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Abstract: The Jizhong Depression is a typical Mesozoic and Cenozoic fault basin located in the northwestern part of the Bohai Bay Basin that has abundant hydrothermal and geothermal resources and enormous development potential. In this study, hydrochemical and isotopic analyses were conducted on water samples from the southern region of the Jizhong Depression. The formation and evolution processes of the deep geothermal water were analyzed, the circulation process of the deep geothermal water was determined, and the genetic mechanism of the geothermal systems was elucidated. The hydrochemical types of the geothermal fluids in the sandstone reservoirs in the research area are mainly Cl·HCO₃⁻Na type, while the geothermal fluids in the carbonate reservoirs are mainly Cl-Na type and Cl·HCO₃⁻Na type. The ion components in the geothermal water are mainly controlled by the dissolution of the carbonate rocks and the alternate adsorption of cations. The elevation of the geothermal water supply area is 763–1063 m, and the main source is precipitation from the mountainous areas in the western Taihang Mountains. The Na-K-Ca temperature scale and multi-mineral equilibrium method have relatively small errors and are suitable for the southern region of the Jizhong Depression, with average errors of 21.44 °C and 32.64 °C, respectively. The depth of the Jxw thermal storage cycle in the research area is 3033–5187 m, and the depth of the Ng thermal storage cycle is 1360-2862 m. The content of the main ions (Na⁺, K⁺, and Cl⁻) in the water samples of the study area is greater in the Jxw thermal storage than in the Ng thermal storage; the Jxw thermal storage water samples have lower $\gamma Na^+/\gamma Cl^-$ values than the Ng thermal storage; and the $\gamma SO_4^{2-}/\gamma Cl^-$ and $\gamma Cl^-/(\gamma HCO_3^- + CO_3^{2-})$ values are greater than those of the Ng thermal storage, indicating that the Jxw thermal storage is located in a geological environment with better sealing, longer flow, slower water circulation, more complete leaching, and higher salinity than the Ng thermal storage. Part of the deep thermal storage is transmitted upwards through the rocks via thermal conduction, and part is transmitted upwards along fault channels via thermal convection, forming a convection-conduction-type geothermal system.

Keywords: Jizhong Depression; hydrogeochemistry; hydrogen and oxygen isotopes; thermal storage temperature

1. Introduction

Geothermal resources refer to geothermal energy, geothermal fluids, and their useful components within the Earth that can be economically utilized by humans. They are a renewable energy source with characteristics such as large reserves, a wide distribution, and clean environmental protection [1–5]. The scientific and reasonable development and utilization of geothermal resources can not only alleviate the pressure on energy resources in China, but also offer an important and practical way to achieve carbon neutrality [6]. The North China Plain, where the Jizhong Depression is located, is a typical sedimentary basin-type geothermal resource distribution area in China. It is rich in medium-low temperature



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (25 °C < T < 150 °C) geothermal resources. Analysis of the genetic mechanism of the geothermal system is crucial to the scientific development of geothermal resources in this region [7].

Characterizing the reservoir temperature and groundwater circulation process in geothermal systems is a prerequisite for the sustainable development of geothermal resources. Water chemistry and isotope research are important tools for the effective exploration of geothermal systems. Stable isotopes (δ^{18} O and δ^{2} H values) and hydrochemistry have been widely applied to trace groundwater sources and to describe the water-rock-gas interaction processes that occur in groundwater systems [8–13]. Reservoir temperature is an important parameter for delineating the genesis type of geothermal system and evaluating the resource potential of geothermal resources, which is determined mainly by ground temperature measurement and calculation methods [14]. The exploration of geothermal resources and the study of the genetic mechanism of geothermal systems in the Jizhong Depression area have been ongoing for decades. Previous researchers have also conducted relevant research on the hydrochemical characteristics and genetic mechanism of the geothermal systems in the Jizhong Depression area using hydrochemical methods, mainly focusing on the Niutuo Town geothermal field in the central part of the Jizhong Depression. Pang et al. [15] studied the source and composition of the geothermal fluids in the Niutuo Town geothermal field based on the geochemical and isotope compositions of geothermal fluids and evaluated the crust–mantle heat flow ratio in the area, providing important information for the crust–mantle thermal structure composition of the Niutuo Town geothermal field. Zhao et al. [16] calculated the thermal storage temperature and thermal cycle depth of the Rongcheng geothermal field and studied the deep cycle mechanism of the geothermal water stored in the Wumishan Formation carbonate rock. Xing et al. [17] conducted geochemical sampling and testing of the geothermal water in five major tectonic units in northern China and found that the geochemical field in this area is mainly influenced by factors such as water–rock interactions, fractures, and reservoir sealing. Zhang et al. [18] analyzed the geothermal genesis model of the Rongcheng Uplift using a combination of hydrochemical methods and rock thermophysical properties and found that the geothermal water came from the supply in the Taihang Mountains and atmospheric precipitation. Regarding the northern region of the Jizhong Depression, Deng et al. [19] analyzed the hydrochemical and isotopic characteristics of the geothermal fluids and found that the geothermal water in the northern region of the Jizhong Depression mainly comes from the atmospheric precipitation in the western Taihang Mountains, which supplies geothermal water from the northwest to southeast through faults, and evaluated the applicability of various temperature scales in the northern part of the Jizhong Depression and concluded that the Na-K and K-Mg scales are suitable for the application in the Jizhong Depression region. Zhao et al. [20] analyzed the geothermal fluid characteristics of the Gaoyang geothermal field in the southern part of the Jizhong Depression using a sampling hydrochemical method and revealed its genetic mechanism. They concluded that the source of the geothermal water supply is the precipitation in the Taihang Mountains and Yanshan Mountains.

Previous research on the Jizhong Depression region has mostly been concentrated in the central and northern regions. In recent years, multiple high-temperature geothermal wells have been drilled in the Gaoyang geothermal field in the central and southern parts of the Jizhong Depression, gradually attracting people's attention. However, research on the hydrochemical characteristics, geothermal water sources, and genetic mechanisms of the geothermal system in the southern region of the Jizhong Depression is still not sufficiently systematic. Therefore, based on research on the geothermal geological conditions in the study area, in this article we analyze the hydrochemical characteristics of geothermal water samples by conducting hydrochemical composition and isotope analyses on the geothermal water samples from thermal reservoirs in the study area. Based on data on the geothermal water characteristic coefficients, recharge elevations, thermal storage temperatures, and thermal cycle depths, we investigate the formation and evolution of the water resources and reveal the genetic patterns of the hydrothermal resources in the study area. The results of this study provide a scientific basis for the rational development and utilization of these geothermal resources.

2. Regional Geological Setting

The Jizhong Depression is a typical Meso-Cenozoic fault basin (Figure 1) located in the northwestern part of the Bohai Bay Basin, which consists of 12 small- to medium-sized half grabens developed on the basement of the Yanshan movement, with the Paleocene as the main sedimentary body, and seven bumps and low bumps jointly [21]. The area is divided into a western depression zone and an eastern depression zone bounded by the Gaoyang-Wuji low relief in the central part of the area, as well as the Niouma Town relief and the Hexiwu tectonic belt, and these tectonic units constitute a "two sag and one uplift" pattern of NNE-NE-oriented spreading [22]. This study includes four tectonic units, which are the Baoding sag, the Gaoyang low bulge, the Lixian slope, and the Rao Yang sag, in order from northwest to southeast. The Jizhong Depression, where the study area is located, has experienced many phases of tectonic activities since the Paleozoic, from the stable depositional stage from the Middle Neoproterozoic to the Paleozoic, to the uplift and folding stage in the Mesozoic, to the rupture stage in the Paleocene, and finally to the stage of depression in the Neocene to the present day, and has developed the metamorphism of the Paleozoic, the marine carbonate rocks from the Middle Neoproterozoic to the Middle Ordovician, the marine and terrestrial interbedded clastics with carbonate rocks in the Permian, and the sandstone and mudstone sediments of the lacustrine and riverine phases in the Paleocene to the Quaternary. The general stratigraphy of the area is characterized by the deposition of metamorphic rocks of the Paleoproterozoic and Palaeoproterozoic (Great Wall and Jixian), Paleoproterozoic (Cambrian and Ordovician), Mesoproterozoic (Jurassic and Cretaceous) and Cenozoic (Paleocene, Neoproterozoic and Quaternary) on top of the crystalline basement of the Palaeoproterozoic-Palaeoproterozoic metamorphic rocks, among which the Paleoproterozoic and Jixian formations are in an angularly unconformable contact. This tectonic pattern of the basin basement and the development of sandstone and carbonate thermal reservoirs provide good geological conditions for the transport and storage of deep heat sources [23,24].



Figure 1. Cont.



Figure 1. (a) Tectonic unit of the Bohai Bay Basin (Modified from Chang et al. [25]); (b) The structure unit division of Jizhong Depression (Modified from Chang et al. [25]); (c) Stratigraphic Profile of the Study Area (Modified from Song et al. [26]).

3. Materials and Methods

3.1. Hydrochemical Sample

There were 36 groups of water samples in this study, and the sampling points were distributed in four tectonic units: Baoding depression, Gaoyang low relief, Lixian slope and Raoyang depression (Figure 1). Among these, 19 groups of sandstone thermal storage geothermal fluids were taken from the Guantao Formation (Ng), and the water samples numbered JN01-19 (sampling depth 1403–2206 m); 14 groups of carbonate thermal storage geothermal fluids were taken from the Wumishan Formation (Jxw), water samples No. JJ01-14 (sampling depth 3200–4000 m). The geothermal water was collected at the corresponding location in the thermal reservoir and obtained by pumping tests. The fluid was relatively clear and not turbid. These samples included 2 groups of shallow groundwater samples, water samples No. JQ01-02; 1 group of surface water samples, water sample No. JS01; and 1 group of atmospheric precipitation, sample No. SP01.

The indoor tests included water quality analysis and hydroxide isotope analysis, and the water quality analysis was based on the national standards of the People's Republic of China, "National food safety standard Methods for examination of drinking natural mineral water" (GB 8538-2016) [27], "Standard examination methods for drinking water-General principles" (GB/T 5750-2006) [28], and the People's Republic of China's Geological and Mining industry standard "Analysis Method of Groundwater uality" (DZ/T 0064-1993) [29]. The water samples were tested using an inductively coupled plasma emission spectrometer (iCAP6300) to detect cations and trace elements, ion chromatography to detect anions, and the anion and cation equilibrium error was controlled to be less than 3%. δ D and δ^{18} O were detected using a water isotope analyzer (L2130i) with Wavelength Scanning-Optical Cavity Decay Spectrometry, and the testing accuracies of δ D and δ^{18} O were ± 1 ‰ and ± 0.1 ‰, respectively. The sample test results are shown in Table 1.

Sample NO.	Stratigraphic	T (°C)	Ph	K*	Na ⁺	Ca ²⁺	Mg ²⁺	Cl-	SO_4^{2-}	HCO ₃ -	TDS	Sr ²⁺	δD_{VSMOW}	$\delta^{18}O_{VSMOW}$	\mathbf{F}^{-}	H_2SiO_3	HBO ₂
JN01	Ng	69.2	7.95	4.6	445.1	9.37	0.83	369.8	102	396.9	1183	0.536	-74	-9.7	1.72	60.89	1.62
JN02	Ng	82	8.16	5.03	416.9	8.83	0.61	303.4	124.2	432.4	1135	0.346	-74	-9.3	2.36	68.02	1.92
JN03	Ng	67	8.04	4	412	11.81	1.11	368	110.4	325.8	1115	0.636	-75	-9.9	1.69	52.62	1.12
JN04	Ng	46.1	8.16	2.74	308.3	7.61	0.75	206.1	94.28	344.8	834.6	0.3	-76	-10.3	1.56	49.46	0.64
JN05	Ng	44.8	8.58	1.97	242.9	5.71	0.68	116	91.4	296.8	661.1	0.116	-76	-10.2	1.33	42.93	0.46
JN06	Ng	62	7.94	4.29	463.6	6.7	0.57	275	108.1	589.4	1209	0.28	-74	-9.4	3.14	62.92	2.3
JN07	Ng	73.4	8.19	2.9	359.6	4.97	0.62	164.1	81.49	527.2	925.7	0.148	-73	-9.4	2.99	56.11	1.26
JN08	Ng	68	8.12	4.29	573.2	6.59	0.73	524.1	18.06	615.5	1487	0.259	-73	-8.9	3.33	55.28	3.72
JN09	Ng	56.1	8.41	1.96	370.5	5.11	0.64	214.3	96.45	438.3	967.7	0.114	-72	-9.1	3.92	43.99	1.76
JN10	Ng	48.2	8.14	5.83	586.5	21.23	3.56	667.7	137.1	271.9	1592	0.965	-73	-9.9	0.79	37.29	0.92
JN11	Ng	52.9	8.17	5.89	937.5	17.69	3.32	1224	26.24	421.8	2465	1.46	-71	-9.3	1.04	38.5	2.77
JN12	Ng	72	8.7	4	310.2	4	1	95	80.3	510.1	1063.1	43.54	/	/	/	/	/
JN13	Ng	79	7.94	3.3	192.9	18.4	3.3	85.1	48.9	373.4	753.6	34.11	/	/	/	/	/
JN14	Ng	80	8.4	2.9	316.9	4.8	1	147.5	73.5	524.7	1114	38.96	/	/	/	/	/
JN15	Ng	80	8.36	3.7	319.7	6.4	1	168.8	93.7	478.4	1125.5	57.46	/	/	/	/	/
JN16	Ng	75	8.81	4.9	401	7.2	0.5	195.7	113.1	578.4	1350	33.29	/	/	/	/	/
JN17	Ng	76	8.45	5.98	441.7	6.74	0.69	211.8	132.8	622.2	1498	79.43	/	/	/	/	/
JN18	Ng	88	7.98	6.39	473.4	8.22	1.08	244.2	135.6	641.7	1585	85.54	/	/	/	/	/
JN19	Ng	76.4	7.78	12.61	1138	25.08	4.22	1453	8	482.1	3193	59.8	/	/	/	/	/
JJ01	Jxw	82	7.46	149.3	1691	88.56	20.08	2387	104.9	838.2	5122	8.611	-72	-6.4	8.43	179.1	90.26
JJ02	Jxw	81.6	7.53	167	1894	77.05	15.09	2746	112.3	761.2	5677	9.714	-71	-5.9	8.42	186	104.2
JJ03	Jxw	66.8	7.03	147.9	1857	106.3	15.6	2675	120.6	906.3	5618	10.74	-73	-6.4	6.58	133.8	91.72
JJ04	Jxw	71	7.34	37.19	823.9	53.59	8.86	996.2	92.81	574.6	2398	3.091	-75	-9.1	2.11	78.78	25.18
JJ05	Jxw	65.6	7.05	73.45	1098	55.31	7.04	1391	104.5	675.3	3212	5.309	-74	-8.2	4.09	100.6	48.17
JJ06	Jxw	100	8.38	186.5	2062	23.03	11.34	3097	116.1	571.6	6461	6.689	-71	-5.9	8.63	204.1	118.1
JJ07	Jxw	84.1	7.08	145.6	1466	88.15	19.6	1978	118.3	852.5	4882	7.97	-72	-6.8	9.45	185	78.48
JJ08	Jxw	87.6	8.4	193.4	2097	16.99	8.7	3096	111.7	473.9	6109	7.327	-70	-5.4	9.68	182.9	120
JJ09	Jxw	88.2	8.46	165.6	1865	18	12.76	2818	94.16	456.1	5563	2.811	-70	-5.6	8.78	204.4	107.2
JJ10	Jxw	100	7.65	150.1	1682	74.08	20.36	2421	159.7	552.2	4968	4.705	-70	-6.5	8.04	129.7	70.36
JJ11	Jxw	83	7.79	124.4	2201.1	65.7	142.5	3034.8	760.7	341.7	6742.6	81.82	/	/	/	/	1,
JJ12	Jxw	81	7.01	107.1	1911	255.4	45.22	2777	741.8	367.3	6297	62.53	/	/	/	/	1,
JJ13	Jxw	75.7	6.9	112.8	1838	274.3	43.13	3000.7	487	371.2	6227.4	63.96	1	/	1	/	/
JJ14	Jxw	89.1	7.46	105.1	1944	221.9	46.39	2827	538.7	356.9	6147	64.61	/	/	/	/	/
JQ01	Q	14.9	7.83	1.2	99.82	82.89	49.34	105.4	327.7	179.5	889.7	0.897	-70	-9.7	0.43	< 0.20	22.97
JQ02	Q	21.5	8.09	3.18	49.05	21.81	6.91	5.25	6.4	209.4	326.7	0.297	-80	-10.6	0.37	< 0.20	21.47
JD01	/	19	5.86	0.45	2.83	4.54	0.81	1.79	7.8	4.74	35.62	0.016	-55	-8.5	0.15	<1.00	<0.20
JB01	/	15.2	8.03	5.44	202.9	57.65	59.1	218.1	97.05	497	1167	0.647	-34	-2.7	0.81	12.89	0.96

Table 1. Main ion concentration (mg/L) of water samples.

3.2. Geothermometer

Geothermal temperature scale is a means of estimating the temperature of deep thermal storage by using the concentration of hot water chemical components related to the temperature of underground thermal storage or the relationship between its ratio and the temperature, and the commonly used geothermal temperature scales include the cationic geothermal temperature scale, SiO₂ temperature scale, and so on [30].

3.2.1. Cationic Geothermal Temperature Scale

Cation temperature scale is a method of calculating thermal storage using the relationship between the ratio between Na, K, Ca, Mg and other cations in the geothermal fluid and the temperature when the equilibrium is reached between the geothermal water and the water–rock action of the minerals in the thermal storage layer at a specific temperature. The common cation geothermal temperature scales are the Na-K geothermal temperature scale, Na-K-Ca geothermal temperature scale, and K-Mg geothermal temperature scale.

The Na-K geothermal temperature scale is based on the temperature-controlled exchange equilibrium of Na⁺ and K⁺ between the geothermal water and alkali feldspar, and this geothermometer is mainly suitable for calculating the temperature of hot water above 150 °C, with the empirical formula [31]:

$$T = \frac{1217}{1.438 + \lg(Na/K)} - 273.15\tag{1}$$

The Na-K-Ca geothermal temperature scale is an empirical method modified on the basis of the Na-K geothermal temperature scale, which is more suitable for calculating the temperature of hot water with high Ca^{2+} content. It makes up for the shortcomings of the unreasonable calculation results of the Na-K geothermal temperature scale in Ca^{2+} -rich hot water, with the empirical formula [32]:

$$T = \frac{1647}{\lg(Na/K) + \beta(\lg(\sqrt{Ca}/Na) + 2.26) + 2.47} - 273.15$$
(2)

The K-Mg geothermal temperature scale is based on the ion-exchange reaction of potassium feldspar transforming into dolomite and chlorite, which is based on the principle that K/Mg is more sensitive to temperature decreases and can react quickly when the water temperature changes. This geothermometer is mainly suitable for calculating the temperature of hot water at low and medium temperatures, with the empirical formula [30]:

$$T = \frac{4410}{13.95 - \log(K^2/Mg)} - 273.15$$
(3)

The Ca-Mg geothermometer assumes the equilibrium of the waters with calcite and dolomite in the reservoir, which is reasonable in this type of system, with the empirical formula [33]:

$$T = \frac{979.8}{3.1170 - \log(Ca/Mg) + 0.07003\log\sum eq} - 273.15$$
(4)

In Equations (1)–(4) *T* is the thermal storage temperature (°C) and each ion concentration is mg/L.

3.2.2. Silicon Dioxide Temperature Scale

 SiO_2 is a mineral commonly found in the lithosphere and hydrosphere, and common SiO_2 minerals include quartz, chalcedony, and fonzanite, etc. Because the physicochemical properties of SiO_2 in water are stable and unaffected by other ions, and the concentration of SiO_2 in water has the characteristic of being sensitive to temperature changes, it has been widely used as a geothermal thermoscan [34]. Silicon dioxide geothermal temperature scale principle SiO_2 solution at low temperatures can be maintained for a long time in a

supersaturated state; SiO_2 is used in a hot water solubility and temperature relationship to estimate the underground heat storage temperature. Nowadays, the commonly used silica geothermal temperature scale includes the quartz geothermal temperature scale and chalcedony geothermal temperature scale, with the empirical formula [35]:

Quartz geothermal temperature scale with no vapor loss:

$$T = \frac{1309}{5.19 - \lg S} - 273.15 \tag{5}$$

Jade chalcedony geothermal temperature scale:

$$T = \frac{1032}{4.69 - \lg S} - 273.15 \tag{6}$$

In Equations (5) and (6) *T* is the thermal storage temperature (°C) and *S* is the SiO₂ concentration (mg/L).

3.3. Multi-Mineral Equilibrium Graphical Method

The multi-mineral equilibrium method refers to the method of determining the deep temperature by analyzing the relationship between the dissolution state and temperature of multiple minerals in the geothermal system. It is based on the principle that at a specific temperature, the temperature at which multiple mineral components in the geothermal fluid are close to dissolution equilibrium at the same time is regarded as the temperature of the deep thermal storage [16].

Mineral saturation index SI = $\log Q/K$, where Q is the ion activity product and K is the reaction equilibrium constant at a specific temperature, using SI to determine the degree of equilibrium between minerals and geothermal water reactions in geothermal systems. If SI > 0, it indicates that the minerals are oversaturated and precipitation occurs in the hot water; if SI = 0, it indicates that the minerals are in equilibrium between dissolution and precipitation; if SI < 0, it indicates that the minerals are not saturated, and dissolution of minerals continues to occur.

3.4. Water–Rock Balance Analysis

Judging whether the ions in the geothermal fluid reach the equilibrium state is a prerequisite for calculating the thermal storage temperature using the geothermal temperature scale; therefore, before using the geothermal temperature scale for calculation, it should be judged whether the geothermal fluid reaches the water–rock equilibrium or not. Nowadays, the Na-K-Mg triangulation diagram is often used to classify the geothermal fluid into three types: fully equilibrated, partially equilibrated, and immature water [36], according to the water–rock equilibrium state and whether there is cold water mixing [34]. The Na, K, and Mg contents in the geothermal fluid samples in the study area were linearly transformed and put into the Na-K-Mg triangular diagram, and according to their position, we can judge whether the ions in the water samples reached the equilibrium state.

4. Results

4.1. Hydrochemical Characteristics

Geothermal fluids can be divided into different geothermal water chemical types according to their chemical composition. Statistical analysis of the main chemical indicators of geothermal fluids in the study area can be seen in Table 1 and Figure 2: Ng geothermal water pH value distribution is more concentrated, with the value range of 7.78–8.58 and the average value 8.3, belonging to the weakly alkaline. The distribution of total dissolved solids (TDS) value is more concentrated, with the value range of 753.6–3193 mg/L and the average value 1390.76 mg/L. The Jxw geothermal water pH value distribution is discrete, with the value range 6.9–8.81 and the average value 8.46, belonging to weak



alkaline. The total dissolved solids (TDS) distribution range is discrete, with the value range 2398-6742 mg/L and the average value 6059.2 mg/L, belonging to saline water.

Figure 2. (a) The PH box plot of water samples; (b) The TDS box plot of water samples.

From Figure 3, it can be seen that the cations of the geothermal fluids of sandstone thermal storage and carbonate thermal storage in the study area are mainly dominated by Na⁺, and the anions are mainly dominated by HCO_3^- and Cl^- . The high concentration of Na⁺ and Cl⁻ in the Jxw thermal storage also reflects the long hot water runoff time in its deeper part and deeper hot water metamorphism [37]. According to Shukarev's classification [38], the hydrochemical types of geothermal fluids in sandstone thermal storage in the study area are mainly of the Cl·HCO₃⁻Na type, the geothermal fluids in carbonate thermal storage are mainly of the Cl-Na and Cl·HCO₃⁻Na types, and the shallow subsurface cold water is of the SO₄⁻Na·Ca and HCO₃⁻Na·Ca type water. According to studies by Apollaro et al. [39], the iso-ionic–salinity (TIS) lines were added in the correlation plot of (Na⁺ + K⁺) vs. (Ca²⁺ + Mg²⁺) to reflect the ionic salinity. As shown in Figure 4, the content of Ca²⁺ and Mg²⁺ is lower than that of Na⁺⁺ K⁺ on the whole, and the total ionic salinity (TIS) of water ranges from 10.95 to 114.05 meq/L.

According to the results of the Schoeller diagram (Figure 5), Ca^{2+} , Mg^{2+} , and HCO_3^{-1} in Jxw hot storage are higher than in Ng hot storage in the study area, which is mainly caused by the difference in lithology of the different hot storages. The lithology of Jxw hot storage is mainly composed of dolomite, and the main mineral fractions are dolomite and calcite; Ca^{2+} , Mg^{2+} , HCO_3^{-} derive mainly from the dissolution of these carbonate minerals. The main ions of the water samples—Na⁺, K⁺, Cl⁻—are greater in Jxw thermal storage than in Ng thermal storage. The reason is that the water circulation path of Jxw thermal storage is longer, the dissolution and filtration is more adequate, and the soluble materials in the surrounding rocks enter into the hot water in large quantities. The ion concentration in the sandstone thermal storage is greater. There is a difference in the trend of ion changes between the geothermal water and the cold groundwater, indicating that they are not clearly hydraulically connected.



Figure 3. The Piper triangular diagram of water samples.



Figure 4. TIS salinity diagram of water samples.



Figure 5. The Schoeller diagram of water samples.

4.2. Estimation of Deep Thermal Storage Temperature

The thermal storage temperatures were calculated by each temperature scale and the results are shown in Table 2. The calculated ranges of Ng thermal storage in the study area using Na-K, Na-K-Ca, K-Mg, Ca-Mg, Quartz, Chalcedony, and the SI Method were 54.48–106.59 °C, 55.18–87.28 °C, 53.23–103.1 °C, 364.31–457.66 °C, 53.23–103.1 °C, respectively, 32.2–155.61 °C, 27.44–131.09 °C and 71–99 °C, while the calculated ranges of Jxw heat storage in the study area were 164.08–106.59 °C, 97–154.32 °C, 129.18–217.57 °C, 265.41–401.85 °C, 133.07–293.81 °C, 105.93–297.4 °C, and 110–153 °C, respectively. According to the comparison results, it can be seen that the Jxw thermal storage temperature derived using each temperature scale calculation method is higher than the Ng thermal storage, i.e., the thermal storage temperature of the deep Jixian carbonate samples is higher than that of the shallow Neoproterozoic sandstone thermal storage.

Tabl	le 2.	Calculatior	results of	therma	l storage	temperature
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Simple No.	Measuring Temperature	Na-K	Na-K-Ca	Ca-Mg	K-Mg	Quartz	Chalcedony	SI Method
JN01	69.2	82.31	78.42	435.31	86.02	138.30	111.72	97
JN02	82	89.43	84.45	457.66	89.70	149.67	124.40	96
JN03	67	79.52	71.62	430.79	75.46	142.80	116.72	92
JN04	46.1	75.64	67.40	428.60	69.72	133.93	106.88	83
JN05	44.8	71.71	61.10	415.00	63.10	132.23	105.00	92
JN06	62	77.40	81.32	438.53	91.81	141.59	115.38	81
JN07	73.4	71.47	70.91	409.49	82.33	126.07	98.22	89
JN08	68	68.33	78.29	416.01	87.54	59.65	27.44	81
JN09	56.1	54.48	61.66	409.05	69.47	135.19	108.27	83
JN10	48.2	80.57	66.86	386.22	78.81	155.61	131.09	82
JN11	52.9	61.20	67.89	376.93	88.48	73.97	42.35	71
JN12	72	92.58	72.84	364.20	96.79	125.29	97.37	99
JN13	79	106.59	55.18	386.59	53.23	100.78	70.77	78

Simple No.	Measuring Temperature	Na-K	Na-K-Ca	Ca-Mg	K-Mg	Quartz	Chalcedony	SI Method
JN14	80	76.91	65.42	375.15	81.70	120.69	92.33	85
JN15	80	87.49	71.02	393.93	83.52	133.59	106.50	96
JN16	75	90.03	86.30	457.45	93.10	144.19	118.27	78
JN17	76	94.92	87.28	423.54	103.10	153.68	128.91	89
JN18	88	94.78	83.29	404.23	101.51	154.94	130.33	98
JN19	76.4	85.48	83.25	383.02	101.74	32.20	125.31	90
JJ01	82	215.20	131.26	362.50	193.24	139.88	113.48	117
JJ02	81.6	215.08	139.65	370.81	197.42	143.78	117.82	125
JJ03	66.8	206.58	135.06	389.33	187.58	147.93	122.46	110
JJ04	71	164.08	101.96	385.29	129.18	133.07	105.93	121
JJ05	65.6	192.67	125.38	401.85	164.22	139.67	113.24	121
JJ06	100	217.26	148.32	321.82	212.80	145.71	119.97	149
JJ07	84.1	225.42	130.85	364.16	189.28	146.80	121.19	115
JJ08	87.6	218.94	154.32	319.99	217.57	143.47	117.47	153
JJ09	88.2	215.68	142.19	306.22	212.13	133.86	106.80	150
JJ10	100	216.11	131.21	351.67	196.20	165.13	141.86	140
JJ11	83	179.97	97.00	265.41	176.87	293.81	297.40	122
JJ12	81	179.36	108.81	376.73	142.28	291.14	293.97	148
JJ13	75.7	186.09	110.99	384.45	141.88	249.93	242.21	148
JJ14	89.1	176.74	107.90	366.57	145.98	259.26	253.74	150

Table 2. Cont.

4.3. Water Rock Balance Results

The Na-K-Mg ternary diagram can be used to determine the degree of equilibrium of the geothermal water and rock mineral reaction as well as to estimate the thermal storage temperature, and this diagram classifies the geothermal water into three types: fully equilibrated water, partially equilibrated or mixed water, and immature water [30]. The Na-K-Mg triangular diagram of the water sample points in the study area was drawn by Aqua-Chem software (Version 3.70) (Figure 6), and most of the water samples of the thermal storage layer fall in the partial equilibrium or mixed water area, indicating that the de-watering rock action has not completely reached equilibrium. Therefore, there is a deviation between the estimation of the thermal storage layer using the cationic geothermal temperature scale and the actual thermal storage temperature, in which the water sample points of the thermal storage layer of the Ng fall in the vicinity of the complete equilibrium line, indicating that the Ng reservoir fall near the complete equilibrium line, indicating that the Ng reservoir fall near the complete equilibrium line, indicating that the Ng reservoir samples are close to the water-rock equilibrium state, and the cationic temperature scale can be used to estimate the thermal reservoir temperature.



Figure 6. The Na-K-Mg triangular diagram of water samples.

5. Discussion

5.1. Analysis of Hydrochemical Evolution

5.1.1. Correlation Analysis of Hydrochemical Components

By analyzing the correlation between the main chemical indicators and ion concentrations of the geothermal water, the groundwater runoff conditions can be obtained, and the possible sources of the hydrochemical components of the geothermal water can be inferred. Cl⁻ can serve as a good tracer in hot water systems. The principle is that Cl⁻ is not easily adsorbed on mineral surfaces or does not form mineral salts in hydrothermal systems and is in a stable state under high-temperature conditions. Therefore, the source of the ions can be determined by analyzing the correlations between Cl^{-} and other ions [20]. According to Table 3, there are significant correlations between the Cl^{-} and Na^{+} , K^{+} , and Ca^{2+} in the Ng thermal storage in the study area, indicating that these three ions have the same source as the Cl^- . There are significant correlations between the Cl^- and Na+ and K^+ in the Jxw thermal reservoir in the study area, indicating that both have the same material source as the Cl⁻, and both are derived from the dissolution of related minerals and some deep Earth materials. However, the correlations between the main ions Ca²⁺, Mg²⁺, SO₄^{2–}, HCO₃[–], and Cl[–] are not good, indicating that these ions only originated from mineral dissolution during hydrothermal processes. HCO₃⁻ has strong correlations with Ca²⁺ and Mg²⁺, indicating that these ions mainly originated from the dissolution of dolomite. The Na⁺, K⁺, and Cl⁻ in the two types of thermal storage exhibit significant positive correlations with the total dissolved solids (TDS), indicating that these three ions have a significant impact on the changes in the TDS content of the geothermal water.

Table 3. Correlation coefficients of geothermal water chemistry indexes.

	T (°C)	pН	K+	Na ⁺	Ca ²⁺	Mg ²⁺	Cl-	SO_4^{2-}	HCO_3^-	TDS
T (°C)	1									
pН	-0.097	1								
K ⁺	0.285	-0.431	1							
Na ⁺	-0.055	-0.433	0.848 **	1						
Ca ²⁺	-0.101	-0.570 *	0.686 **	0.678 **	1					
Mg ²⁺	-0.097	-0.459 *	0.618 **	0.645 **	0.951 **	1				
CĨ-	-0.162	-0.462 *	0.788 **	0.976 **	0.769 **	0.740 **	1			
SO_4^{2-}	0.026	0.246	-0.273	-0.494 *	-0.359	-0.473 *	-0.555 *	1		
HCO_3^-	0.611 **	0.116	0.209	0.094	-0.401	-0.353	-0.101	-0.034	1	
TDS	0.099	-0.365	0.911 **	0.973 **	0.674 **	0.662 **	0.931 **	-0.460 *	0.196	1
T (°C)	1									
pН	0.661 *	1								
Γ̈́K ⁺	0.606 *	0.619 *	1							
Na ⁺	0.513	0.444	0.717 **	1						
Ca ²⁺	-0.128	-0.648 *	-0.349	0.144	1					
Mg ²⁺	0.044	-0.048	-0.137	0.441	0.259	1				
CĨ-	0.509	0.427	0.713 **	0.982 **	0.215	0.357	1			
SO_4^{2-}	0.017	-0.253	-0.275	0.428	0.679 **	0.823 **	0.397	1		
HCO ₃ -	-0.305	-0.265	0.18	-0.348	-0.363	-0.512	-0.382	-0.699 **	1	
TDS	0.481	0.308	0.638 *	0.976 **	0.309	0.474	0.974 **	0.527	-0.384	1

Note: ** Significant correlation at the 0.01 level (two-tailed). * Significant at the 0.05 level (two-tailed).

According to the hydrochemical analysis of the samples from the study area, the main trace elements in the geothermal water are F^- , Sr^{2+} , metaboric acid, and metasilicic acid, which are especially enriched in the Jxw thermal reservoirs. These trace elements are mainly derived from hydrothermal processes or deep hydrothermal fluids. By plotting the relationships between Cl⁻ and F⁻, Sr²⁺, metaboric acid, and metasilicic acid, the main sources of the trace elements in the deep geothermal water can be determined. According to Figure 7, the correlations between Cl⁻ and F⁻ and F⁻ and metasilicic acid –in the Ng thermal storage are poor. It is speculated that the Cl⁻ has different material sources, and the

contents of Sr^{2+} and metasilicic acid in this aquifer are relatively low, indicating that these trace elements in the Ng geothermal water mainly come from the dissolution of minerals during hydrothermal processes. There are good positive correlations between Cl^- and F^- , metaboric acid, and metasilicic acid in the Jxw thermal storage, suggesting that these three trace elements have material sources similar to that of the Cl^- . The content of metaboric acid in geothermal water is directly proportional to the intensity of the runoff [40]. The content of the metaboric acid in the Jxw hot water in the area is significantly higher than that in the Ng hot water, indicating that the geothermal water in the Jxw thermal storage has a longer runoff path, a slower flow velocity, and a weaker runoff intensity.



Figure 7. The relationships between trace elements and chlorine concentration.

5.1.2. Characteristic Coefficients of Geothermal Water

The study of ionic ratios in formation water can reflect the degree of metamorphism, desulfurization, and salinization of groundwater. The metamorphic coefficient $\gamma Na^+/\gamma Cl^-$ is used to describe the degree of groundwater metamorphism, the hydrogeological and geochemical environment of thermal reservoirs, and their sealing properties. The smaller the metamorphic coefficient is, the better the sealing of the aquifer is, and the higher the degree of metamorphism is. The desulfurization coefficient $100 \times \gamma SO_4^{2-}/\gamma Cl^-$ is used to indicate the degree of sulfate removal from the groundwater, and its reaction process is $SO_4^{2-} + 2C + 2H_2O \rightarrow H_2S + 2HCO_3^-$ [41]. If the desulfurization coefficient is smaller, the environment in which the geothermal water is located is sealed better and has higher reducibility. If the desulfurization coefficient is less than 1, the environment in which the aquifer is located has been completely restored. The salinization coefficient $\gamma Cl^-/(\gamma HCO_3^- + CO_3^{2-})$ can reflect the degree of salinity of the groundwater, and the larger the salinity coefficient is, the higher the degree of salinity of the groundwater is. The characteristic coefficient values of the geothermal water are presented in Table 4.

Sample No.	Stratigraphic	$\gamma Na^+/\gamma Cl^-$	$100 imes \gamma SO_4^{2-}/\gamma Cl^-$	$\gamma Cl^{-}/(\gamma HCO_3^{-}$ + $CO_3^{2-})$
JN01		1.86	20.33	1.60
JN02		2.12	30.26	1.21
JN03		1.73	22.16	1.94
JN04		2.31	33.73	1.03
JN05		3.23	58.10	0.67
JN06	Ng	2.60	28.99	0.80
JN07		3.38	36.72	0.54
JN08		1.69	2.57	1.46
JN09		2.66	33.22	0.84
JN10		1.35	15.14	4.22
JN11		1.18	1.59	5.00
JJ01		1.09	3.24	4.90
JJ02		1.06	3.02	6.21
JJ03		1.07	3.33	5.08
JJ04		1.28	6.87	2.98
JJ05	INTAG	1.22	5.56	3.54
JJ06	JXW	1.03	2.77	9.32
JJ07		1.14	4.41	3.99
JJ08		1.04	2.67	11.24
JJ09		1.02	2.47	10.63
JJ10		1.07	4.88	7.54
JQ01	0	2.72	127.10	0.60
JQ02	Q	1.44	32.85	0.75

Table 4. Geothermal water characteristic coefficients.

The metamorphic coefficient of the Ng geothermal water in the research area is 1.18–3.38, and that of the Jxw geothermal water in the research area is 1.02–1.28. The results indicate that the Jxw thermal reservoir has better sealing performance and a higher degree of metamorphism, and the environment it is located in has a stronger reducibility. The metamorphic coefficients of both the Ng and Jxw reservoirs are greater than 1, indicating that atmospheric precipitation affects the formation of the hot water in both reservoirs, but the Ng reservoir is more strongly affected.

The desulfurization index of the Ng thermal storage in the research area ranges from 1.59 to 58.1, and the desulfurization index of the Jxw thermal storage ranges from 2.47 to 6.87, both of which are lower than those of shallow groundwater, indicating that both reservoirs have undergone a certain degree of desulfurization. The Jxw thermal storage has better sealing performance than the Ng thermal storage, and its geological environment is more reducible.

The salinity coefficient of the Ng hot water in the study area ranges from 0.54 to 5.00, with an average of 1.76. The salinity coefficient of the Jxw hot water ranges from 2.98 to 11.24, with an average of 6.54, indicating that the Jxw geothermal water has a longer runoff path, slower water circulation speed, and higher salinity than the Ng geothermal water.

5.1.3. Main Ion Sources of Geothermal Water

During the deep circulation process of groundwater, differences in the hydrochemical components occur due to water–rock reactions with surrounding rocks [42]. By identifying the sources of the major ions, the evolution process of the hydrochemistry can be revealed. The source of Na⁺ can be obtained using the γ Na⁺/ γ Cl⁻ ratio. It can be seen from Figure 8a that the Na⁺ contents of all of the water samples from Ng and Jxw are slightly higher than the Cl⁻ contents, and the data plot near the y = x ray, indicating that the Na⁺ in the geothermal water in the study area mainly comes from salt rock dissolution. The main sources of the Ca²⁺ and Mg²⁺ in the groundwater can be analyzed using the γ (Ca²⁺ + Mg²⁺)/ γ (HCO₃⁻ + SO₄²⁻) ratio, which is based on the principle that the Ca²⁺ and Mg²⁺

in groundwater generally come from the weathering and dissolution of carbonate rocks, silicates, and evaporites. It can be seen from Figure 8b that the $\gamma(Ca^{2+} + Mg^{2+})/\gamma(HCO_3^- + SO_4^{2-})$ ratios of the Jxw thermal storage are greater than those of the Ng thermal storage, and the water samples are generally distributed below the y = x line. Therefore, it is concluded that the Ca²⁺ and Mg²⁺ in the Ng thermal storage water and the Jxw thermal storage water both originate from the dissolution of carbonate minerals. The $\gamma(SO_4^{2-} + Cl^-)/\gamma HCO_3^-$ ratio can be used to identify the control ratio of carbonate and salt rocks during rock dissolution [43]. The $\gamma(SO_4^{2-} + Cl^-)/\gamma HCO_3^-$ ratios of the water samples from the research area are shown in Figure 8c. Most of the Jxw and Ng thermal storage water samples plot above the y = x ray, indicating that the SO₄²⁻ and Cl⁻ in the thermal storage water are mainly come from the dissolution of evaporate salt rocks. The larger ratio of the Jxw water indicates that the SO₄²⁻ and Cl⁻ in the Jxw thermal storage water are mainly from the dissolution of evaporate salt rocks.



Figure 8. (a) Plots of $\gamma Na^+ / \gamma Cl^-$ of the water samples; (b) Plots of $\gamma (Ca^{2+} + Mg^{2+}) / \gamma (HCO_3^- + SO_4^{2-})$ of the water samples; (c) Plots of $\gamma (SO_4^{2-} + Cl^-) / \gamma HCO_3^-$ of the water samples; (d) Plots of CAI-1/CAI-2 of the water samples.

Cation alternating adsorption is an important process in the chemical evolution of groundwater [44]. The cation alternating adsorption process in groundwater can be characterized by the chlor-alkali index (CAI-1, CAI-2), and the calculation formulas for CAI-1 and CAI-2 are as follows:

$$CAI - 1 = \frac{Cl^{-} - (Na^{+} + K^{+})}{Cl^{-}}$$
$$CAI - 2 = \frac{Cl^{-} - (Na^{+} + K^{+})}{SO_{4}^{2-} + HCO_{3}^{-} + CO_{3}^{2-} + NO_{3}^{-}}$$

Positive CAI values indicate ion exchange between the Na⁺ and K⁺ in groundwater and the Ca²⁺ and Mg²⁺ in the surrounding rocks. If all of the CAI values are negative, the ion exchange direction is opposite [45]. The absolute value of the CAI represents the degree of cation exchange between the groundwater and surrounding rock, and its value is directly proportional to the degree of exchange. It can be seen from Figure 8d that the CAI values of the Jxw thermal storage water are all positive, indicating that the Na⁺ and K⁺ in the Jxw thermal storage water undergo ion exchange with the Ca²⁺ and Mg²⁺ in the surrounding rock. The CAI values of the Ng thermal storage water are often negative, indicating that the alternating adsorption process of the cation ions in the geothermal water involves the exchange of the Ca²⁺ and Mg²⁺ in the geothermal water with the Na⁺ and K⁺ in the surrounding rocks. The absolute CAI-1 and CAI-2 values of the Ng geothermal water are mostly greater than those of the Jxw geothermal water, indicating a higher degree of cation alternating adsorption.

5.1.4. Source of Geothermal Water Supply

Hydrogen and oxygen isotopes are good tracers, and the recharge and elevation of groundwater during circulation can be represented by their distribution characteristics [7]. Using the hydrogen and oxygen isotope standards (Standard Mean Ocean Water, SMOW) determined by Craig [46] and the global atmospheric waterline equation ($\delta D = 8\delta^{18}O + 10$), the study area can be divided into Ng geothermal water, Jxw geothermal water, and shallow groundwater. A plot of δD versus $\delta^{18}O$ is shown in Figure 9. The solid line in Figure 9 represents the global atmospheric water line (GMWL), while the dashed line represents the deuterium excess parameter (d), where d can be used to measure the degree of exchange of ¹⁸O between the geothermal water and rocks. The smaller the d value is, the smaller the runoff velocity of the geothermal water is, the longer the retention time in the aquifer is, and the stronger the water–rock reaction is. The expression for d is d = $\delta D - 8$. The ¹⁸O and d values are not affected by factors such as the season and height, and their values are constant [47].



Figure 9. $\delta D - \delta^{18} O$ plot for water samples.

For the Ng geothermal water in the research area, δD is between -76% and -71%, and $\delta 18O$ is between -10.3% and -8.9%. For the Jxw geothermal water, δD is between -75% and -70%, and $\delta^{18}O$ is between -9.1% and -5.4%. In Figure 7, the overall distributions of the hydrogen and oxygen isotopes in the Ng geothermal water and shallow groundwater plot near the GMWL, indicating that atmospheric precipitation is the main source of the water supply. The hydrogen and oxygen isotopes of the Ng and Jxw thermal storage water shift toward the atmospheric waterline, resulting in oxygen drift, indicating that the source of the geothermal water supply is not directly supplied by local atmospheric

precipitation and may have been supplied from a distance through long-term underground lateral flow [48]. It can be seen from the graph that the oxygen drift of the Jxw thermal storage is more pronounced than that of the Ng thermal storage. This is due to the higher recharge elevation of the deep Jxw thermal storage, which is supplied laterally from the distant high mountains, while the Ng thermal storage is supplied in the lower elevation piedmont plain. The d values of the Ng thermal storage in the study area are significantly lower than those of the Jxw thermal storage, indicating that the Jxw geothermal water has a slower runoff rate, longer retention time in the aquifer, and stronger water–rock reaction.

5.1.5. Elevation of Geothermal Water Supply

Liu et al. [49] found that as water vapor rises and cools, the δ^{18} O and δ D values decrease as the elevation increases. Therefore, the elevation of the geothermal water supply can be calculated from the hydrogen and oxygen isotopes of atmospheric precipitation, and the location of the geothermal water supply area can be inferred. The formula for calculating the supply elevation is as follows:

$$H = \frac{\delta_{G} - \delta_{P}}{K} + h \tag{7}$$

where H is the elevation of the geothermal water supply area (m); δG is the $\delta^{18}O$ or δD value of the geothermal water sample (‰); δP refers to $\delta^{18}O$ or δD value of the atmospheric precipitation (‰); K is the $\delta^{18}O$ or δD elevation gradient of the atmospheric precipitation (‰ /100 m); and H is the elevation of the sampling point (m).

One atmospheric precipitation sample was collected in the research area and the test results were obtained. The δD value is -55%, and the $\delta^{18}O$ value is -8.5%. Due to the enrichment of ¹⁸O in the geothermal water, oxygen drift is more severe. The elevation error of the $\delta^{18}O$ calculation for replenishment is relatively large, so δD was selected for the calculation of the atmospheric precipitation. The elevation gradient K of δD is taken as -2%/100 m [50]. According to the formula, the elevation of the geothermal water supply area in the study area was calculated (Table 5). The geothermal water supply elevation is 763–1063 m, which is consistent with the elevation of the Taihang Mountains in the western part of the Jizhong Depression. It is speculated that the geothermal water in the study area is mainly supplied by precipitation in the mountainous areas of the western Taihang Mountains.

Sample No.	Supply Elevation (m)	Sample No.	Supply Elevation (m)
JN01	963	JJ01	863
JN02	963	JJ02	813
JN03	1013	JJ03	913
JN04	1063	JJ04	1013
JN05	1063	JJ05	963
JN06	963	JJ06	813
JN07	913	JJ07	863
JN08	913	JJ08	763
JN09	863	JJ09	763
JN10	913	JJ10	763
JN11	813		

Table 5. Calculation results for the recharge elevation of the geothermal groundwater samples.

5.2. Deep Thermal Cycling Process

5.2.1. Deep Thermal Storage Water–Rock Equilibrium State

According to the distribution of the water sample points on the Na-K-Mg ternary diagram (Figure 6), the geothermal water samples in the study area all plot in the partially balanced and mixed water fields, and the water–rock interaction has not reached complete equilibrium. The reason for this is that cold water enters the thermal reservoir, and after

mixing with the hot water, the water–rock interaction has not reached equilibrium. The Ng geothermal water samples plot near the full equilibrium waterline, and the cation temperature scales can be used to calculate the thermal storage temperature.

Due to the lack of accurate aluminum content data for water quality analysis, in this article, the fixed aluminum method was used to calculate the mineral saturation index [51]. A Ng thermal water storage sample that tended to balance water and rock was selected from each of the four structural units in the study area (Figure 10): the Baoding depression (JN03), Gaoyang low uplift (JN06), Lixian slope (JN08), and Raoyang depression (JN10). Common minerals such as calcite, quartz, chalcedony, dolomite, potassium feldspar, and chlorite in the study area were selected [30]. PHREEQC software (Version 3.7.3) was used to simulate the saturation index of each mineral in the geothermal system at 0–200 °C. The temperature was plotted as the abscissa, and the saturation index (SI) was plotted as the ordinate. The relationship between the saturation index and temperature is shown in Figure 8. On the SI-T diagram, multiple mineral lines intersect with SI = 0, which is the predicted deep temperature value. Based on this method, the study area samples were predicted. The results are presented in Table 2. The Ng thermal storage temperature predicted using the multi-mineral equilibrium method is 71–99 °C, and the Jxw thermal storage temperature is 110–153 °C.



Figure 10. SI-T diagram for geothermal water.

5.2.2. Thermal Storage Temperature

By using various geothermal temperature scales to calculate the thermal storage temperatures of the sample points, it was found that when different temperature scales were applied to the same sample point, different thermal storage temperatures were obtained. The calculation of the thermal storage temperature based on each temperature scale and the actual temperature error value was carried out (Table 6). Based on the comparison diagram of the measured temperature and estimated temperature (Figure 11), it can be seen that the Na-K-Ca temperature scale and the multi-mineral equilibrium method yield overall temperature estimates that are the closest to the measured temperature. The average errors for these methods are 21.44 °C and 32.64 °C, respectively. The K-Mg temperature scale, quartz temperature scale, Na-K temperature scale, and chalcedony temperature scale yield

results that are relatively close to the actual temperature for the Ng thermal storage, but there is a significant deviation in estimating the Jxw thermal storage temperature. The average error in calculating the thermal storage temperature using the Ca-Mg temperature scale is 312.32 °C, which is larger than the measured temperature of the thermal storage in the study area, indicating that the scale is not applicable to the study area. Based on Table 6 and Figure 11, the Na-K-Ca temperature scale and multi-mineral equilibrium method have relatively small errors and are suitable for the southern region of the Jizhong Depression. However, when applied to geothermal development, some points still have significant errors. Further condition analysis of the temperature scale is needed to identify the appropriate methods to reduce the differences and provide a reliable reference basis for geothermal development.

No.	Temperature Scale Type	Error Range (°C)	Average Error (°C)
1	Na-k	$\pm 0.33 - 141.32$	57.52
2	Na-K-Ca	± 0.84 -68.26	21.44
3	K-Mg	$\pm 1.7 - 129.97$	50.06
4	Ca-Mg	$\pm 181.42 - 382.50$	312.32
5	Quartz	$\pm 8.35 - 210.81$	73.82
6	Chalcedony	$\pm 8.23 - 214.4$	53.73
7	SI Method	$\pm 1.00-72.3$	32.64

Table 6. Estimated and actual temperature error values of each temperature scale.



Figure 11. Comparison of measured temperature and estimated temperatures.

5.2.3. Thermal Cycle Depth

The North China Plain, where the Jizhong Depression is located, is a typical sedimentary basin-type geothermal resource area. The temperature of the geothermal water is positively correlated with the depth of the thermal storage cycle. The formula is as follows [52]:

$$\mathbf{H} = \frac{\mathbf{t}_1 - \mathbf{t}_2}{\mathbf{I}} + \mathbf{h} \tag{8}$$

where H is the depth of the thermal cycling (m); t_1 is the thermal storage temperature (°C); t_2 is the local annual average temperature (°C); I is the ground temperature gradient (°C/100 m); and h is the thickness of the constant temperature zone (m).

The average depth of the constant temperature zone in the research area is 25 m, the annual average temperature is 14.5 °C, and the geothermal gradient is 2.9 °C/100 m [26]. The calculation results of the K-Mg temperature scale presented in Table 2 were selected as the thermal storage temperature. The depth of the Jxw thermal storage cycle in the research area was calculated to be 3033–5187 m, with an average depth of 4268 m. The depth of the Ng thermal storage cycle was calculated to be 1360–2862 m, with an average depth of 2306 m.

5.3. Conceptual Circulation of the Thermal Waters

- Heat source: The destruction of the North China Craton causes thinning of the lithosphere and uplift of the Moho surface at the bottom of the depression, which is more conducive to the conduction of deep heat.
- (2) Thermal reservoirs: The research area contains multiple layers of high permeability thermal reservoirs in the Neogene Guantao Formation (Ng), while in the hidden bedrock uplift area, there are underlying thermal reservoirs in the Middle Neoproterozoic Jixian Wumishan Formation (Jxw), which contain abundant geothermal resources.
- (3) Channel: The structural pattern of the alternating concavity and convexity in the research area has formed large and deep faults, and the widely developed fractures in the deep carbonate thermal reservoirs provide good channels for the migration of groundwater and thermal conduction.
- (4) Cover layer: The thermal reservoir in the southern part of the Jizhong Depression is covered by a Neogene-Paleogene sandstone layer, which has a low thermal conductivity. The upper part is covered by the Quaternary system, and the lithology is mainly composed of clay and sand layers, which have a poor thermal conductivity. Therefore, the thermal insulation effect is significant. The research area is covered with a double insulation layer, which makes the heat of the thermal reservoir less likely to dissipate and provides a good insulation effect for the heat in the thermal reservoir.

The geothermal genesis model of the study area is as follows. The atmospheric precipitation in the Taihang Mountains infiltrates and migrates along the deep faults in front of the mountain. The thermal reservoir water is supplied laterally from northwest to southeast. After a long and slow flow process, it undergoes water–rock interaction with the surrounding rock, making the chemical composition of the thermal storage water complex. Due to the shallow Moho surface in the study area, the thermal flow in the rock and the radioactive heat generated in the rock continuously heat the groundwater, resulting in local thermal convection. The water temperature gradually increases as it flows through the rock, forming deep thermal storage resources. Under the influence of multiple tectonic activities, the large and deep faults formed in the area provide good water channels, and the hot water flows along the fault channels and transfers some of the heat upwards via convection, forming shallow geothermal resources. The overlying Neogene sandstone and Quaternary cover layer in the area have a low thermal conductivity, forming a good insulation cover layer and ultimately allowing for the development of a good geothermal resource area (Figure 12).



Figure 12. Genetic model for the geothermal water in the study area.

6. Conclusions

- (1) According to the geochemical and isotopic analyses of geothermal water samples from the study area, the hydrochemical types of the geothermal fluids in the sandstone thermal storage are mainly the Cl·HCO₃⁻Na type, while the geothermal fluids in the carbonate rock thermal storage are mainly the Cl-Na type and Cl·HCO₃⁻Na type. The content of the main ions (Na⁺, K⁺, and Cl⁻) in the water samples from the Jxw thermal storage is greater than that in the Ng thermal storage. The reason for this is that the Jxw thermal storage has a longer water cycle path, it experiences more complete leaching and filtration, and a large amount of soluble substances in the surrounding rock enter the hot water. According to the ion ratios, the components of the geothermal water are mainly controlled by dissolution and cation adsorption of the carbonate rocks. According to the calculated characteristic coefficients, the geological environment where the Jxw thermal storage is located is more enclosed than that of the Ng thermal storage, with a longer flow path, slower water circulation, and higher salinity.
- (2) By analyzing the hydrogen and oxygen isotope compositions of the thermal storage water in the study area, it was found that the main source of the Ng thermal storage water and shallow groundwater is atmospheric precipitation. The Jxw thermal storage water undergoes a more rightward oxygen drift compared to the Ng thermal storage water. This is due to the higher elevation of the deep Jxw thermal storage, which is recharged laterally from the distant high mountains, while the Ng thermal storage is recharged in a small amount in the lower altitude piedmont plain. The elevation of the geothermal water supply area in the research area is 763–1063 m, which is consistent with the elevation of the Taihang Mountains in the western part of the Jizhong Depression. It is speculated that the geothermal water is mainly supplied by precipitation in the mountainous areas of the western Taihang Mountains.

- (3) The measured temperature of the Ng thermal storage in the research area is 69.2–88 °C, and the measured temperature of the Jxw thermal storage is 82–100 °C. The Na-K-Ca temperature scale and the multi-mineral equilibrium method have relatively small errors and are suitable for the southern region of the Jizhong Depression, with average errors of 21.44 °C and 32.64 °C, respectively. The depth of the Jxw thermal storage cycle in the research area is 3033–5187 m, and the depth of the Ng thermal storage cycle is 1360–2862 m. The geothermal water sample is in partial equilibrium or is mixed water due to the entry of cold water into the thermal reservoir, and the water-rock interaction does not reach equilibrium after mixing with the hot water.
- (4) The geothermal genesis model for the study area is as follows. The precipitation in the Taihang Mountains infiltrates via faults and is supplied laterally from northwest to southeast. During the long-term runoff process, the groundwater undergoes waterrock reactions and changes in hydrochemical type and is continuously heated by the deep heat flow and radioactive heat from the rocks to form geothermal water. Some of the geothermal water forms thermal convection locally, while the rest is transferred upwards along the fault channel. Heat accumulation occurs in the structural bulge area, resulting in the formation of a convection–conduction-type geothermal system.
- (5) The bedrock thermal storage in the study area is widely distributed and has a great resource potential. Karst fissures are relatively well developed, but there are problems such as strong sealing of the geothermal water and long supply cycles. It is difficult to meet large-scale development needs by relying on natural supply. Therefore, the characteristics of the reservoir fissure development should be utilized, and artificial recharge should be conducted to achieve sustainable utilization of the thermal resources in this area.

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