Article

Recharge Sources and Genetic Model of Geothermal Water in Tangquan, Nanjing, China

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Abstract: This paper introduces a method to study the origin of geothermal water by analysis of hydrochemistry and isotopes. In addition, the genetic mechanism of geothermal water (GTW) is revealed. The study of the origin of geothermal water is useful for the sustainability of geothermal use. As an example, Tangquan is abundant in GTW resources. Elucidating the recharge sources and formation mechanism of the GTW in this area is vitally important for its scientific development. In this study, the GTW in Tangquan was systematically investigated using hydrochemical and isotopic geochemical analysis methods. The results show the following. The GTW and shallow cold water in the study area differ significantly in their hydrochemical compositions. The geothermal reservoir has a temperature ranging from 63 to 75 °C. The GTW circulates at depths of 1.8–2.3 km. The GTW is recharged by the infiltration of meteoric water at elevations of 321–539 m and has a circulation period of approximately 2046–6474 years. The GTW becomes mixed with the shallow cold karst water at a ratio of approximately 4–26% (cold water) during the upwelling process. In terms of the cause of its formation, the geothermal system in the study area is, according to analysis, of the low-medium-temperature convective type. This geothermal system is predominantly recharged by precipitation that falls in the outcropping carbonate area within the Laoshan complex anticline and is heated by the terrestrial heat flow in the area. The geothermal reservoir is composed primarily of Upper Sinian dolomite formations, and its caprock is made up of Cambrian, Cretaceous, and Quaternary formations. Through deep circulation, the GTW migrates upward along channels formed from the convergence of northeast–east- and north–west-trending faults and is mixed with the shallow cold water, leading to geothermal anomalies in the area.

Keywords: geothermal water; hydrogeochemistry; origin of geothermal water; genetic model

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1. Introduction

Geothermal resources, consisting of heat, minerals and water, are types of green resources [1,2]. The development of geothermal has been popular all over the world. However, geothermal water extraction without scientific planning will destroy geothermal resources, which will cause a decline of the hydraulic head and the reservoir temperature [3].

One famous hot spring is located in Tangquan, Nanjing, which north of the Yangtze River. The geothermal water (GTW) is quite abundant. With a discharge rate of 4590 t per day and a maximum temperature of 47 °C, the GTW in Tangquan contains over 30 trace elements beneficial to the human body. The development of geothermal resources in Tangquan began in the 1960s. By 2010, a series of geothermal and geological surveys, detailed surveys, and explorations had been conducted in this area. These efforts yielded a relatively deep understanding of the formation conditions and geological structures in this area, determined its geothermal zone, and provided preliminary estimates of the quantity of GTW resources. However, the temperature of the geothermal reservoir (T_R) and the

age, recharge source, circulation process, and formation mechanism of the GTW in this area have yet to be systematically investigated. In recent years, Tangquan Township has mounted vigorous efforts to build a hot spring resort and has unremittingly expanded the application and development scope of its GTW. As a result, hot springs have ceased to overflow at some locations during the dry season. Thus, further determination of the recharge sources and formation mechanism of the GTW in this area is an essential precondition for guiding its scientific development and sustainable utilization. Geothermal system modeling is an important means for analyzing the formation mechanism of GTW resources. China's hydrogeothermal resources can be categorized into convective geothermal resources in uplifted mountainous areas (volcanic and deep-circulation geothermal resources) and conductive geothermal resources in sedimentary basins (those in Mesozoic and Cenozoic graben basins, Mesozoic and Cenozoic depression basins, and Cenozoic depression basins), of which low-medium-temperature geothermal resources are the primary type [4]. Hydrochemical and isotopic geochemical methods are used extensively to study the recharge sources of GTW; determine whether groundwater (GW) originates from precipitation, magmatic water, or seawater [5]; calculate GTW recharge elevations; and analyze the mixing ratios of water from different types of sources [6]. These methods, combined with dating indices (e.g., ^{14}C), can be employed to further determine the age or recharge period of GTW. Based on a mixing model, Zhang et al. estimated that the T_R of the Gulu high-temperature geothermal system in Tibet ranged from 195 to 260 °C and that cold water was mixed at a ratio of 52–74% [7]. Ke et al. comprehensively studied the type of the geothermal system in the layered carbonate geothermal reservoir in an uplifted mountainous area at the Gujishan anticline in Beijing using geological and hydrochemical methods [8]. They found that the water in the geothermal reservoir originated from the karst fissure water in the dolomite of the Wumishan Formation of the Jixian System and that the geothermal reservoir was heated by the decay heat of radioactive elements from deep granitic masses. Yan et al. examined the characteristics and formation mechanism of the GTW resources in the basins in the basalt area of the Changbai Mountains based on stable D and O isotopes and geophysical survey data. They determined the heat source, the caprock, the geothermal reservoir, and the recharge source and circulation depth Z of the GTW [9]. Zhang and Yang et al. determined GTW recharge elevations and sources by comparing the linear relationships between the D and O isotopes in GTW and atmospheric precipitation [10,11].

This study examined the hydrochemical and environmental isotopic characteristics of the GTW in Tangquan and systematically analyzed the reservoir, caprock, source, and circulation conditions required for its formation to determine its formation mechanism and mode of occurrence, with the objectives of improving the understanding of the GTW system in Tangquan and providing a scientific basis for its sustainable development and utilization.

2. Materials and Methodology

2.1. Materials

The sampling campaign was implemented in April 2019; a total of 15 water samples were collected, including 6 GTW samples and 9 cold groundwater samples from civil wells. Figure 1 shows basic information about the sampling sites. All samples for hydrochemical analyses were filtered with a 0.45 µm membrane before bottling. Samples for cation analysis were acidified with ultra-purified HNO_3 to adjust the sample to $\text{pH} < 2$. A total of 60 mL of filtered water was collected into High Density Polyethylene (HDPE) vials for anion analyses. A total of 20 mL of filtered water was collected into screw-capped HDPE vials for stable $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses, whereas 1000 mL of unfiltered water was collected into screw-capped HDPE bottles for $\delta^{13}\text{C}$ and $\delta^{14}\text{C}$ analyses, 200 mL of water for $^{87}\text{Sr}/^{86}\text{Sr}$ analyses, and 1000 mL of water for $\delta^{34}\text{S}$ analyses. K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , and H_2SiO_3 were tested at the Nanjing Supervision and Testing Center for Mineral Resources. ^2H , ^{18}O , ^{87}Sr , ^{86}Sr , and ^{14}C were tested at the Ministry of Land and Resources of China

and the Institute of Geographic Sciences and Natural Resources Research at the Chinese Academy of Sciences.

Figure 1. Schematic diagram of tectonic structures and sampling sites in the study area (1: Overturned anticline; 2: Anticline; 3: Measured (inferred) normal fault; 4: Measured (inferred) reverse fault; 5: Measured (inferred) fault of undetermined nature; 6: Geothermal water (GTW) sampling sites and ID; 7: Cold groundwater (GW) sampling sites and ID).

2.2. Methodology

Quartz geothermometers were used in this study to calculate T_R . The circulation depth (Z) value of the geothermal fluid at each sampling site can be calculated based on T_R using the following equation [12]:

$$Z = Z_0 + (T_R - T_0) / \text{grad}T \quad (1)$$

where Z is the circulation depth (m), Z_0 is the depth of the constant-temperature zone (m), T_R is the temperature of the geothermal reservoir ($^{\circ}\text{C}$), T_0 is annual average the temperature of the constant-temperature zone ($^{\circ}\text{C}$), and $\text{grad}T$ is the geothermal gradient ($^{\circ}\text{C}/\text{hm}$).

The following equation shows how to calculate the GW recharge elevation based on the elevation effect of the ^{18}O isotope in precipitation [13]:

$$H = \frac{\delta^{18}\text{O}_{\text{GW}} - \delta^{18}\text{O}_r}{\text{grad}\delta^{18}\text{O}} + H_r \quad (2)$$

where H is the GW recharge elevation (m), $\delta^{18}\text{O}_{\text{GTW}}$ is the isotopic composition of the sample collected at the GW sampling site, $\delta^{18}\text{O}_r$ is the isotopic composition of the sample of precipitation at the reference site, $\text{grad}\delta^{18}\text{O}$ is the average gradient in the low-latitude southern region of China ($-0.3\text{‰}/100\text{ m}$) [14], and H_r is the ground elevation at the GW reference site (i.e., the Nanjing Observation Station of the GNIP) (26 m).

The mixing relationship between the GTW and the cold GW in the study area was examined using a binary mixing model based on Sr and $^{87}\text{Sr}/^{86}\text{Sr}$, as shown below [15–18]:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_m \times [\text{Sr}]_m = f \times \left(\left[\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right]_1 \times [\text{Sr}]_1\right) + (1 - f) \times \left(\left[\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right]_2 \times [\text{Sr}]_2\right) \quad (3)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})_m$, $(^{87}\text{Sr}/^{86}\text{Sr})_1$, and $(^{87}\text{Sr}/^{86}\text{Sr})_2$ are the Sr isotope ratios for the mixed sample, end member 1, and end member 2, respectively; $[\text{Sr}]_m$, $[\text{Sr}]_1$, and $[\text{Sr}]_2$ are the Sr

contents of the mixed sample, end member 1, and end member 2, respectively; and f is the mixing ratio for end member 1.

The age of the GTW in Tangquan was determined by ^{14}C using the following equation [19]:

$$t = -8267 \cdot \ln\left(\frac{\alpha_t}{\alpha_0}\right) \quad (4)$$

where α_0 and α_t are the initial ^{14}C activity and the ^{14}C activity after a time period t , respectively. However, the dissolution of carbonate minerals dilutes the initial ^{14}C activity of the dissolved inorganic carbon (DIC) in GW, resulting in an older ^{14}C age.

3. Results

3.1. General Information of Tangquan

Tangquan is located to the west of the main urban area of Nanjing and within the Yangtze Platform Fold Belt of the Yangtze Paraplatform. In terms of geotectonic elements, Tangquan encompasses low mountains and hills. All the hot springs and geothermal wells in Tangquan are distributed at the junction of the Laoshan Uplift and the Liuhe–Quanjiao Sag (Figure 1), where the terrain is high in the southeast and low in the northwest and faults and fissure structures have developed. The Laoshan complex anticline on the south side is distributed along the east–northeast (ENE) direction and covers an area of approximately 100 km². In addition, the highest altitude of the Laoshan complex anticline is 442 m at its main peak, Longdongshan (also known as Dalashan), and the altitudes of the remaining areas are mostly 180–390 m. The transition zone of the plain polder area sits at altitudes of 15–40 m. Outcrops of Upper Sinian dolomite and limy dolomite are present at the core of the Laoshan complex anticline and plunge to the piedmont hilly and plain area. With developed karst fissures and a relatively large thickness, this series of carbonate formations is the main geothermal reservoir being developed and used in the study area, which is overlain by thin-bedded Upper Cambrian dolomite, Upper Cretaceous silty and fine sandstone, and Neogene and Quaternary loose sedimentary formations.

In the study area, two main groups of faults control the Mesozoic and Cenozoic sedimentary characteristics and are closely related to the geothermal system. (1) ENE-trending Tangquan–Fanji Fault (F1). Located on the northwest side of Mount Laoshan, the Tangquan–Fanji Fault is a large normal fault that dips northwestward, cuts deep into the ground, and is composed of multiple parallel faults. (2) Northwest (NW)-trending Tangquan–Lulang Fault (F21) and East Tangquan–Jiangning Township Fault (F22). Formed in a relatively later period, this group of faults is large in size, cuts deep into the ground, and offsets earlier-formed northeast (NE)-trending faults. Figure 2 shows their planar locations [20].

Figure 2. Geological scheme of the study area (Z_{2d} —Sinian Dengying Formation; Z_{1h} —Sinian Huangxu Formation; E_3O_{1g} —Cambrian Guanyintain Formation; K_{2c} —Cretaceous Chishan Formation; K_{2p} —Cretaceous Pukou Formation; Q—Quaternary).

3.2. Hydrochemical and Isotopic Composition

Table 1 summarizes some of the test results. The temperatures of the GTW samples ranged from 32 to 46 °C (the temperature of sample H3 was relatively low due to an insufficient water discharge time).

Table 1. Hydrochemical and isotopic test data.

Sample ID	Depth m	Wellhead Temp °C	pH	Electric μs/cm	TDS mg/L	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	H ₂ SiO ₃	δD	δ ¹⁸ O
														‰	
H1	>200	37.0	7.04	2320	2794.00	6.77	12.4	682.0	102.0	5.55	301	1789	55.1	−54.9	−8.83
H2	>200	46.0	6.89	2350	2420.00	6.96	12.2	566.0	108.0	6.93	299	1523	60.2	−56.2	−8.71
H3	>200	22.0	8.30	979	776.00	3.60	11.8	174.0	33.9	20.8	134	444	20.3	−49.9	−8.00
H4	>200	32.4	7.02	1970	1954.00	4.92	12.0	464.0	84.4	6.93	332	1178	48.0	−54.3	−8.62
H5	>200	35.5	7.12	2030	1959.00	5.31	13.2	457.0	88.4	10.4	332	1180	46.8	−54.2	−8.74
H6	>250	41.4	6.96	2250	2513.00	6.38	12.6	541.0	98.9	6.93	314	1489	54.5	−55.8	−9.27
C1	12.00	15.8	7.68	1752	1610.00	4.79	21.7	368.0	71.2	41.6	343	904	32.6	−46.6	−7.85
C2	10.00	15.2	8.30	875	647.00	0.81	17.4	138.0	35.0	24.3	270	230	32.0	−46.8	−7.98
C3	10.00	14.8	7.83	820	524.00	61.80	50.5	66.5	21.3	54.1	339	75.5	30.0	−43.9	−7.58
C4	10.00	16.2	7.98	721	468.00	0.64	98.9	52.8	10.8	69.3	257	49.9	27.0	−46.0	−7.16
C5	10.00	14.6	7.30	498	312.00	1.63	21.7	58.6	22.1	41.6	157	62.9	31.9	−44.2	−7.69
C6	3.00	16.5	7.65	1012	694.00	2.93	63.6	126	32.7	70.7	389	139	35.3	−44.4	−7.47
C7	15.00	16.5	8.52	835	532.00	2.05	67.3	92.8	19.4	54.1	299	115	23.7	−42.9	−7.11
C8	6.00	16.2	8.58	798	478.00	4.10	46.6	84.5	23.0	61.0	213	96.4	36.2	−45.0	−7.14
C9	10.00	15.6	8.00	679	1335.31	3.39	66.4	57.2	20.5	61.0	163	69.8	42.4	−44.1	−7.30

3.2.1. Hydrochemical Composition

The Total Dissolved Solids (TDS) of the GTW ranged from 776 to 2794 mg/L, with an average of 2070 mg/L. Hydrochemically, the GTW was primarily of the SO₄-Ca type. The TDS of the cold GW was relatively low at 312–1610 mg/L, with an average value of 733 mg/L. The Piper diagram in Figure 3 shows the hydrochemistry of the GW in the study area. Hydrochemically, the cold GW was primarily of the SO₄-HCO₃-Ca/HCO₃-SO₄-Ca-Na type. Sampling site C1 was close to GTW well H1, which reaches to depths where carbonate rocks are distributed. As a result of the dissolution of carbonate rocks, hydrochemically, the sample collected from sampling site C1 was of the SO₄-Ca-Mg type.

Figure 3. Piper diagram of the hydrochemistry of different bodies of water in Tangquan.

As demonstrated by the hydrochemistry represented by the Piper diagram, the cold-GW sampling C1–C9 points are scattered and distributed in areas different from those where the GTW H1–H6 are distributed. These differences in hydrochemical composition show that the GTW and shallow cold GW undergo different reactions with rocks, and that the formation of deep GTW is not closely hydraulically linked with the shallow cold GW.

3.2.2. Estimation of the Geothermal Reservoir Temperature (TR) and Depth (Z)

The concentrations of the major elements in the GTW in a geothermal reservoir depend heavily on the temperature, the variation of which significantly affects the cationic ratios and the concentration of water-soluble SiO_2 in the GTW. Two main types of geothermometers are commonly used, namely cationic geothermometers (e.g., Na-K and Na-K-Ca geothermometers), which are obtained based on the relationship between the K-Ca-Na-Mg concentration ratio and the temperature [21–23], and SiO_2 geothermometers [24], which depend on the solubility of minerals (e.g., quartz and chalcedony) that control water-soluble SiO_2 . All the GTW samples collected from the study area fall into the immature water area on the Na-K-Mg ternary diagram shown in Figure 4. Thus, the GTW in the study area has not reached equilibrium with feldspar silicate minerals such as Na, K, and Mg silicate materials. This finding suggests that general cationic geothermometers, such as Na-K, K-Mg and Na-K-Ca, are unsuitable for the study area.

Thus, quartz geothermometers were used in this study to calculate T_R . Table 2 summarizes the calculation results. The T_R values calculated using the amorphous silicon, α -cristobalite, and β -cristobalite geothermometers are lower than those measured in the field. Some of these calculated T_R values are even negative and are therefore inconsistent with real-world conditions. The T_R values calculated using the chalcedony geothermometer are slightly higher than those at the mouths of the wells and are consistent with real-world conditions and thus are the most reliable. T_R in Tangquan, Nanjing, ranges from 63 to 75 °C, suggesting the presence of low-medium geothermal resources in normal geothermal background conditions. Well H3 was undisturbed prior to sampling in this study. The field sampling conditions precluded extraction of water for a protracted period of time. As a consequence, samples of hot water with a relatively low temperature (approximately

20 °C), which reached temperature equilibrium with the shallow water, instead of the in situ GTW, were collected. Thus, the T_R values measured in the field and those calculated using the chalcedony geothermometer are relatively low.

Figure 4. Giggenbach Na-K-Mg ternary diagram of the GTW.

Table 2. T_R values calculated using SiO_2 geothermometer/°C.

Sample ID	Wellhead Temp	Amorphous Silica	α -Cristobalite	β -Cristobalite	Chalcedony
		Fournier, 1977			
H1	37.0	−15	50	3	70
H2	46.0	−12	54	7	75
H3	22.0	−49	10	−33	27
H4	32.4	−20	44	−2	64
H5	35.5	−21	43	−3	63
H6	41.4	−16	50	3	70

According to the heat-flow data for the study area, $\text{grad}T$ is 2.4 °C/hm, Z_0 is 12–20 m, and the annual average temperature is 17 °C [25]. Thus, the GTW in the study area circulates at depths of approximately 1.8–2.3 km. Table 3 summarizes the calculation results.

Table 3. Z values for the GTW/m.

Sample ID	Depth/m
H1	2117
H2	2292
H3	417
H4	1854
H5	1807
H6	2096

3.2.3. Characteristics of Stable D and ^{18}O Isotopes

Fifteen isotope samples of D and ^{18}O were collected from the GW in the study area. The test data for the D and ^{18}O isotopes were plotted to show the δD – $\delta^{18}\text{O}$ relationship (Figure 5). The local meteoric water line (LMWL) was produced by linear regression of the isotope data for monthly precipitation (Lu et al. 2018) provided by the Nanjing Observation Station of the Global Network for Isotopes in Precipitation (GNIP). As demonstrated in Figure 5, the δD (‰) and $\delta^{18}\text{O}$ (‰) values for both the GTW and the cold GW fall near the global meteoric water line and the LMWL for Nanjing. This suggests that the GTW and the cold GW are primarily recharged by the infiltration of atmospheric precipitation.

Figure 5. δD – $\delta^{18}\text{O}$ relationship for the water samples collected from Tangquan.

The δD and $\delta^{18}\text{O}$ values for the GTW range from -42.89‰ to -53.21‰ and from -7.11‰ to -8.40‰ , respectively. The projected points are located in the lower left section in Figure 5. This result suggests that the GTW is recharged by the infiltration of atmospheric precipitation at relatively high elevations and with more depleted δD and $\delta^{18}\text{O}$ values and is tenuously linked with the shallow cold GW.

Table 4 summarizes the calculated GW recharge elevations. The elevation calculated for the sample collected from well H3 is relatively low due to the mixing of cold GW and is unable to reflect the real-world recharge elevation. The recharge elevations calculated for the remaining samples range from 321 to 539 m, which are close to the elevation of the main body of Mount Laoshan.

Table 4. Calculated GTW recharge elevations in Tangquan/m.

Sample ID	$\delta^{18}\text{O}/\text{‰}$	$\delta^2\text{H}/\text{‰}$	Recharge Elevation/m
H1	−8.83	−54.9	392
H2	−8.71	−56.2	354
H3	−8.00	−49.9	116
H4	−8.62	−54.3	321
H5	−8.74	−54.2	362
H6	−9.27	−55.8	539

3.2.4. Mixing Ratio for a Mixing Model Based on Sr and $^{87}\text{Sr}/^{86}\text{Sr}$

GTW inevitably mixes with shallow cold GW during the upwelling process [26]. The aforementioned results reveal a certain mixing effect between the GTW sample collected from well H3 and the cold GW.

Karst GTW is insubstantially linked and highly unlikely to mix with fissure water in clastic rocks. However, it is possible that karst GTW becomes mixed with shallow cold karst water during the upwelling process. Here, the sample ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709417$, $\text{Sr} = 1060 \mu\text{g/L}$) collected from sampling site C2 near the GTW is treated as a cold-water end member. In addition, the sample with the highest temperature and the highest Sr content of all the GTW samples (i.e., the sample collected from well H2) is treated as a hot-water end member. The above mixing model was used to calculate the mixing ratios for the other GTW samples. Table 5 summarizes the calculation results. The cold-water mixing ratio (87%) for the sample collected from well H3 is the highest. This result agrees with the aforementioned analysis. The cold-water mixing ratios for the other samples are relatively low (<30%).

Table 5. Calculated mixing ratios for the GTW samples collected from Tangquan.

Sample ID	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr /($\mu\text{g}\cdot\text{L}^{-1}$)	Thermal Water Fraction	Cold Water Fraction
H1	0.708876	4890	96%	4%
H2	0.709041	5060	100%	0%
H3	0.709299	1580	13%	87%
H4	0.708916	4100	76%	24%
H5	0.708901	4020	74%	26%
H6	0.708997	4740	92%	8%

3.2.5. Age of the GTW

Figure 6 shows the $\delta^{14}\text{C}$ – $\delta^{13}\text{C}$ relationship of the GTW in the study area. Overall, there is a negative correlation between $\delta^{14}\text{C}$ and $\delta^{13}\text{C}$, demonstrating the dilution effect of the dissolution of carbonate minerals. In this study, the Pearson model, which takes into consideration the isotopic fractionation of CO_2 and DIC in soils [27], was employed to correct the ^{14}C age. Table 6 summarizes the calculation results. As demonstrated in Table 6, the GTW in the study area is relatively old, with an age varying from 2046 to 6474 aBP. As a result of its mixing with cold water, the age of the sample collected from well H3 is relatively young. Based on the calculated T_R as well as the locations of the wells, the age of the sample collected from well H3 should be similar to that of the sample collected from well H1 [28,29].

Table 6. Corrected ^{14}C ages of the GTW/aBP.

Sample ID	^{13}C /‰ VPDB	^{14}C /pMC	Uncorrected	Pearson Model No. 2
H1	−3.8	11.06	18,203	6474
H2	−2.03	8	20,880	3709
H3	−2.99	35.49	8564	Modern water
H4	−5.09	25.15	11,411	2046
H5	−5.69	24.28	11,702	3417
H6	−4.43	13.11	16,797	6206

Figure 6. $\delta^{14}\text{C}$ – $\delta^{13}\text{C}$ relationship of the GTW.

4. Discussion

4.1. Analysis of the Heat Source

The terrestrial heat flow rate in Tangquan is approximately $58\text{--}62 \text{ mW/m}^2$, which is close to the arithmetic mean ($61.5 \pm 13.9 \text{ mW/m}^2$) of heat flow rate measurements for Mainland China [30]. The geothermal gradient in Tangquan is approximately $24 \text{ }^\circ\text{C/km}$. According to the temperature measurements obtained by drilling in adjacent areas, in the study area, $Z_0 = 12\text{--}20 \text{ m}$ and $T_0 = 17 \text{ }^\circ\text{C}$.

In the following section, radioactive heat sources are discussed. Let us assume that radioactive elements are uniformly distributed in the topmost 10 km of the Earth's crust. The upper limit A of the average heat generation rate of the Earth's crust in the study area is $1.6 \text{ } \mu\text{W/m}^3$ [31]. Thus, the upper limit of the heat generated by radioactive decay within the topmost 10 km of the Earth's crust is as follows: $\Delta q = A\Delta z = 16 \text{ mW/m}^2$ [11]. The average heat generated by the decay of radioactive heat sources will be even lower. Thus, radioactive heat sources do not constitute special heat sources of the geothermal system in the study area.

In addition, there are no young magmatic intrusions within the shallow crust in the study area. Thus, there are no additional heat sources, such as magmatic heat. The contribution of the mechanical frictional heat generated by active faults and earthquakes to the terrestrial heat flow is extremely low and can be considered negligible. Thus, the geothermal system in Tangquan is of the nonvolcanic type and is heated by normal terrestrial heat flow. As a result, within the accessible depth (3 km), the conditions required for forming high-temperature geothermal resources are lacking, and the geothermal resources are low-temperature resources ($<90 \text{ }^\circ\text{C}$).

4.2. Geothermal Reservoirs and Caprock Conditions

The Sr isotope ratio of the GTW in Tangquan, Nanjing, ranges from 0.708876 to 0.709299, with an average of 0.709005. This result suggests that the GTW primarily flows through carbonate (Sr isotope ratio = 0.708–0.710) formations [32]. As the main constituent of the main body of Mount Laoshan, Upper Sinian dolomite, which is rich in carbonate minerals, outcrops in the middle of Mount Laoshan and becomes concealed in the piedmont zone at a depth that gradually increases northwestward from the piedmont zone. From the perspective of geological development, during the Late Sinian, the sedimentary dolomite of

the Dengying Formation was elevated and underwent regression as a result of the Tongwan Movement and was subsequently subject to weathering and erosion. In addition, the Earth's crust was intensely active during the Mesozoic. This series of carbonate formations underwent multiple episodes of fault activity, uplifting, erosion, and karstification during the Yanshanian period [33]. This process led to the development of karst fissures, which are favorable spaces for storing fluids.

At the northern foot of Mount Laoshan, a series of ENE-trending, NW-dipping tectonic fault zones with the downthrown side to the north have developed. In this area, sandstone sediments of the Cretaceous Chishan and Pukou Formations have been deposited, and their thickness increases northwestward. The abovementioned clastic assemblage and Quaternary loose sedimentary formations have a low permeability and a low thermal conductivity (generally 0.71–0.92 W/m°C), which is far lower than that (2.01 W/m°C) of limestone (dolomite), and can form good caprocks for geothermal reservoir aquifers [20,28].

4.3. Tectonic Control

Tangquan is located on the southeastern margin of the Liuhe–Quanjiao Sag within the Mesozoic Fault Depression. The mountains south of Tangquan are a complex anticline structure composed of the Sinian formations of the Laoshan Uplift. The ENE-trending faults that control the distribution of the geothermal water wells in Tangquan are relatively large in size and are offset by later-formed NW-trending faults. These faults jointly form a tectonic framework that stores and diverts water and heat. The fracture zone is formed from the convergence and cutting of the nearly EW-trending Tangquan–Fanji Fault Zone (F1) and the NW-trending Tangquan–Lulang Fault (F21); the East Tangquan–Jiangning Township Fault (F22) is the main channel for the GTW and home to the majority of the existing geothermal water in Tangquan.

In addition, the GTW in the middle of Mount Laoshan is recharged at relatively high elevations (321–539 m), which differ relatively considerably (by approximately 40 m) from those (281–499 m) of the hot spring discharge zone in Tangquan. The resulting hydraulic pressure difference causes subsequent forced circulation of the infiltrated water.

4.4. Genetic Model

The geothermal resources currently being developed and used in Tangquan, Nanjing, are from a low-medium-temperature convective geothermal system. There are no local special heat sources in the shallow crust. Under the normal geothermal background of the area, the GW brings deep heat to the discharge zone on the north side of Mount Laoshan through deep circulation.

Atmosphere precipitation infiltrates in the outcropping carbonate area of Mount Laoshan and subsequently recharges the GW. The infiltrated water penetrates deep into the solution fissures in the Upper Sinian dolomite and tectonic fractures as it continuously absorbs heat from the rocks and gradually becomes heated. At a depth of 2.3 km, the infiltrated water reaches a temperature of approximately 75 °C, forming a deep geothermal reservoir. In addition, the infiltrated water reaches chemical equilibrium with the deep surrounding rocks during the prolonged seepage process. Eventually, GTW of the SO₄-Ca type is formed. The ENE- and NW-trending tectonic faults on the north side of Mount Laoshan and their combinations form upwelling channels for the GTW. As a result of the hydraulic pressure difference, the GTW rises and becomes mixed with the shallow cold karst water in the discharge zone where the faults meet. The ENE- and NW-trending tectonic faults on the north side of Mount Laoshan and their combinations form upwelling channels for the GTW. As a result of the hydraulic pressure difference, the GTW rises and becomes mixed with the shallow cold karst water in the discharge zone where the faults meet. The mixed water forms a geothermal reservoir due to obstructions by upper low-permeability formations (e.g., Cretaceous and Quaternary formations) or rises to the surface and forms hot springs at locations where the caprock is discontinuous. Based on

the above analysis, a genetic model is proposed for the geothermal system in Tangquan, Nanjing, as shown in Figure 7.

Figure 7. Schematic diagram of the proposed genetic model for the geothermal system in Tangquan, Nanjing (1: Quaternary clay; 2: Sandstone of the Cretaceous Chishan Formation; 3: Argillaceous sandstone of the Cretaceous Pukou Formation; 4: Thin-bedded dolomite of the Cambrian Guanyintain Formation; 5: Karstified dolomite of the upper segment of the Sinian Dengying Formation; 6: Karstified dolomite of the lower segment of the Sinian Dengying Formation; 7: Migration of cold water; 8: Migration of hot water; 9: Mixing of hot and cold water; 10: Terrestrial heat flow; 11: Inferred fault; 12: Hot spring).

5. Conclusions

- (1) The temperature of the GTW in Tangquan, Nanjing, ranges from 32 to 46 °C. Thus, the GTW in this area is low-temperature hot water. Hydrochemically, the GTW in Tangquan is of the SO₄-Ca type. T_R ranges from 63 to 75 °C. The GTW circulates at depths of 1.8–2.3 km.
- (2) The GTW in the study area originates from meteoric water, has a depleted D and O isotopic composition compared to the cold GW, and is recharged at elevations of 321–539 m, close to the elevation of the main body of Mount Laoshan. During the upwelling process, the GTW becomes mixed with the shallow cold karst water at a ratio of approximately 4–26% (cold water). At a relatively low cold-water mixing ratio, the temperature of the GTW is relatively high, and vice versa. The age of the GTW in the study area is approximately 2046–6474 a.
- (3) The geothermal system in the study area is of the low-medium-temperature type. Atmospheric precipitation infiltrates in the high-elevation outcropping carbonate area of the Laoshan complex anticline and flows mainly through Upper Sinian dolomite formations. Under the background of the normal terrestrial heat flow, the infiltrated water is gradually heated by the surrounding rocks. Through long-term deep circulation, the GTW rises in the relatively low-lying area on the northwest side of Mount Laoshan, where the ENE- and NW-trending faults meet. During the upwelling process, the GTW becomes mixed with some shallow cold karst water. The mixed water forms a geothermal reservoir overlain by Cretaceous and Quaternary formations or rises to the surface at locations where the caprock is discontinuous and forms geothermal anomalies in the study area.
- (4) In order to ensure the sustainable development and utilization of GTW, it is suggested to further strengthen the dynamic monitoring of groundwater and the control of extraction amounts. A comprehensive plan for cascading development and utilization

should be established—mainly for medical treatment, tourism, and bathing—and the management mode of GTW should be improved.

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