Research Article

Fault-Affected Fluid Circulation Revealed by Hydrochemistry and Isotopes in a Large-Scale Utilized Geothermal Reservoir

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A new significant aspect in the utilization of hydrothermal energy in China is the large-scale exploitation using multiwells from a single geothermal site. This requires detailed hydrogeochemical investigations to gain insight about deep groundwater circulation. At the Xiongxi karst geothermal site in North China, where the demonstration project of large-scale utilization was conducted, 40 boreholes with depths from 1000 to 1800 m were drilled in a region of 50 km². A total of 25 water samples were collected, and temperature loggings were conducted in 16 of these wells. At the site scale, the hydraulic head was observed to decline from SW to NE, i.e., orthogonal to that at the regional scale. Moreover, the geothermal groundwater temperature, borehole temperature gradient, and heat flow in the caprock all exhibited the same spatial trend with the groundwater head. Based on the hydrogeochemical and temperature logging data, this was explained by mixing of lateral recharging groundwater with ascending thermal fluids through the Xiongxi Fault, after excluding the causes of pumping activities and geologic structure. In addition, geothermal groundwater ⁸¹Kr age was estimated to be approximately 760 kyr, which is much older than the ¹⁴C age of 20 to 30 kyr. The older ⁸¹Kr age implies a low renewability of deep groundwater circulation, which should be considered in terms of sustainable management in relation to the large-scale utilization of geothermal resources.

1. Introduction

The geothermal energy from the hydrothermal systems (hydrothermal energy) has been utilized by mankind since its existence [1]. The utilization of hydrothermal energy is undergoing a rapid development, and steady growth can be further expected in China [2]. In January 2017, the National Energy Board released the “13th Five-Year Plan” of China, where a target on the total development and utilization capacity of geothermal resources of 70 Mt standard coal by 2020, based on approximately 20 Mt standard coal in 2015, was reported. Large-scale utilization of hydrothermal energy in a specific geothermal field was one of the main achievements.

The following several issues must be considered to achieve sustainable use of large-scale hydrothermal energy: (1) long-

term return on investment, (2) maintenance of groundwater temperature and level related to exploitation and injection, and (3) geological hazards of subsidence and/or seismic events resulting from pumping and injection activities.

Deep karst aquifers are ideal targets for the large-scale utilization of geothermal energy due to their favorable characteristics, such as high well yield, low salinity, easy reinjection, and minor environmental impacts [3, 4]. Although geotemperature, reservoir, and caprock features could be measured directly, the water source and its flow path are difficult to delineate. Hot water in the karst aquifer may be supplied by the lateral recharge and ascending deep fluids through transmissible pores and fractures or faults [5]. Among these origins, the up-flowing deep fluids generally have high temperatures and could significantly warm up the overlying

aquifers [6, 7]. However, due to the complex geometry of geological stratification in the karst reservoirs, it is difficult to identify the groundwater origins and their flow paths. In this regard, hydrochemical data and isotopic information are very helpful [8], considering that they are critical in evaluating the long-term behavior of the karst aquifer system.

The hydrothermal energy exploitation at the Xiongxian karst geothermal site is the demonstration project of hydrothermal energy utilization in China [9, 10]. In Xiongxian, approximately 2.8 million m² (more than 90%) of the total heating area is supplied with hydrothermal energy (Zheng et al., 2015; [11]). Xiongxian is located on top of the Niutuozen Uplift of Bohai Bay Basin (BBB) (Figure 1(a)). The reservoir is composed by midtemperature karst bedrock with a large amount of fractures (Figure 1(b)), allowing groundwater flow to modify the heat distribution [12]. Wang et al. [13] and Chen et al. [14] concluded that the heat flow in the North China Plain (NCP, the main part of BBB) generally has higher values in the uplift and lower values in the depression. The Hydrogeology and Engineering Geology Group in Hebei Province built a conceptual model for groundwater flow in the Niutuozen Uplift based on geological and geochemical data [15]. They concluded that geothermal groundwater in the Niutuozen Uplift was mainly fed via the precipitation in the Taihang and Yanshan Mountains, and that it had a regional flow pattern from northwest to southeast. Pang et al. [10] found that the mantle-derived heat fraction at the surface heat flow in the Niutuozen Uplift accounted for 48 to 51%, using the gas ³He/⁴He values from 0.24 to 0.60 Ra. They further discussed the hydrochemical difference between the groundwater in the sandstone and karst reservoirs. However, for the sustainable utilization of geothermal energy in this region, knowledge on the deep groundwater circulation inside the karst reservoir, the main reservoir for exploitation, is required. Although the Xiongxian karst reservoir has already been exploited for more than 30 years, large-scale utilization was initiated only in 2009. More than 40 boreholes (approximately 25 production wells and 15 reinjection wells), with depths ranging from 1000 to 1800 m, were installed in a region of 50 km² in the karst geothermal field. Until now, there have been no detailed investigations on the groundwater inside the reservoir and hydrochemical data have not been systematically acquired.

In this study, we conducted detailed temperature logging and hydrochemical and isotopic analysis of water samples at the Xiongxian site. Two different isotopes of old groundwater dating, including carbon-14 (dating age of <50,000 years) and krypton-81 (dating age of >50,000 years albeit less than 1 million years), were utilized in assessing the renewability of geothermal groundwater. The main objectives of this study are to (1) characterize the hydrochemistry of geothermal groundwater at the Xiongxian sector of the Niutuozen Uplift and (2) present a conceptual model of fluid circulation of the study area.

2. Geological and Hydrogeological Background

Xiongxian is located 108 km to the south of Beijing, 100 km west of Tianjin, and in the NW sector of the BBB (see

Figure 1(b)). The Xiongxian sector is located in the SW region of the Niutuozen Uplift, which is to the N of the Jizhong Depression (Figure 1(b)), the latter being part of one of the major petroleum and gas producing areas in eastern China. It covers both the coastal regions around the Bohai Bay and the Bohai Bay itself. Altogether, its total area is approximately 200,000 km². It is a large Mesozoic-Cenozoic intracratonic sedimentary basin filled with Paleocene, Neogene, and Quaternary continental sediments. It was formed in the Tertiary on the basement of the North China Platform, and it consists of several separate Paleogene faulted depressions. During the Neogene period, the whole area subsided to form a single large depression [16].

The boundary of the Niutuozen Uplift consists of four main faults (Figures 1(c) and 2), i.e., the Niudong Fault in the E, the Niunan Fault in the S, the Rongcheng Fault in the SW, and the Daxing Fault in the NW. They were formed by folding movement from the Late Jurassic to the Cretaceous periods, during the Himalayan orogenesis, and all these faults reach the crystalline basement.

The Xiongxian Fault sits in the W of Xiongxian (Figure 1(d)) and cuts through the karst strata to the crystalline basement. It is an inferred normal inclined fault striking NW and dipping SW with an angle of approximately 45°. The throw (vertical displacement) of the fault is approximately 600 m whereas the heave (horizontal displacement) is approximately 500 m.

From the surface downwards, the Niutuozen Uplift is characterized by Quaternary alluvial sandstones and clays, Neogene fluvial and inland lacustrine sandstones, Eocene inland lacustrine sandstones and clays, Cambrian-Ordovician marine carbonates, Proterozoic (Jixian and Changcheng) dolomites, and the Archean basement, which consists of gneiss, granulite, and quartzite (Figure 2). In the Xiongxian sector, the Eocene units were missing due to erosion processes, and thus, the Jixian formation (with a thickness more than 1500 m) was directly overlaid by Neogene (with thicknesses ranging from approximately 500 to 600 m) and Quaternary deposits (with thicknesses ranging from approximately 400 to 500 m). The dolomite rocks belonging to the Jixian formation were exposed at the surface, and consequently, they suffered multikarstification stages that increased their permeability.

The geothermal reservoirs in the Xiongxian region are porous Neogene sandstone and Jixian karst-fissured dolomite bedrock. In this study, we focused on the karst aquifer because it is the main geological formation exploited for geothermal energy production in Xiongxian.

3. Materials and Methods

3.1. Borehole Logging. In the Xiongxian region, geothermal fluid produced from the karst reservoir is utilized for space heating from November 15 to March 15. To avoid the interruption of groundwater extraction, the hydrothermal logging was carried out in Xiongxian in June and October 2013. The DS 200 borehole logging system was used to measure the temperature with a precision of 0.1°C. Temperature readings were recorded every 0.05 m. The drop of the temperature sensor was controlled at a speed ranging between 6.5 and

FIGURE 1: (a) Location of Bohai Bay Basin (BBB) in China; (b) location of Niutuozen Uplift in the BBB; (c) location of Xiong-xian geothermal sector in the Niutuozen Uplift (cross section A–A' and the color legend are depicted in Figure 2); (d) location of all water samples including cold groundwater and geothermal groundwater.

7.5 m/min, to allow thermal equilibrium between the sensor and groundwater. In June, a total of 16 wells were measured from zero to approximately 1000 m in depth, whereas in October, three wells (i.e., XH02, XH05, and XH08) were measured from zero to more than 1400 m in depth. The temperature logging data and computed geothermal gradient (43.9 to 72.2°C/km) and heat flow (66.55 to 95.99 mW/m²) were reported by Li et al. [17]. The hydraulic head was obtained through the temperature profile because the temperature suddenly increased when the sensor reached the water table.

3.2. Water Sampling and Analysis. In total, nine geothermal and thirteen cold water samples were collected from Xiong-xian in March 2013 (Table 1). In addition, to compare the hydrochemistry of groundwater on both sides of the Xiong-xian Fault, two geothermal waters on the west of Xiong-xian Fault were also collected. The cold aquifer was sampled from the Quaternary deposits whereas the geothermal water was collected from the Jixian karst aquifer. The sampling depth (between 60 and 1800 m) is also listed in Table 1. The casing

was installed inside the cold groundwater boreholes, whereas the geothermal boreholes were not encased in the Jixian aquifer. Near the geothermal production wells, there were reinjection wells. The reinjected water remained as the geothermal water even after it flowed through the 3 μm filter devices and heat exchangers. Therefore, its dissolved ions were left unchanged. Prior to the water sampling, the wells were pumped for approximately 30 min until both the electrical conductivity (EC) and temperature were stable. All the samples were filtered in situ at 0.23 μm prior to collection in HDPE bottles and sealed using parafilm. Samples for the determination of major cations and trace elements were preserved with 6 N of subboiled HNO₃ with pH of less than 2.0. Meanwhile, the unacidified samples were collected for anion and water isotopes.

Temperature, pH, dissolved oxygen (DO), Eh, and EC were measured in the field. The samples were later analyzed at the Water Isotopes and Water–Rock Interaction Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences. δ²H and δ¹⁸O were measured using laser absorption water isotope spectrometer analyzer (Picarro L2120-i).

FIGURE 2: Cross section A-A' of the Xiongxiian geothermal sector (depth unit: m; revised based on [15]).

All $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were expressed in relation to the Vienna Standard Mean Ocean Water (V-SMOW) in ‰. The measurement precisions were $\pm 0.5\text{‰}$ and $\pm 0.1\text{‰}$ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, respectively. The water chemistry was completed through ion chromatography in the Analytical Laboratory of Beijing Research Institute of Uranium Geology. Cations were determined according to the National Analysis Standard DZ/T0064.28-93, whereas the anions were determined using DZ/T0064.51-93. Alkalinity was measured using an automatic titrator (785 DMP™). Analytical precision was $\pm 3\%$ of concentration based on the reproducibility of samples, and the detection limit was 0.1 mg/L. The trace elements were determined through ICP-MS (7500C, Agilent), with analytical precision less than 0.5%. The carbon isotopic compositions (i.e., ^{14}C and ^{13}C) were determined by Beta Analytic, Inc., using accelerator mass spectrometry (AMS) and isotope ratio mass spectrometry (IR-MS), respectively. The analytical precision for the AMS ^{14}C results was $\pm 0.1\%$. The ^{14}C ages were corrected using the $\delta^{13}\text{C}$ mixing model (Clark and Fritz, 1997):

$$t = -8267 \cdot \ln \left(\frac{C_t}{q \cdot C_0} \right), \quad (1)$$

$$q = \frac{\delta^{13}\text{C}_t - \delta^{13}\text{C}_d}{\delta^{13}\text{C}_s - \delta^{13}\text{C}_d}, \quad (2)$$

where t is the groundwater age; C_t is the measured ^{14}C activity; q is the correction factor; and $\delta^{13}\text{C}_t$, $\delta^{13}\text{C}_d$, and $\delta^{13}\text{C}_s$ represent the measured $\delta^{13}\text{C}$ values for the groundwater, the dissolved calcite (0‰), and soil (-23‰), respectively.

To compare with the ^{14}C age, the dissolved gas samples for radio-krypton (^{81}Kr) analysis were collected from two geothermal wells through vacuum cylinder extraction method

[18–20] in March 2018. The gas was processed and purified in the laboratory to produce pure krypton for analysis. According to Yang et al. [21] and Li et al. [18], the abundance ratios of purified $^{81}\text{Kr}/\text{Kr}$ were analyzed through Atom Trap Trace Analysis at the University of Science and Technology of China. All the measured data are listed in Table 1.

4. Results

4.1. Local Hydrothermal Pattern. The geothermal borehole logging data were used to show the local hydrothermal pattern. In the studied region (less than 50 km^2), the plain was very flat. The difference between the ground altitudes of each well was less than the uncertainty of altitude measurement. Therefore, we were able to assume that all the wells have the same ground altitude and that the water table could be used to indicate the direction of groundwater flow. Figure 3 illustrates that the groundwater table declined from SW to NE, whereas the direction of local groundwater flow was orthogonal to the direction of regional groundwater flow, which is from NW to SE. Similar to the local groundwater table pattern, groundwater wellhead temperature declined from SW (80.1°C) to NE (61.6°C) (Figure 3). Based on the logging and collected data reported by Li et al. [17], the temperature gradient and heat flow in the caprock were calculated as 43.9 to $72.2^\circ\text{C}/\text{km}$ and 66.55 to $95.99\text{ mW}/\text{m}^2$, respectively (Figure 4). Temperature gradient and heat flow in the SW of the Xiongxiian geothermal site were higher than those in the NE, thereby resembling the spatial variation of the water table.

4.2. Water Chemistry. The cold and geothermal waters from the Quaternary aquifer and the deep Jixian karst aquifer, respectively, are plotted in Figure 5.

With regard to the cold groundwater, they were dispersed in the Piper diagram with large variability (Figure 5 and

TABLE 1: Isotopic and chemical data at the Xiongxi and Rongcheng geothermal sites.

Sample label	WD (m)	pH	T (°C)	EC (μ S/cm)	Li (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	SiO ₂ (mg/L)	B (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	$\delta^{13}\text{C}$ (‰)	^{14}C (pmc)	^{81}Kr (pm Kr)
XH01	1500	8.0	61.6	4730	1.75	821.0	52.5	44.8	30.9	31.5	1.80	1129.0	1.0	695.0	-8.5	-73	-5.3	1.1 $\pm$ 0.1	10 $\pm$ 1
XH02	1500	8.0	63.5	4570	1.60	822.0	48.3	48.7	20.4	37.1	4.68	1129.0	1.2	658.0	-8.5	-73	-6.0	1.7 $\pm$ 0.1	
XH03	950	8.0	67.3	4780	1.59	858.0	52.7	59.5	23.5	34.1	4.26	1121.0	9.7	684.0	-8.6	-73			
XH04	1500	7.5	71.1	4660	1.58	852.0	48.4	48.4	19.6	37.3	3.32	1134.0	0.9	666.0	-8.4	-73			
XH05	1800	8.0	72	4690	1.66	812.0	48.8	45.5	20.9	37.9	5.10	1106.0	2.4	668.0	-8.4	-73			
XH06	1600	8.0	74.6	4640	1.71	871.0	53.9	49.7	23.2	38.8	5.10	1140.0	1.8	663.0	-8.5	-73	-7.7	1.4 $\pm$ 0.1	
XH07	1700	8.0	80.1	4630	1.74	870.0	52.2	51.0	17.7	46.1	5.27	1090.0	3.4	636.0	-8.5	-73	-8.1	1.4 $\pm$ 0.1	
XH08	1600	7.0	76.2	4400	1.53	870.0	53.2	50.4	19.9	42.2	5.09	1141.0	5.2	645.0	-8.5	-72			
XH09	1000	7.0	>60	4700	1.67	929.0	47.7	42.7	21.3	40.5	4.61	1284.0	0.8	487.0	-8.9	-74	-7.5	2.1 $\pm$ 0.1	10 $\pm$ 1
RH01	1028	8.0	56	4270	1.05	769.0	40.0	61.0	25.7	31.5	2.12	1069.0	1.8	677.0	-8.6	-73	-8.9	1.3 $\pm$ 0.1	
RH02	1851	7.0	48.5	3900	1.25	692.0	36.9	55.2	25.9	27.2	4.44	941.0	2.7	658.0	-8.6	-73			
XC01	200	7.0	<20	687	0.01	119.0	0.4	20.1	10.1	13.2	0.04	54.0	55.3	249.0	-10.6	-80			
XC02	200	6.5	<20	890	<0.01	114.0	0.4	10.4	4.3	12.5	0.04	35.0	35.3	236.0	-10.8	-82			
XC03	200	6.5	<20	567	<0.01	113.0	0.6	12.0	3.9	12.8	0.04	33.0	32.5	236.0	-10.9	-81			
XC04	200	6.5	<20	556	<0.01	85.9	0.6	19.5	6.8	13.4	0.01	41.0	35.6	206.0	-11.1	-83	-13.1	15.5 $\pm$ 0.1	
XC05	200	7.0	<20	424	<0.01	84.1	0.5	10.4	3.3	13.2	0.03	15.0	32.2	194.0	-11.1	-84			
XC06	200	7.0	<20	488	<0.01	85.4	0.4	9.5	3.1	12.9	0.03	18.0	31.8	193.0	-11.3	-84			
XC07	200	6.5	<20	865	0.01	127.0	1.3	33.0	10.9	13.3	0.03	133.0	53.4	210.0	-10.9	-82			
XC08	200	7.0	<20	729	0.01	117.0	0.7	28.0	9.4	13.7	0.04	85.0	52.1	223.0	-11.1	-83			
XC09	300	6.5	<20	360	<0.01	53.2	1.0	15.0	7.0	13.5	0.02	6.0	21.9	194.0	-11.3	-82	-13.1	7.7 $\pm$ 0.1	
XC10	60	7.0	<20	1001	0.01	90.8	0.5	44.6	56.1	16.1	0.13	56.0	73.7	493.0	-9.7	-70			
XC11	80	6.5	<20	750	<0.01	71.2	0.5	45.0	39.2	15.9	0.12	13.0	25.1	467.0	-8.9	-66			
XC12	280	6.0	<20	325	<0.01	35.6	0.9	24.4	9.8	16.9	0.03	2.0	9.2	212.0	-10.6	-76			
XC13	100	6.5	<20	730	0.01	28.3	1.6	68.1	49.2	20.6	0.06	57.0	33.0	372.0	-8.5	-62	-17.1	50.0 $\pm$ 0.2	

Note: WD represents well depth.

Table 1). The total dissolved solids (TDS) of cold groundwater ranged from 0.2 to 0.6 g/L, and their water type was Na-HCO₃. The pH was between 6 and 7. The principal cation of this group was Na⁺ (28.3–127.0 mg/L), while K⁺ (0.4–1.3 mg/L) was very low. The principal anion was HCO₃⁻ (28.3–127.0 mg/L), whose concentration was greater than SO₄²⁻ (9.2–55.3 mg/L) and Cl⁻ (2.0–133.0 mg/L).

With regard to the geothermal groundwater, they are located in the alkali corner of the Piper diagram (Figure 5). The TDS of geothermal groundwater in karst aquifers was between 1.9 and 2.6 g/L, and they were Na-Cl. They had very similar chemical compositions with pH between 7 and 8 (Table 1). The principal cation was Na⁺ (692.0–929.0 mg/L), which was higher than Ca²⁺ (42.7–61.0 mg/L), K⁺ (36.9–53.9 mg/L), and Mg²⁺ (19.6–30.9 mg/L). The principal anions were Cl⁻ (941.0–1284.0 mg/L) and HCO₃⁻ (487.0–695.0 mg/L), which account for more than 90% of the total anions, while SO₄²⁻ was close to zero.

4.3. Water Isotopes. The stable isotopes of the cold groundwater in Quaternary aquifers and the geothermal groundwater in Jixian aquifers ranged from -11.3‰ to -8.5‰ as well as from -8.9‰ to -8.4‰ for δ¹⁸O and from -84.1‰ to -62.4‰ as well as from -73.5‰ to -72.4‰ for δ²H, respectively (Figure 6). The local meteoric water line (LMWL) in North China has been observed to be quite similar with the global meteoric water line (GMWL) [22, 23]. Therefore, in this study, we used the GMWL instead of the LMWL. Cold groundwater samples were distributed along the GMWL, whereas geothermal groundwater samples were located away from the GMWL. However, cold groundwater can be divided into two groups according to well depth and stable isotopes. Groundwater with well depth of less than 200 m (shallow cold groundwater) has larger isotopic values than that with well depth of more than 200 m (deep cold groundwater). The δ¹⁸O values of geothermal groundwater were less negative than those of deep cold groundwater. Moreover, the δ²H of geothermal groundwater was satisfactory between the two groups of cold groundwater.

4.4. Groundwater Dating. Radioactive ¹⁴C and ⁸¹Kr isotopes were used to assess the geothermal groundwater renewability. The ¹⁴C groundwater age was calculated and corrected using the δ¹³C mixing model, based on the assumption that the dissolved inorganic carbon (DIC) comes from soil CO₂ and carbonate dissolution. Table 1 shows that the cold groundwater had ¹⁴C activity higher than 7.7 ± 0.1 pmc and that the geothermal groundwater had ¹⁴C activity less than 2.1 ± 0.1 pmc. Moreover, for the cold groundwater samples, the water ¹⁴C activity (50 ± 0.2, 15.5 ± 0.1, and 7.7 ± 0.1 pmc) decreased in relation to well depth (100, 200, and 300 m), thereby illustrating the increasing trend of groundwater age in relation to circulation depth. Geothermal groundwater with ¹⁴C activity less than 2.1 pmc corresponded to an age of more than 22 k yr after the correction. However, groundwater samples with less than 2 pmc of ¹⁴C turned out to be uncertain in dating, provided that it was almost beyond the application limit of the ¹⁴C method (Matsumoto et al., 2018). Therefore,

we collected the gas samples to determine the ⁸¹Kr age for the geothermal groundwater.

Kr is a nonreactive gas, which is solely derived from atmospheric sources ([19]; Matsumoto et al., 2018). Converting measured ⁸¹Kr into groundwater age was comparatively simple because the ratio of ⁸¹Kr/Kr in atmospheric air was already known and was probably constant over the past hundred thousand years [24]. Primarily, there were no other sources that could have affected the input ratio, unlike in the ¹⁴C method wherein the “initial value problem” must always be addressed. Table 1 shows that both geothermal groundwater samples had ⁸¹Kr ratio of 10 ± 1 pm Kr. With the ⁸¹Kr decay constant (λ_{Kr} = 3.03 × 10⁻⁶ yr⁻¹), the ⁸¹Kr age was calculated to be 760 ± 30 k yr. Evidently, the ⁸¹Kr age was much older than the ¹⁴C age. Such an old ⁸¹Kr age implied that the results of the ¹⁴C method were unconvincing. It reminded us that the use of the ¹⁴C method near its dating limit should be done with caution.

5. Discussion

5.1. Factors Controlling the Hydrochemistry and Isotopes. The geothermal water chemistry was formed during the process of deep circulation. Compared with cold groundwater, geothermal groundwater had higher salinity, elevated Na, K, Cl, Li, B, and Si content, and lower SO₄²⁻ and a slightly lower Mg²⁺ composition (Table 1). The higher values of chemical compositions resulted from the interaction of infiltrating water with the shallow clay and deep limestone through which it flowed. The lower values of SO₄²⁻ should be attributed to the hydrochemical processes in the deep aquifers, which will be discussed together with the hydrogen isotope.

The difference in the stable isotopes between the two groups of cold groundwater (Figure 6) is attributed to a cool climate in the late Pleistocene period (6 to 9°C cooler than the current temperature, [25]). In their counterpart research on shallow groundwater in the NCP, Chen et al. [25] claimed that the values regarding the groundwater recharged by precipitation in the late Pleistocene period were in the ranges of -9.4 to -11.7‰ for δ¹⁸O and -76‰ to -85‰ for δ²H, whereas those recharged by precipitation in the Holocene period were in the ranges of -7.7‰ to -10.2‰ for δ¹⁸O and -63‰ to -73‰ for δ²H values. Figure 6 shows that isotopes from deep cold groundwater and shallow cold groundwater were well-defined in the ranges of the late Pleistocene and Holocene precipitation isotopes, respectively. The differences in isotopic data between deep and shallow cold groundwater suggest that groundwater beneath and above the depth of 200 m were in independent systems with weak hydraulic connectivity between them.

To explain the geothermal water isotopes, the effect of reinjection is to be discussed. The isotope fractionation of groundwater was observed after reinjection in the Larderello vapor-dominated geothermal field in Tuscany, Italy, due to (1) mixing between the reinjected water and reservoir fluid as well as (2) evaporation of reinjected water [26–28]. However, both processes could not happen in our study area, where the reservoir has lower temperature than the boiling point and a closed system is run with no fluid mixing and

FIGURE 3: Groundwater temperature (T) and water table (WT) in Jixian aquifers of Xiongxiian geothermal sector.

FIGURE 4: The bubble map of (a) temperature gradient and (b) heat flow based on the borehole data at Xiongxiian geothermal sector.

phase change. Therefore, we considered the water isotope as unchanged during the reinjection. Thereafter, several reasons may be used to address the location of geothermal groundwater points in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram.

The first possible reason is the paleoprecipitation. The ^{81}Kr age of 760 kyr belongs to the period of mid-Pleistocene climate transition (MPT), which marks the evolution of asym-

metric climate cycles defined by a slow expansion of continental ice sheets towards the midlatitudes followed by rapid melting culminating in interglacial warmth [29]. During the MPT, the $\delta^{18}\text{O}$ values varied with the paleoclimate and may have led to the observed geothermal groundwater isotopes in Figure 6. However, precipitation during the MPT should be less enriched in heavy isotopes than those in the Holocene

FIGURE 5: Piper diagram of groundwater at Xiongxian geothermal site. Black open triangles: hot groundwater; blue open circles: cold groundwater.

FIGURE 6: Isotopes of cold groundwater and geothermal groundwater at Xiongxian. The dashed lines are the possible processes: red line indicates the oxygen shift due to water-rock interaction (WRI); the dashed blue line shows the hydrogen shift due to inferred bacterial sulphate reduction (BSR); and the dashed black line is the mixing line.

[30], when the precipitation falls to form groundwater with well depth less than 200 m (Figure 6).

The second possible reason is the water-rock interaction. The enrichment of ^{18}O , which is called the oxygen shift and is produced by the exchange of oxygen between the water molecule and silicate and carbonate minerals, is commonly found in the geothermal system. With regard to the ^2H isotope exchange, it is generally found between water and clay minerals in sedimentary basins [5]. Although no clay minerals are manifested in the karst aquifer, the SO_4^{2-} content of the geothermal groundwater was lower than that of the cold groundwater. Moreover, with the depth increasing from the cold groundwater reservoir of around 200 m to the geothermal groundwater reservoir of more than 1000 m, the process of bacterial SO_4^{2-} reduction (BSR) might occur in a reduction environment with a reservoir temperature of less than 100°C . Moreover, high contents of H_2S were found in the Jinxian Sag near the Xiongxian region [31]. The released H_2S causes the ^2H enrichment [32, 33]. Figure 6 shows that the geothermal groundwater had more enriched ^2H 2–10‰ than that of the deep cold groundwater. Therefore, the process of BSR probably led to the alteration of both SO_4^{2-} and $\delta^2\text{H}$ in the geothermal water. However, the reduction of 1 g SO_4^{2-} at subsurface conditions will generally bring

FIGURE 7: Temperature profiles of XH02, XH05, and XH08 wells at Xiongxiang geothermal site. The arrows illustrate the extent of different rock types; the solid rectangle shows the sudden temperature rise in XH08.

an increase of 0.1‰ in ^2H [34]. The reduction of SO_4^{2-} (less than 55 mg/L) in our case was not enough to alter ^2H , thereby implying that other processes may have affected the water isotopes.

The abovementioned led to the other reason, i.e., the geothermal water was mixed by deep cold groundwater and ascending thermal fluids. The Xiongxiang Fault, striking NW and dipping SW (Figures 1(b) and 2), provides the flow path for the thermal fluids. Figure 6 shows a mixing line to support this explanation. The thermal fluids should be enriched in heavy isotopes; however, it must not be the andesitic water because (1) the mixing line in Figure 6 is not oriented towards the andesitic water isotopes and (2) the andesitic water was mainly identified near plate boundaries [35], whereas the Xiongxiang geothermal sector was located inside a sedimentary basin. Although more investigations are needed to explain the water isotopes of thermal fluids, the mixing process can be supported by the identified local hydrothermal pattern, as shown in the following section.

5.2. Explanation on the Local Hydrothermal Pattern. Several hypotheses were proposed to explain the deviation of the local hydrothermal pattern from the regional pattern.

The first reason is the long-term pumping activities. The groundwater flow pattern may have been modified due to exploitation during the past 30 years. From 1987 to 2009, the annual pumping rate increased from $1.6 \times 10^4 \text{ m}^3$ to $181.4 \times 10^4 \text{ m}^3$. Generally, the groundwater exploitation should lead to the drawdown around the production well. However, the pattern of the water table was not related to the locations of the wells (Figures 3 and 4). There is no available data till now that shows more groundwater is extracted in the NE than in the SW. Moreover, the temperature in the reservoir should not be significantly interrupted by the pumping activities. Provided that the groundwater

temperature changed only slightly in the past decades, the long-term pumping is an insufficient explanation for the local thermal pattern.

The second reason is the geological structure. The overall heat flow pattern in the BBB is consistent with the Mesozoic-Cenozoic tectonic-thermal evolution of the lithosphere (Hu et al., 2000; [9]), i.e., higher in the uplift and lower in the graben, as a result of heat transfer and accumulation. For example, the heat flow in the Niutuozen Uplift was almost twice higher than that in the surrounding grabens [17]. However, at the local scale, the study area was at the top of the Niutuozen Uplift, within a horizontal and vertical distance of 5 km and 300 m (to the bottom of overlying layer), respectively. The difference of heat transfer at each position was too low to generate a temperature difference of 20°C.

The last reason is the ascending water through the Xiongxiang Fault, which results into the observed hydrothermal pattern.

5.2.1. Evidence from Temperature Profiles. The temperature profiles of the XH02, XH05, and XH08 wells (Figure 1(d)) were used to support our hypothesis on the Xiongxiang Fault effect. Among the three wells, XH02 and XH08 were reinjection wells, whereas XH05 was a production well. Figure 7 illustrates that the groundwater temperature, at the same well depth above the karst (dolomite) aquifer, is quite different in the three wells. It declined in the sequences of the XH08, XH05, and XH02 wells. Compared with Figure 1(d), the foregoing three wells keep the distance to the Xiongxiang Fault, with the nearest one being the XH08 well, then the XH05 well, and, finally, the XH02 well, which is the farthest from the fault. Moreover, there was a sudden change in the groundwater temperature profile of the XH08 well, where the groundwater temperature suddenly increased (from 80 to 85°C with an increase in depth of 30 m) when the XH08

FIGURE 8: FixAl graph for the geothermal groundwater (a) XH01, (b) XH03, (c) XH04, and (d) XH08 at the Xiongxian site. The Al concentration is fixed by microcline saturation, and the process of degassing is corrected.

well met the karst aquifer. However, in the temperature profiles of the other two wells, there were no similar temperature changes. Thus, we concluded that the ascending thermal fluids through the Xiongxian Fault caused the high groundwater temperature around the fault.

5.2.2. Evidence from Lithium and Boron. The two useful indicators of deep groundwater circulation are Boron (B) and Lithium (Li). According to Giggenbach et al. [36], much of the B is transported by the subducted sediments absorbed onto clay particles. The transfer of Li from rock to water generally requires intense water-rock interaction at high temperatures [37]. Therefore, the groundwater that circulated through the deep fault should have had higher contents of B and Li. It can be clearly seen that the B and Li compositions of geothermal groundwater were much higher than those of cold groundwater. Furthermore, the geothermal groundwater to the east of the Xiongxian Fault had higher contents of Li (1.64 mg/L) and B (4.36 mg/L) than the geothermal groundwater to the west of the Xiongxian Fault, i.e., Li (1.15 mg/L) and B (3.28 mg/L). Because the regional groundwater flow direction is from the NW to the SE, geothermal groundwater to the west of the Xiongxian Fault could be used as the proxy

for geothermal groundwater that was not affected by the Xiongxian Fault. In this context, the higher contents of Li and B are considered as one of the evidence that geothermal groundwater has been mixed with ascending thermal fluids through the Xiongxian Fault.

5.2.3. Evidence from the Estimated Reservoir Temperature. The reservoir temperature of the Jixian aquifer was estimated using different geothermometers which utilized the software provided by Powell and Cumming [38] as well as the SOLVEQ-XPT program [39]. The calculated temperature using quartz geothermometers varied within the range of 82 to 99°C, whereas the results of the chalcedony geothermometer were close to the measured wellbore temperature of 62 to 80°C. The ordinary Log (Q/K) graphs had poor convergence, owing to degassing and incorrect Al concentration. As such, we corrected the same using the FixAl method [40]. Equal amounts of moles of HCO_3^- and H^+ , ranging from 0.005 to 0.01 mol/L, with an increasing interval of 0.001 mol/L, were added into the geothermal waters to calculate the Log (Q/K) values of minerals. The results of samples XH01, XH03, XH04, and XH08 were selected to make the plot of Log (Q/K). As shown in Figure 8, the saturation index (SI)

FIGURE 9: Conceptual model of hydrothermal genesis of Xiongxiang karst geothermal reservoir.

curves of the seven common hydrothermal minerals, except for chalcedony, in the geothermal reservoirs excellently converged to approximately 85 to 95°C. Thus, the reservoir temperature estimated via the FixAl method is consistent with the quartz geothermometers, which were both slightly higher than the measured borehole temperature.

The Na-K and Na-K-Ca geothermometers indicated a much higher temperature range of approximately 166 to 199°C. The temperature (94 to 102°C) estimated using the K-Mg geothermometer was not as high as the one measured with the Na-K geothermometer, but they were still higher than the one measured using the SiO₂ geothermometer. Given that the application of the SiO₂ geothermometer was under the assumption that there were no mixing processes for the geothermal groundwater, the calculated difference between the geothermometers could be attributed to the mixing of ascending thermal fluids with the lateral recharging groundwater. This is further supported by the estimated 141 to 165°C based on the CO₂-CH₄ isotope geothermometer in the same reservoir [10], which implies an upward migration of thermal fluids.

5.3. Conceptual Model of Fluid Circulation and Implications for Geothermal Energy Exploitation. Previous studies on the Niutuozen Uplift showed that the groundwater in the karst aquifers was recharged from the Taihang and Yanshan Mountains, flowed toward the SE, and then accumulated in the Niutuozen Uplift [12, 14, 15]. In our study, we highlighted the mixing of lateral regional recharge with the ascending thermal fluids through the Xiongxiang Fault (Figure 9). In addition, we emphasized the chemical compositions of geothermal water resulting from the processes, such as mineral dissolution, water-dolomite interaction, and BSR.

The distance from the Taihang and Yanshan Mountains to Xiongxiang is approximately 150 km. Consequently, we

could obtain the average regional flow velocity of 0.2 m/yr based on the ⁸¹Kr age, which is much lower than the one of 0.8–1 m/yr in the shallow Quaternary aquifer in the central part of the BBB (Matsumoto et al., 2018). In contrast, the tracer test through reinjection in the karst reservoir at the Xiongxiang geothermal sector showed that the groundwater velocity could reach as high as 359 m/d inside a small region of 1.5 km² [41]. This is supported by the similar contents between different geothermal groundwater samples (Figure 5), which revealed the high transmissibility of the developed karst rocks in the sampling region. Therefore, reinjection is essential in maintaining the reservoir pressure because the regional recharge is limited.

6. Conclusions

Based on a systematic data framework, including temperature logging, as well as hydrochemical and isotopic data, the conceptual model of fluid circulation at the Xiongxiang geothermal sector was developed. The direction of groundwater flow in the Xiongxiang karst reservoir was observed to be from SW to NE, with water table values ranging from -89 to -95 m, orthogonal to the regional one from NW to SE. Additionally, groundwater wellhead temperature declined from SW (80.1°C) to NE (61.6°C). Moreover, both borehole temperature gradient and heat flow in the caprock were maximum in the SW and minimum in the NE. This is attributed to the mixing of ascending thermal fluids through the Xiongxiang Fault. The chemical and isotopic values were similar among the geothermal groundwater in the karst reservoir, where the water mixing and hydrochemical processes, including BSR and water-dolomite interaction, were identified as plausible explanations in causing the hydrogen and oxygen shift of geothermal groundwater.

Our study highlights the importance of the Xiongxi Fault in affecting the local hydrothermal pattern. We further emphasized that the regional groundwater velocity for the Jixian karst geothermal reservoir is approximately 0.2 m/yr based on the ^{81}Kr age, thereby representing poor renewability. Therefore, in the future designing and planning for the large-scale utilization of geothermal resources, a detailed investigation on the local geology, as well as geophysical and geochemical investigation, should be conducted at the geothermal site scale, even though the regional data has already been obtained.

Data Availability

The hydrochemical and isotopic data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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