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Origin and Classification of Geothermal Water from Guanzhong Basin, NW China: Geochemical and Isotopic Approach

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ABSTRACT: Combined with tectonic evolution, a multi-isotopic method (δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and ^{14}C) and hydrochemistry data have been used to study the origin and classification of geothermal water in the Guanzhong Basin. The study shows that geothermal water of Xianli terrace primarily came from north-west direction when accepting recharge. A small amount supply source of geothermal water in Xi'an City is from Qinling Mountain and the principal supply source comes from the west direction, but geothermal water of Chang'an District mainly accepts supply from Qinling Mountain. Based on geothermal environment is open or not, the degree of water-rock interaction, and the origin of geothermal water, geothermal water of the study area can be divided into four types: A, geothermal water of Gushi depression, perfect closed thermal environment and significant water-rock interaction, belonged to residual sedimentary water origin; B, geothermal water of Xianyang City, good closed environment and relatively significant water-rock interaction, belonged to residual sedimentary water origin mixed with fossil leaching water; C, geothermal water of Xi'an City, half closed environment and some water-rock interaction, belonged to fossil leaching water origin; D, geothermal water of Chang'an District, open environment and mixed with modern precipitation, belonged to fossil leaching water origin.
KEY WORDS: geothermal waters, isotope and geochemistry, classification, groundwater type.

0 INTRODUCTION

Geothermal resources can provide clean green energy and have recently received considerable attention (Wang et al., 2013). Nowadays, geothermal water in the central part of Guanzhong Basin is being used on a fairly large scale (Qin et al., 2005) and the utilization of geothermal water has a history of more than 1 000 years (Liu, 1975). Wells had been drilled to supply geothermal water for bathing, space heating and fish farming.

Research on the origin and evolution of deep geothermal water is a great forefront of contemporary earth science research. Hydrogeochemical investigation methods, some of which are based on stable isotopes, such as ^{18}O, ^{2}H, ^{14}C and $^{87}Sr/^{86}Sr$ (Cartwright et al., 2012; Thomas and Rose, 2003; Jorgensen and Banoeng-Yakubo, 2001; Wang et al., 1996; Banner et al., 1994), could be used to study the origin and evolution of the various fluid components (Kanduč et al., 2014; Négrel et al., 2001). Strontium isotope ratios had been applied to hydrogeology and environmental geology study since the 1990s (Barbieri et al., 2005; Bullen et al., 1996), unlike the istope ^{18}O and ^{2}H that have been used in hydrology for a long time (Ma et al., 2010; Leybourne et al., 2006; Craig, 1961). Strontium dissolves in the groundwater though dissolution or ion exchange. Hence, $^{87}Sr/^{86}Sr$ ratios are sensitive to water-rock interaction (Naftz et al., 1997) and could be used as an ideal tracer of supply source and flow path (Cartwright et al., 2012; Palmer and Edmond, 1992). $^{87}Sr/^{86}Sr$ ratios could also help to determine thermal environment of deep geothermal water, study the relations of deep and shallow geothermal water and distinguish different geothermal water cycle systems (Ye et al., 2008).

Geothermal water in the Guanzhong Basin has been well researched. Previous studies of isotopic composition of hydrogen and oxygen had shown that geothermal water with highest measured temperature (120 ºC) had a significant $\delta^{18}O$ isotope shift, showing the sealed or semi-sealed condition (Ma et al., 2010; Qin et al., 2005), and geothermal water of Xi'an was recharged from the Qinling Mountain at high elevations (Qin et al., 2005). Furthermore, combined the results of isotopic study and chemical analysis, geothermal water of Weihe Basin was classified into three groups: the shallow and fast circulating system, the semi-circulating system and the deep and slow circulating system (Ma et al., 2010).

A multi-isotopic approach (δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and ^{14}C) and hydrogeochemical method are applied in the present work for the characterization of geothermal water in the Guanzhong Basin. The aim of this study is to acquire the supply source, flow path and classification of geothermal water in the Guanzhong Basin.

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1 GEOLOGICAL SETTINGS

The Guanzhong Basin, located in the middle of Shaanxi Province, NW China with rich geothermal water, is surrounded by North Mountain with highest elevation of 1 678 m a.s.l. and Qinling Mountain with highest elevation of 3 767 m a.s.l. (Fig. 1). The area of the basin is about 1.9×10^4 km^2. Xi'an is the capital city of Shaanxi Province with 0.923 billion m^3 of exploitable geothermal waters with buried depth of 1 000–4 000 m. As a rapid sedimentary and buried Cenozoic basin, the maximum sedimentary thickness reaches 7 000 m.

Quaternary and modern earthquakes were well developed; many faults striking from the east to the west, and from the north to the south were active with the activity rate of 0.4 to 0.8 mm/year on average. The Qinling foreland fault (F1), Chang'an-Lintong fault (F2) and Weihe fault (F3), are the major discharge channels of geothermal water based on the distribution of geothermal springs (Fig. 1). Owing to frequent recent tectonic movement, a series of large-scale heaves and hollows appeared and three fractured blocks were identified in Guanzhong Basin. These are Xi'an depression, Gushi depression, Xianli terrace. The basement structure was divided into two zones at the boundary of Weihe fault (F3), one was made of metamorphic rock and another was made of carbonate rock (Fig. 2).

Presently, major geothermal reservoirs discovered include the Zhangjiapo Group, the Lantian-Bahe Group and the Gaoling Group of Tertiary System from the top (Fig. 2). Geothermal reservoir of Zhangjiapo Group (N_2z) consists of grey-hazel mudstone, grey sandstone, and foliar siltstone. Average depth, temperature and artesian flux are 1 506.7 m, 68 °C, 794.44 m^3/d, respectively; geothermal reservoir of Lantian-Bahe Group

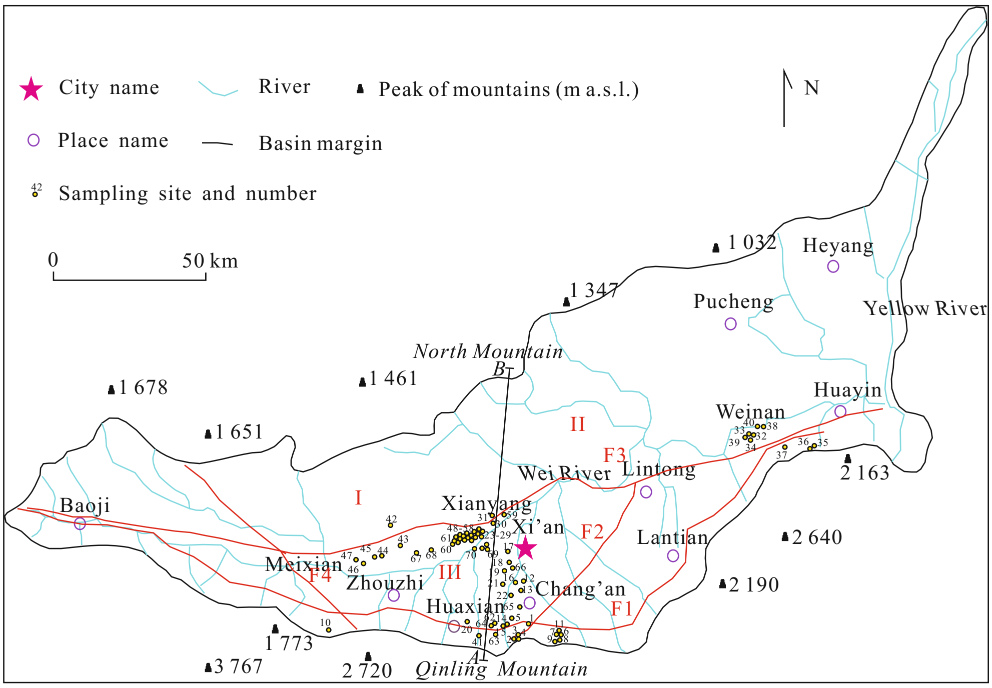

Figure 1. The geographic map of Guanzhong Basin with sampling sites and numbers. I, II, and III, respectively represent Xianli terrace, Gushi depression and Xi'an depression. F1, F2, F3, and F4 represent Qinling foreland fault, Chang'an-Lintong fault, Weihe fault, and Longxian-Yabo fault, respectively.

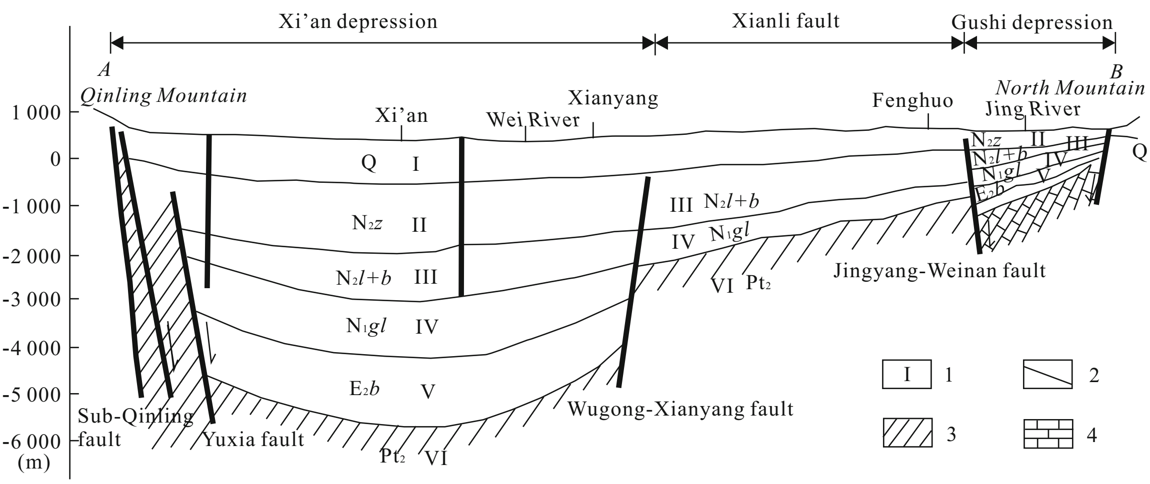

Figure 2. Geological-cross section of Guanzhong Basin. 1. Geothermal reservoir number; 2. major faults; 3. Proterozoic metamorphic rocks (Pt_2); 4. carbonate rock; Q. Quaternary; N_2z. Pliocene-Zhangjiapo Group; N_2l+b. Pliocene-Lantian-Bahe Group; N_1gl. Miocene-Gaoling Group; E_2b: Paleogene-Bailuyuan Group.

(N_2l+b), as the main exploitation geothermal aquifer in the basin, consisted of fluvial and marine sediments. Lantian-Bahe Group was made up of mudstone and middle sandstone. Average depth, temperature and artesian flux were 2 127.85 m, 88.6 ºC, 2 320.08 m^3/d, respectively; the major lithology of Gaoling Group (N_2gl) is red brown and brick red mudstone, arenaceous mudstone with some red brown and French grey fine sandstone, middle sandstone and grit. Average depth of 2 486 m, temperature of 90.25 ºC and artesian flux of 6 335.76 m^3/d, were found in N_2l+b and N_1gl mixed group.

2 SAMPLING AND TESTING

A total of 70 water samples were collected from surface water and the different depths of geothermal reservoir in the Guanzhong Basin between November and December of 2012. Chemical analyses were performed at the Central South Metallurgical Geology Test Center. Cations (Na^+, Ca^{2+}, Mg^{2+}, and Sr^{2+}) were analyzed by AA-100 atomic absorption spectrometer, and total dissolved solids were analyzed by gravimetry. The analytical accuracy of these methods ranged from 2% to 5%.

Water samples for isotopic determination were collected in acid-washed polyethylene bottles. Samples were acidified with pure nitric acid down to pH<2 for Sr stored. $^{87}Sr/^{86}Sr$ ratios of samples were analyzed by thermal ionization mass spectrometer MAT-261 in the China Geological Survey, Yichang Institute of Geology and Mineral Resources and the analytical error (expressed as 2σ) was ±0.000 02 through repeated analyses of the NBS987 standard. Isotopic composition of oxygen and hydrogen ($\delta^{18}O$ and δD) were analyzed in the Isotope Laboratory, the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, and the results were reported in δ% units vs. the international V-SMOW standard (Craig, 1961). Measurement accuracies were within 0.02% for the ^{18}O test, 0.1% for the He test based on the groundwater quality inspection methods DZ/T0064-93. The ^{14}C samples were analyzed by Liquid Scintillation Counter, due to the rapid and accurate testing method. All test results are shown in Table 1.

3 RESULTS AND DISCUSSION

3.1 Supply Source and Flow Path of Geothermal Water Based on Ion Chemistry and Stable Isotope (^2H, ^{18}O, $^{87}Sr/^{86}Sr$)

The changing $^{87}Sr/^{86}Sr$ ratio of geothermal water samples is related to lithology of the basin which the geothermal water flows through. Taking the Wei River as the boundary, Sr isotope distributions between the south and the north of the river indicates that there are obvious lithological differences between two regions (Fig. 3). Strontium concentration and $^{87}Sr/^{86}Sr$ ratio of geothermal water samples in the Xi'an depression gradually increase from north to south. This evidence shows significant accumulation of Sr over time. The $^{87}Sr/^{86}Sr$ ratio of recharge area in the Xianli terrace is relatively higher (0.711 77–0.725 20) (Fig. 3b), while the Sr concentration is low (Fig. 3a), which is consistent with the feature of aluminosilicate; compared with Xi'an depression and Xianli terrace, Gushi depression has the characteristics of higher Sr concentration and lower $^{87}Sr/^{86}Sr$ ratio, suggesting that water-rock interaction is active (Naftz et al., 1997). Strontium concentration of Huayin geothermal water in the Gushi depression is up to 143–255 mg/L, which may due to the ion exchange of Ca^{2+} and Sr^{2+}.

In order to study distribution characteristic of Sr isotope, Fig. 4 is divided into Part I and Part II and the distribution of two parts is quite different.

Part I has the characteristic of stable low Sr concentration (0.02–3.99 mg/L) and higher yet volatile $^{87}Sr/^{86}Sr$ ratios (0.707 50–0.712 48) (Fig. 4), and includes geothermal water of Xi'an depression and surface water in piedmont of Qinling Mountain. The $^{87}Sr/^{86}Sr$ ratios of geothermal water in Xi'an City (samples 12, 13, 16, 17, 18, 19) are higher than those of Chang'an District (samples 14, 15). Flowing through metamorphic rock basement with higher $^{87}Sr/^{86}Sr$ ratio and Tertiary sandstone with higher Rb concentration, $^{87}Sr/^{86}Sr$ ratios of samples in the Xi'an depression show the following characteristics: from Qinling Mountain to Xi'an depression, $^{87}Sr/^{86}Sr$ ratios of geothermal water increase in the flow direction, which demonstrates the accumulation of strontium isotope over time. Whereas $^{87}Sr/^{86}Sr$ ratios of surface water in the north of Qinling Mountain vary greatly, because water flow though different environment. The $^{87}Sr/^{86}Sr$ ratios of geothermal water in the Chang'an District increase from south to north, which suggests that the recharge of shallow geothermal water is from the Qinling Mountain.

Part II, mainly consisting of deep geothermal water samples in Xianli terrace, has the characteristic of moderate and stable $^{87}Sr/^{86}Sr$ ratio (0.710 10–0.711 00) and volatile of Sr concentration (0.02–37.2 mg/L) (Fig. 4), due to carbonate rock with low $^{87}Sr/^{86}Sr$ ratio and high Sr concentration and unconsolidated sediment with high $^{87}Sr/^{86}Sr$ ratio and low Sr concentration. The similar $^{87}Sr/^{86}Sr$ ratio between Xi'an City and Xianli terrace shows that they have a common supply source. $^{87}Sr/^{86}Sr$ ratios of geothermal water in the southeast Xianli terrace are consistent with that of the northwest Xianli terrace, indicating that geothermal waters have a common supply source; however, Sr concentration increases from the northwest to the southeast, as the result of the gradually strengthening process of water-rock interaction (Barbieri et al., 2005) from the recharge area to the retention area, indicating that supply source was probably from the west of the study area (Fig. 3). This is the first time to know the supply source of geothermal water in the Xianli terrace.

The Sr-Ca is used to indicate flow paths and the process of water-rock interaction. Three groups of Sr/Ca are positively correlated, but the ratios are different (Fig. 5a), suggesting that geothermal water of each group type has similar thermal environment and water-rock interaction. The geothermal water which supplied Xianyang City in the southeast of Xianli terrace comes from the north and the west of the study area respectively, and the Sr/Ca ratio of flow in the north is greater than that of water flow in the west. Geothermal water in the north of Xianli terrace, such as Zhangyujiuzhuang, Zhouling Town, is the main supply source for geothermal water in the southeast of Xianli terrace.

Figure 5b shows that geothermal waters of Xi'an City in the south of Xi'an depression have the similar $^{87}Sr/^{86}Sr$ ratio, but Na^+ gradually increases from the south to the north, as the result of water-rock interaction, indicating that geothermal water is recharged from the piedmont of Qinling Mountain. Whereas

Table 1 Chemical and isotopic characteristics of geothermal water and surface water in the Guanzhong Basin

No.	District	Sampling place	T (ºC)	Well depth (m)	TDS (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)	$^{87}Sr/^{86}Sr$	^{14}C (a)	δD (‰)	$\delta^{18}O$ (‰)
1	Qinling surface water	Xiangyu Gate		0		5.06	38.60	7.29	0.22	0.708 912		-70.9	-9.9
2		Caihong Fall		0		1.66	10.41	2.71	0.03	0.711 021		-81.1	-11.4
3		Shihuatan		0		1.70	9.32	1.81	0.02	0.711 021		-80.1	-11.3
4		Cableway Station		0		1.66	9.92	2.04	0.03	0.710 913		-82.0	-11.4
5		Taiping Restaurant		0		1.70	11.12	2.16	0.03	0.710 838		-82.1	-11.8
6	The piedmont of Qinling Mountain	Airport Hotel		800.0		736.02			1.15	0.709 322			
7		Tezhong Fishery		1 000.0		736.05			0.98	0.707 969			
8		Nanshi Village		1 000.0		782.12			1.23	0.708 228			
9		Dao Hot Spring Hotel		1 000.0		805.22			1.06	0.716 931			
10		Tangyu Hot Spring Hotel		350.0	546	146.51	8.01	0.91	2.33	0.711 766		-72.3	-10.6
11		Dongda Town Resort	51	500.0	352	106.90	3.98	0.10	0.10	0.708 068		-80.9	-8.7
12	South Xi'an depression	Chunxiaoyuan Community	90	3 450.0	2 934	859.60	44.12	7.27	1.32	0.710 282		-78.4	-7.8
13		Northwest Hotel	56	1 556.5		135.99	2.40	0.19	0.01	0.710 519			
14		Modern College NWU	75	1 950.0	544	153.89	7.01	0.61	0.65	0.707 542			
15		NWPU Chang'an campus	62	1 993.5	410	125.60	6.02	1.24	0.09	0.708 208		-90.0	-11.3
16		Xi'an diving venues	82	3 300.0	1 904	610.81	29.06	0.62	0.50	0.710 541		-81.7	-9.5
17		Yahe spring garden 2#		3 505.8	4 164	1 375.01	10.05	1.23	2.33	0.710 543		-84.4	-9.9
18		Xi'an Mineral Hall	86	2 550.0	2 992	1 009.99	22.00	2.91	1.32	0.710 328			
19		Sports Academy				31 050.10			1.82	0.710 523			-8.9
20		Jingzhao Community				5 842.07			0.28	0.712 476			-8.9
21		Shaanxi Hotel		3 854.5		1 725.05	44.12	4.30	1.90				
22		Changle Community	72			1 770.01	114.21	23.11	2.80		13 585	-82.6	-9.3
23	Southeast Xianli terrace	SP2		3 558.0	5 000	1 877.19	85.23	15.79	13.57	0.710 674	15 788	-70.6	-4.5
24		202 Institute		2 471.0	5 504	1 635.00	75.20	15.41	14.80	0.710 742	23 652	-66.3	-3.8
25		185 Geological Team	74	2 000.0	7 536	2 649.99	132.32	34.61	37.20	0.710 411	20 251	-69.3	-4.4
26		795 Factory	98	3 094.0	5 324	1 886.98	66.08	11.50	18.40	0.710 808			
27		Wenre 4	81	2 908.2	4 400	1 645.81	67.12	13.99	7.68	0.710 504		-90.1	-5.8
28		Business School		3 500.3	3 704	1 222.50	10.02	0.50	0.80	0.710 652	26 290	-70.9	-5.3
29		Zhaojia Village				246.01	8.12	2.86	0.14	0.710 989		-89.1	-10.7
30		Auxiliary Factory 2	90			40 995.20			14.03	0.710 723			
31		Zhouling Town	71	2 818.0	4 886	1 835.99	56.12	12.19	4.22		22 717	-68.1	-6.7
32	Gushi depression	Weire 1#		3 200.0	4 091	1 225.99	8.48	1.81	2.73	0.710 881		-85.1	-0.7
33		Weire 2#	123	3 806.5	4 748	1 423.40	10.03	0.62	1.33	0.711 942		-87.9	-2.1
34		Weire 3#		3 546.0		1 071.29	75.20		1.67				

Table 1 Continued

No.	District	Sampling place	T (ºC)	Well depth (m)	TDS (mg/L)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)	$^{87}Sr/^{86}Sr$	^{14}C (a)	δD (‰)	$\delta^{18}O$ (‰)
35		Shaohua Mountain 720				20.24	64.41	8.26	3.99	0.706 420		-71.1	-10.0
36		Shaohua Mountain 1200				4.51	52.12	8.16	3.88	0.710 073		-76.2	-10.5
37		051	105	2 600.0	30 120	7 375.00	3 476.92	170.11		0.708 568	20 048	-61.1	-3.2
38		Wei River				35.95	51.82	15.96	0.57				
39	Weinan	Weire 4								0.708 781		-80.2	-3.0
40		Wei River (Weinan)										-65.9	-8.7
41	River water	Feng River										-67.1	-10.2
42	Northwest Xianli terrace	Liquan R5	53	1 901.7	512	106.49	57.72	25.30	0.95	0.719 432		-61.5	-9.4
43		Jinlang Hot Spring Company	80	2 100.0	3 608	1 301.00	35.12	6.69		0.711 138	25 911	-70.8	-9.1
44		Wugong 3		3 200.0		1 689.99	259.02	5.81	25.44	0.710 993		-87.8	-9.0
45		Wugong 2		3 160.0		1 231.96	179.08	5.71	10.73	0.710 667		-90.2	-9.1
46		Yangling Resort	86	2 930.0	4 312	1 475.01	191.40	3.00	5.47	0.710 641		-71.5	-9.3
47		Fufeng R6	48	1 048.3	1 038	271.11	84.65	24.09	3.15	0.725 204		-88.2	-10.9
48	Southeast Xianli terrace	Recharge Well 1	60		8 270	2 931.51	167.32	44.41	26.85				
49		SP1	91	2 975.5	5 960	2 204.50	90.24	24.31	13.13				
50		Hot Spring Company	68		6 824	2 425.01	79.20	13.39	14.80				
51		Weidian Village	68		6 616	2 325.00	96.25	26.66	16.50				
52		Chengjian Group Company	72		8 360	2 975.00	142.32	42.79	27.00		20 219	-71.6	-6.0
53		Shaanxi Technical College	89	2 813.2	6 696	2 362.49	102.21	24.91	21.00		22 263	-66.0	-3.7
54		Wenre 1	82	2 773.0	9 850	2 804.30	142.32	38.90	23.57				
55		Wenre 2	82	2 600.0	7 830	2 804.30	142.32	43.70	23.87				
56		Wenre 3	84	2 900.0	5 490	1 896.31	80.24	24.31	0.71				
57		WR5	73	2 978.6	7 296	2 442.60	118.26	38.30	24.40				
58		Wenre 6	85	3 062.6	5 700	1 799.41	84.28	20.11	13.20				
59		Zhangyu Chateau	83	2 625.0	4 315	1 593.01	50.12	3.02	7.46				
60		Huatai Community	85	2 861.0	6 402	2 148.29	100.29	14.59	23.10				
61		Auxiliary Factory 1	90	2 745.2	4 880	1 782.42	68.12	15.78	14.03				
62	The piedmont of Qinling Mountain	Chang'an Dongda Fishery										-88.5	-12.0
63		Chang'an Dongda Town	80	341.0								-84.6	-9.9
64		Chang'an Dongda Well 2										-88.1	-12.1
65		Changan Liupu	68									-83.7	-11.9
66	Xi'an depression	Coal Board								0.710 438		-86.9	-3.3
67	Northwest Xianli terrace	Chenjia Village								0.711 662		-85.8	-11.1
68		Zhaojia Village										-89.1	-10.7
69	Southeast Xianli terrace	Haiquan Bay										-87.3	-4.1
70		Jin Well 2										-87.1	-2.3

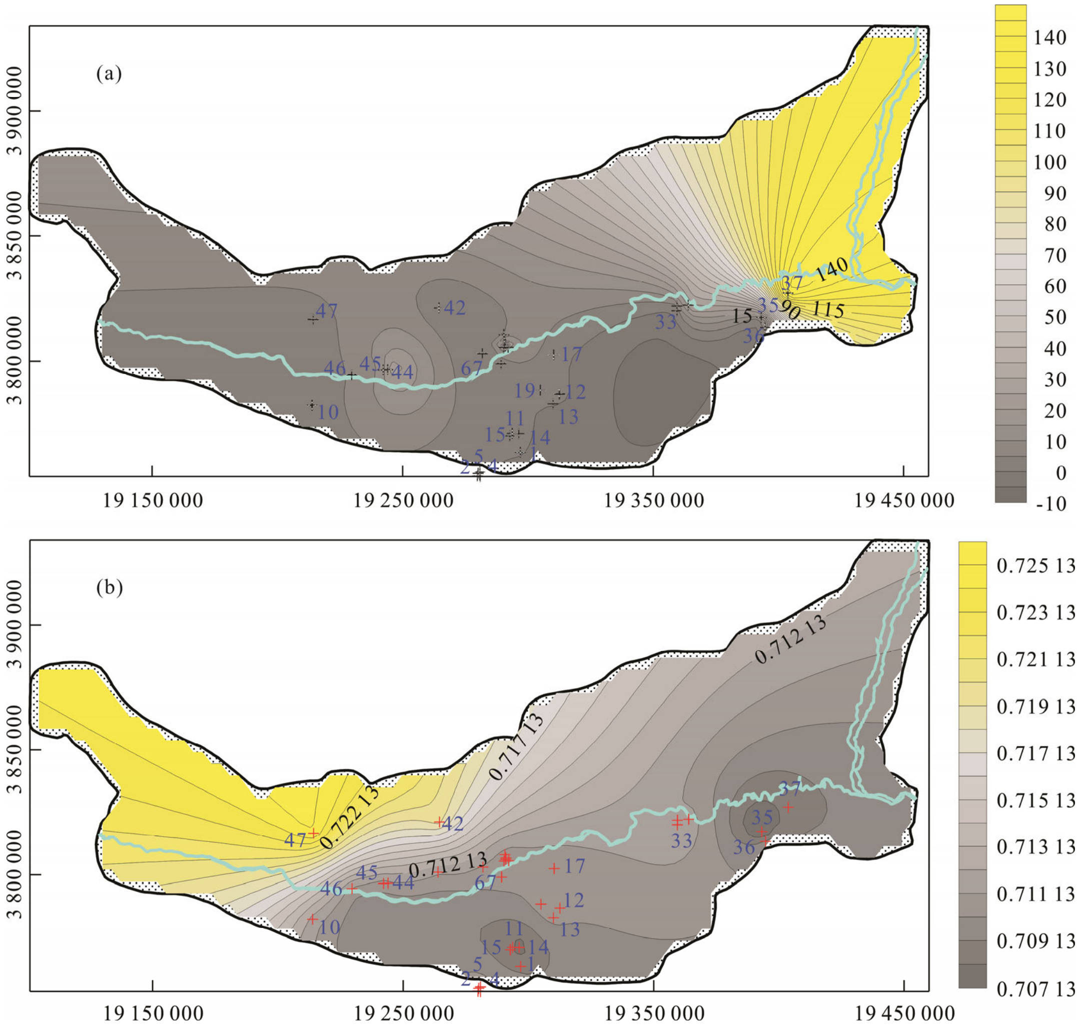

Figure 3. The contour maps of Sr^{2+} (a) and $^{87}Sr/^{86}Sr$ (b). The unit of Sr^{2+} (a) was mg/L; the data of Sr^{2+} and $^{87}Sr/^{86}Sr$ showed in Table 1; the maps were plotted using SUFER software, version 8.0.

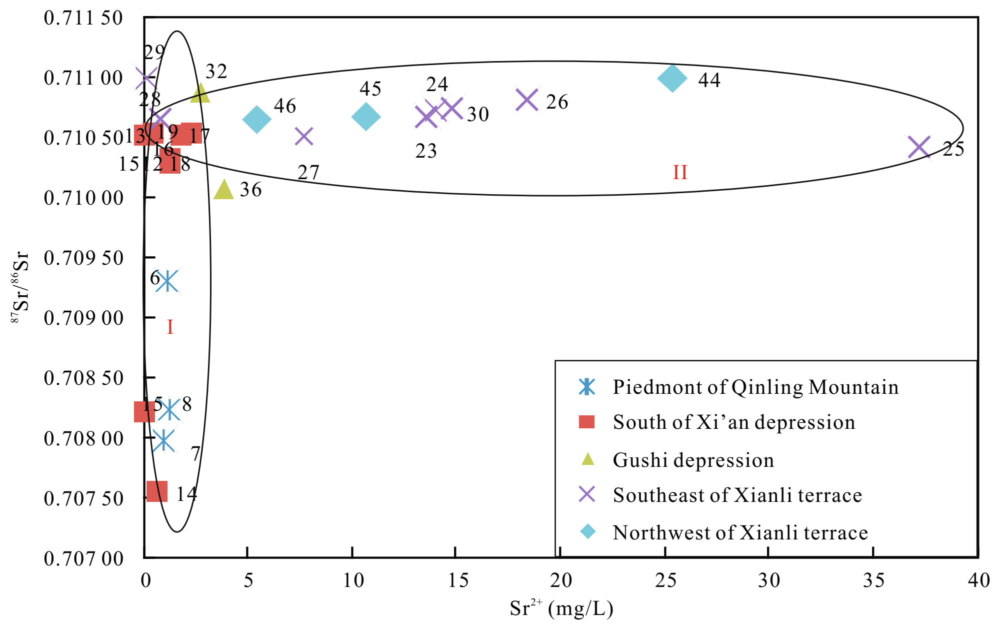

Figure 4. Plot of $^{87}Sr/^{86}Sr$ vs. Sr^{2+} of samples in the Guanzhong Basin. Numbers refer to Table 1.

$^{87}Sr/^{86}Sr$ ratio of Chang'an District geothermal water in the south of Xi'an depression differs from that of Xi'an City geothermal water (Fig. 5b), suggesting that they have different main flow directions. Previous research had drawn a conclusion that geothermal water of Xi'an was recharged from the Qinling Mountain at high elevations (Qin et al., 2005), but they did not differentiate Chang'an District and Xi'an City.

The Sr/Ca and Sr/Mg ratios reflect flow path and the intensity of water-rock interaction. The Sr/Ca and Sr/Mg ratios of geothermal water gradually increased with flow distance and time, from the recharge area to the retention area. Therefore, Sr/Ca and Sr/Mg ratios could be used as tracers. The Sr/Ca and Sr/Mg ratios of geothermal water (respectively, 0–0.15 and 0–0.9) in Xi'an depression from the south to the north and Xianli terrace from the northwest to the southeast present that the water is flowing from recharge area to retention area (Figs. 5c, 5d). The Sr/Ca-TDS of Xi'an depression has no obvious correlation with that of the southeast of Xianli terrace, indicating that they have different supply sources. Geothermal waters in the south of Xi'an depression and the northwest of Xianli terrace have a common supply source. The supply source of geothermal water in Xi'an depression probably comes from the west and Qinling Mountain. However, 051 sample of geothermal water in Gushi depression has the highest value of TDS (30 120 mg/L) compared with other samples of Guanzhong Basin, their difference being about an order of magnitude (Table 1). The reasons for that may be significant water-rock interaction in the perfect closed geothermal environment and the supply of geothermal water came from strong evaporated ancient water during geological history. The origin of geothermal water in the Gushi depression is very interesting and more works should been done in the future.

In order to further confirm the supply source of geothermal water in Chang'an District, samples of atmospheric precipitation from different elevation of Qinling Mountain were collected to analyse stable isotopes ($\delta^{18}O$, δD). Results were summarized in Table 2. The average recharge elevation of geothermal water in the Chang'an District is 1 153.91 m, indicating that supply source of shallow geothermal water in the Chang'an District partly comes from modern atmospheric precipitation of Qinling Mountain.

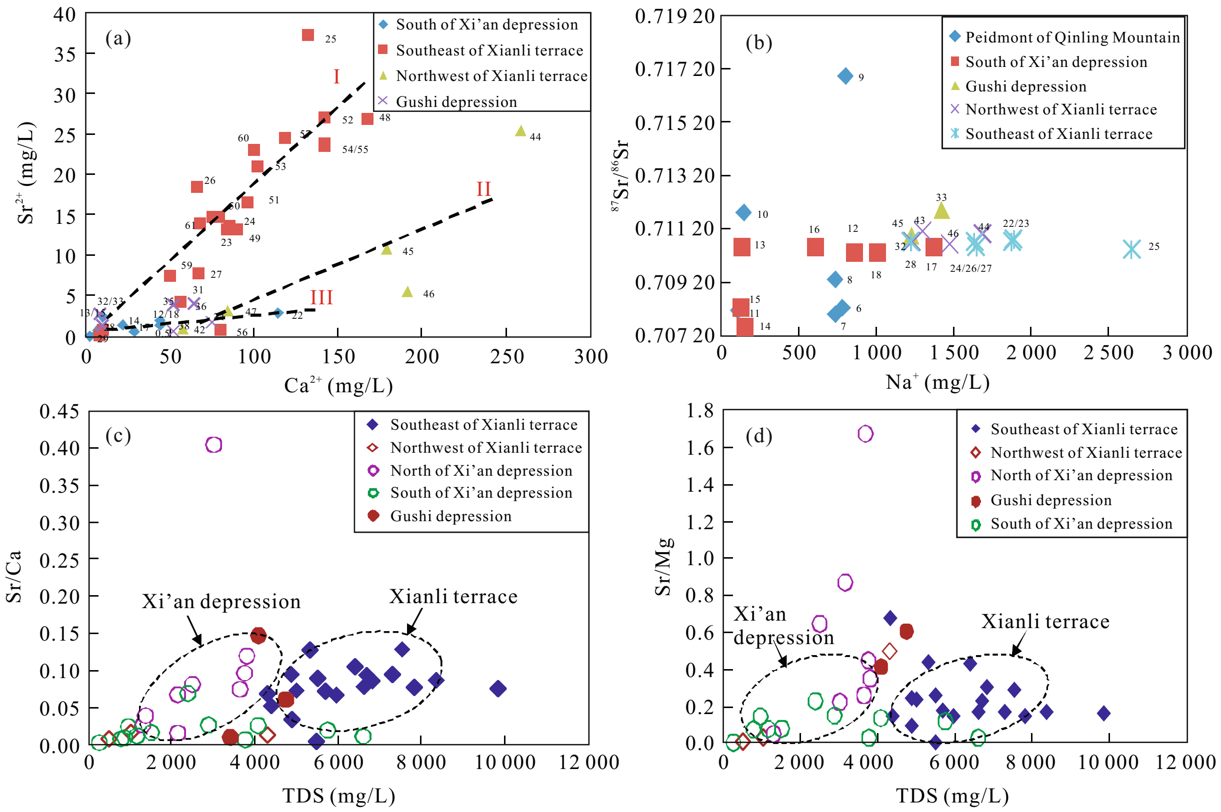

Figure 5. Plot of Sr^{2+} vs. Ca^{2+} (a), $^{87}Sr/^{86}Sr$ vs. Na^{+} (b), Sr/Ca vs. TDS (c), and Sr/Mg vs. TDS (d) of samples in the Guanzhong Basin. Numbers refer to Table 1.

Table 2 Isotope composition (δD and $\delta^{18}O$) of sampled waters in the north of Qinling Mountain

Place	Elevation (m a.s.l.)	δD	$\delta^{18}O$
Xiangyu Park Ticket Office	770	-70.9	-9.9
Caihong Fall	1 674	-81.1	-11.4
Shihuatan	1 488	-80.1	-11.3
Shaohua Mountain	717	-71.1	-10.0
Shaohua Mountain	988	-76.2	-10.3
Shaohua Mountain	1 200	-76.3	-10.5

3.2 Classification of Geothermal Water Based on $\delta D/\delta^{18}O$, ^{14}C and $^{87}Sr/^{86}Sr$

As showed in Fig. 6, points of geothermal water sampled from deep thermal environment in the Xi'an depression and Xianli terrace fall bellow local meteoric water lines (LMWL) showing that $\delta^{18}O$ shift happened with similar δD values and different degree of water-rock interaction existed (Wang et al., 2013). The stable isotopic data indicate that geothermal waters were of meteoric origin when recharge took place. In other words, shallow geothermal water was intermixed with local modern meteoric water and deep geothermal water had hydraulic interaction with shallow geothermal water to some degree (Ma et al., 2010).

The points distribution of surface water and river samples is displayed along the global meteoric line (Fig. 6), indicating that the water receive recharge from meteoric water; some shallow water points (Chang'an District) in the south of Xi'an depression are situated below the global meteoric line. The annual average temperature of supply water was 0.49 ºC (Hu et al., 2009) and recharge elevation was 1 153.91 m, revealing that the shallow geothermal water mixing with some modern meteoric water was recharged from the north of Qinling Mountain in the cold and damp environment before Holocene. The degree of $\delta^{18}O$ drift in Xi'an City geothermal water is at a moderate level among Chang'an District, Gushi depression and Xianli terrace, indicating that thermal environment was half closed and geothermal water was of fossil leaching water origin. The points of geothermal water in the southeast of Xianli terrace (Xianyang City) was far away from global meteoric water line and $\delta^{18}O$ drift was significant, suggesting that geothermal environment was closed and geothermal water was of residual sedimentary water and fossil leaching water origin. The points in the northwest of Xianli terrace have a slight $\delta^{18}O$ drift, showing the characteristics of recharge area. The $\delta^{18}O$ drift was extremely significant in the Gushi depression, inferring that the thermal environment was completely closed and geothermal water was probably of residual sedimentary water origin mixed with fossil leaching water.

In the study area, geothermal water temperature of Xianyang City (the southeast of Xianli terrace) and Xi'an City (the south of Xi'an depression) ranges from 71 to 98 ºC and 56 to 90 ºC, respectively, indicating that thermal environment of Xianyang City is relatively closed than that of Xi'an City. Geothermal water of Gushi depression has the highest temperature, due to the perfect closed geothermal environment.

The reason of using ^{14}C is to provide evidence for the origin of geothermal water and the geological time of isotope hydrogeochemical evolution. ^{14}C of geothermal water in the north of Xi'an depression and the southeast of Xianli terrace is older, indicating that geological environment of geothermal water in these regions was relatively closed (Fig. 7a). There was a few sampling points collected from Huayin region in the Gushi depression to make satisfied inference. The ^{14}C age of the geothermal water was the oldest in the study area; therefore, thermal environment of geothermal water in Gushi depression is perfect closed.

Previous research showed that combining the results of isotopic study and chemical analysis, geothermal water of Weihe Basin was classified into three groups: the shallow and fast circulating system, the semi-circulating system and the deep and slow circulating system (Ma et al., 2010). $^{87}Sr/^{86}Sr$ ratio reflects the process of water-rock interaction and $\delta^{18}O$ reflects the degree of water-rock interaction (Cartwright et al., 2012). Those studies could be used as the basis of study area classification (Fig. 7b). Based on whether geothermal environment is open or not, the degree of water-rock interaction and the origin of geothermal water, geothermal waters in the Guanzhong Basin could be further divided into four types (Fig, 7b). Geothermal water of Type A, represented by 051 sampling place, has the characteristic of highest $\delta^{18}O$ (-3.2‰– -0.7‰) and relative stable $^{87}Sr/^{86}Sr$ ratios

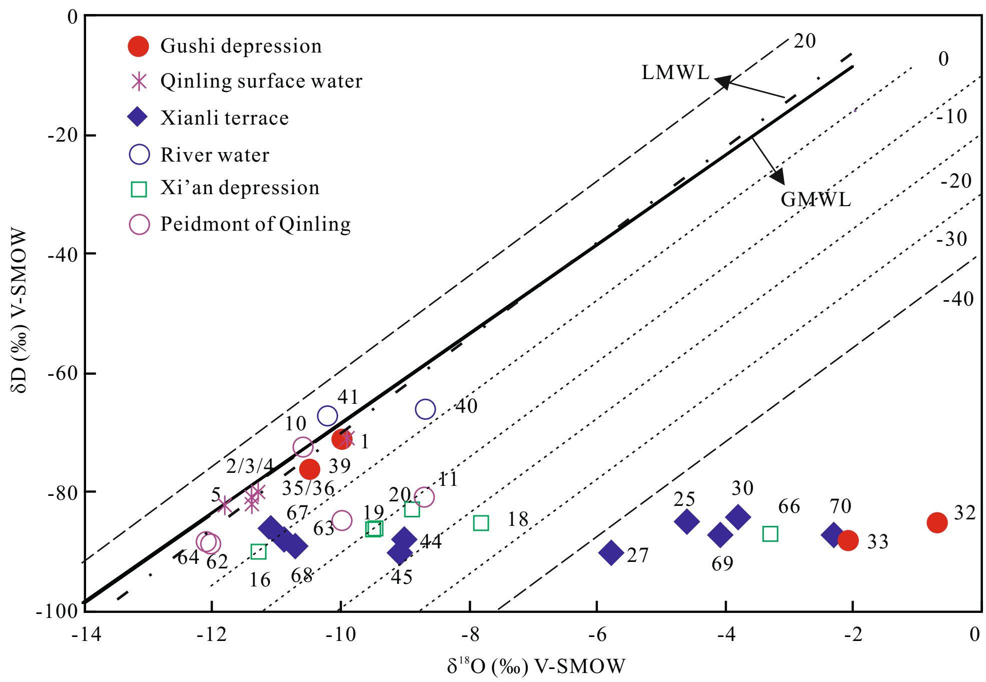

Figure 6. Plot of δD vs. $\delta^{18}O$ showing the stable isotope composition of the geothermal waters, indicating the effects of rock-water interaction. The dashed line is the global meteoric water line (GMWL), $\delta D=8\delta^{18}O+10$ (Craig, 1961). The solid line is the local meteoric water line (LMWL), based on the data from the GNIP network at Xi'an station, $\delta D=7.5\delta^{18}O+6.1$. Numbers refer to Table 1.

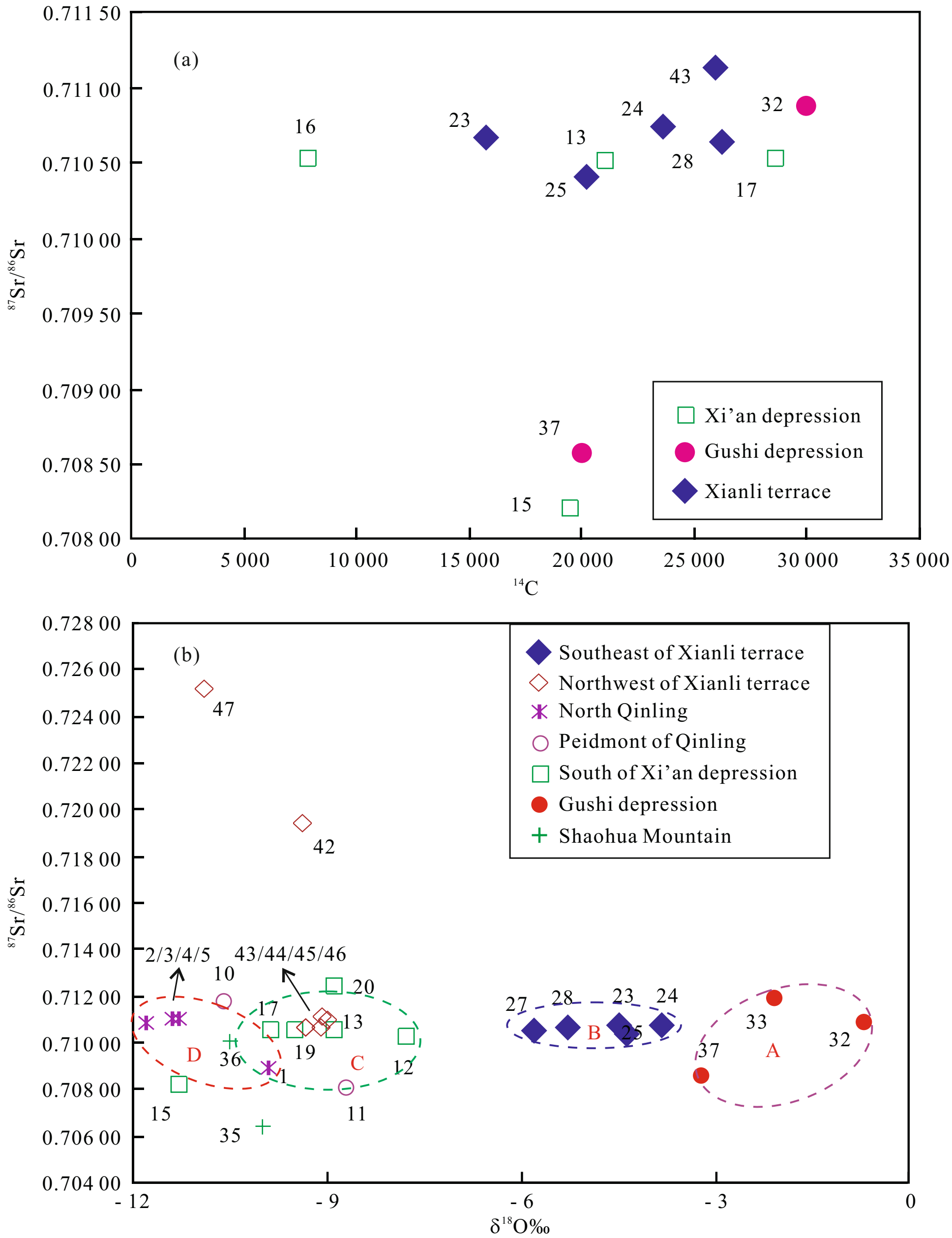

Figure 7. Plots of $^{87}Sr/^{86}Sr$ vs. ^{14}C (a) and $^{87}Sr/^{86}Sr$ vs. $\delta^{18}O$‰ (b). Numbers refer to Table 1.

(0.708 57–0.711 94), indicating the thermal environment is perfect closed and water-rock interaction is significantly, the geothermal water derived from residual sedimentary water. Geothermal water of Type B, represented by sampling places in Xianyang City, has relative higher $\delta^{18}O$ (-5.8‰– -3.8‰) and stable $^{87}Sr/^{86}Sr$ ratios (0.710 41–0.710 74) characteristic, indicating the thermal environment is good closed and water-rock interaction is relative significantly, the geothermal water derived from residual sedimentary water mixed with fossil leaching water. Geothermal water of Type C, represented by sampling places in Xi'an City, has low $\delta^{18}O$ (-9.9‰– -7.8‰) and relative stable $^{87}Sr/^{86}Sr$ ratios (0.710 28–0.712 48) characteristic, indicating the thermal environment is half closed and it exists some water-rock interaction, the geothermal water belonged to the origin fossil leaching water. Geothermal water of Type D, represented by sampling places in the Chang'an District, has relative lower $\delta^{18}O$ (-11.3‰– -8.7‰) and stable $^{87}Sr/^{86}Sr$ ratios (0.708 07–0.708 21), indicating that thermal environment is open and it basically does not exist water-rock interaction, the geothermal water derived from fossil leaching water mixed with modern precipitation.

4 CONCLUSION

The origin and flow path of geothermal water in the Guanzhong Basin by using the ion chemistry and stable isotope (^2H, ^{18}O, $^{87}Sr/^{86}Sr$) methods have been confirmed. The supply source and flow path of geothermal water in the Chang'an District and Xi'an City were different: for Chang'an District, geothermal water was recharged from surface water and precipitation of Qinling Mountain; for Xi'an City, geothermal water was recharged from groundwater flow of the southwest of the study area. The flow direction of deep geothermal water in the southeast of Xianli terrace along the Wei River was consistent with that of geothermal water in the Xi'an City. When accepting recharge, supplywater mainly came from the west of study area.

The classification of geothermal water in the Guanzhong Basin had been confirmed based on the isotopic approach (δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ and ^{14}C). According to whether geothermal environment is open or not, the degree of water-rock interaction and the origin of geothermal water, geothermal water of the study area could be divided into four types: type A geothermal water of Gushi depression, which is featured by highest temperature, perfect closed thermal environment and significant water-rock interaction, belongs to the origin of residual sedimentary water; type B geothermal water of Xianyang City in the southeast of Xianli terrace, which is featured by higher temperature, good closed thermal environment and distinct water-rock interaction, belongs to the origin of residual sedimentary water mixed with fossil leaching water; type C geothermal water of Xi'an City, which is featured by high temperature, half closed thermal environment and the existence of some water-rock interaction, belongs to the origin of fossil leaching water; type D geothermal water of Chang'an District, which is featured by relatively low temperature and open thermal environment, belonged to the origin of fossil leaching water mixed with modern precipitation.

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