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Indication of hydrogen and oxygen stable isotopes on the characteristics and circulation patterns of medium-low temperature geothermal resources in the Guanzhong Basin, China

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Abstract: Guanzhong Basin is a typical medium-low temperature geothermal field mainly controlled by geo-pressure in the west of China. The characteristics of hydrogen and oxygen isotopes were used to analyze the flow and storage modes of geothermal resources in the basin. In this paper, the basin was divided into six geotectonic units, where a total of 121 samples were collected from geothermal wells and surface water bodies for the analysis of hydrogen-oxygen isotopes. Analytical results show that the isotopic signatures of hydrogen and oxygen throughout Guanzhong Basin reveal a trend of gradual increase from the basin edge areas to the basin center. In terms of recharge systems, the area in the south edge belongs to the geothermal system of Qinling Mountain piedmont, while to the north of Weihe fault is the geothermal system of North mountain piedmont, where the atmospheric temperature is about 0.2℃-1.8℃ in the recharge areas. The main factors that affect the geothermal water $\delta^{18}O$ drifting include the depth of geothermal reservoir and temperature of geothermal reservoir, lithological characteristics, water-rock interaction, geothermal reservoir environment and residence time. The $\delta^{18}O$-δD relation shows that the main source is the meteoric water, together with some sedimentary water, but there are no deep magmatic water and mantle water which recharge the geothermal water in the basin. Through examining the distribution pattern of hydrogen-oxygen isotopic signatures, the groundwater circulation model of this basin can be divided into open circulation type, semi-open type, closed type and sedimentary type. This provides some important information for rational exploitation of the geothermal resources.

Keywords: Guanzhong Basin; Hydrogen-oxygen isotopes; Storage characteristics; Circulation model

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Introduction

China's geothermal resources are characterized by wide distribution, huge potential and the presence of mainly low to mid temperature geothermal fields. It is reported that 85% of hydrothermal resources are found in 15 large and medium-sized sedimentary basins, including North China Basin, Songliao Basin and Guanzhong Basin (Wang et al. 2017; Jiang et al. 2017; Pang et al. 1990). Methods of geochemistry and stable isotope are the important way to study the geothermal sources, paths, extension, reservoir, as well as the circulation and renewal of underground hot water in geothermal areas (Giggenbach et al. 1992; Diamond et al. 2000; Majumdar et al. 2005, 2009; Pinti et al. 2013; Dotsika, 2010, 2012; Tan et al. 2012). The hydrogen-oxygen stable isotopes are widely used in the study of geothermal system, as they are the most widely distributed elements in nature. For example, hydrogen has three isotopes including H, D and ^3H, the isotopic abundance ratios for H and D is 99.984 4% and 0.015 6% respectively, with ^3H in rare existence.

The isotopic data are often used to study the source of geothermal water and describe the hydro-

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geochemical process in the liquid movement. Majumdar et al. (2005) analyzed the seasonal changes of ^{2}H and ^{18}O in geothermal water and surface water of Bakreswar and Tantloi geothermal fields, and discussed the recharge source of local geothermal water. Pinti et al. (2013) used inert gas isotope, hydrogen-oxygen stable isotopes and carbon and strontium isotopes as tracers to study the evolution of Los Azufres geothermal field and the heat source of salt in geothermal water. Many researches have been conducted in the recent years focus on studying and evaluating geothermal resources through comprehensive use of different environment isotope techniques (Clayton et al. 1975; Chandrajith et al. 2013). Craig (1961;1966), through identifying the linear relationship between δD and $\delta^{18}O$ of meteoric water for the first time, namely global meteoric water line, pointed out that geothermal water in hydrothermal system mainly came from meteoric water, and discovered that the noticeable phenomenon of "oxygen drifting" happened in the high-temperature hydrothermal system (Sun et al. 2001; Pang et al. 1990; Zhao.1994). Afterwards, Clayton (1975) used hydrogen-oxygen stable isotopes to study the water-rock interaction in geothermal system and hydrothermal mineralization process. The isotope data in recent years are mainly used to study the source of geothermal water and describe the hydrogeochemical process with the movement of the geothermal water. Chandrajith et al. (2013) concluded that the source of geothermal water in Sri Lanka was the meteoric water. Giggenbach (1992) studied the characteristics of hydrogen-oxygen isotopes on the convergent boundary of plates, and concluded that the geothermal water was the result of the mixing of local meteoric water and magmatic water; Ma (2007) used the hydrogen-oxygen isotope technique in Taiyuan basin to indicate that geothermal water originated from paleo-atmospheric precipitation and underwent different degrees of evaporation and concentration, and geothermal water in different flow systems had different periods of recharge; Komatsu et al. (2021) observed that most of the unused geothermal water in Okayama Prefecture was attributed to the mixing of meteoric water and sea water, by analyzing the signatures of D, ^{18}O and Sr isotopes in the thermal water (Sun et al. 2015; Richard et al. 2019; Komatsu S et al. 2021).

The application of hydrogen-oxygen isotopes in studying China's geothermal resources mainly focus on the convective geothermal systems of uplifted mountain areas in Zhangzhou, Tibet, Jiangxi province and other regions (Pang et al. 1990; Guo et al. 2017; Zhang et al. 1989; Qin et al. 2005; Ma et al. 2006, 2008; Wang et al. 2020). Pang et al. (1990) analyzed the tritium characteristics and formation conditions of geothermal water and other natural water in Zhangzhou Basin, who calculated the age of geothermal water in Zhangzhou Basin by using the "piston model" method. Their research provided an approach towards clarifying the patterns of groundwater recharge, flow and discharge on a basin scale, which also revealed the genesis of geothermal water. The isotopes study of geothermal water in Guanzhong area was conducted in more than a decade time from the end of the 1980s to the beginning of the 21st century. After analyzing the changes of hydrogen-oxygen stable isotopes in meteoric water of Shaanxi province, Zhang (1989) conducted a research to look into the factors that affect the change of δ value, including that from precipitation, temperature and evaporation, and proposed the correlation of hydrogen-oxygen isotopes of precipitation recharge with groundwater. Qin et al. (2005) examined the hydrochemical and isotopic compositions of geothermal water in the wells at the depth from 300 m to 3 000 m in Xi'an city, and pointed out that the recharge area of the geothermal water in Xi' an was located in Qinling Mountains; in addition, they estimated the average velocity of groundwater according to the ^{14}C age difference in the geothermal wells. After analyzing the composition of hydrogen-oxygen isotopes of geothermal water in the south of Guanzhong area, Ma et al. (2006) stated that the water at a normal temperature was attributed to the mixing of more than 50% surface water with the geothermal water, as there was an average temperature gap of about 16℃ between the recharge source and modern precipitation of net hot water in the study area. They suggested that the recharge source was glacial water of the Quaternary Period, located above the altitude of 1 800 m in Qinling Mountains. They further explored the hydraulic connection among all the major aquifers in the area and found that the deep fractured zone on the basin edge is the key factor to control the hydraulic connection in the south of Guanzhong Basin(Luo et al. 2017; Liu et al. 2009). In addition, this research indicated that the geothermal water in Xi'an and Xianyang areas belongs to different geothermal systems with different recharge sources (Wang et al. 2004; Wang et al. 1989; 1996; Hu et al. 2009). Li Xiucheng et al. (2016) used the isotope-based hydrogeochemical method to study the Dongda Geothermal Field of Guanzhong Basin, and discovered that the highest temperature of the geothermal reservoir was 110℃, with the largest circulation depth of 3 120 m. However, due to the restriction of sampling conditions, limited water samples were collected for geochemical analysis, resulting in the isotopic researches only conducted for a single geotectonic unit in the Guanzhong basin, left behind the other units without any researches to examine the sources and circulation of the thermal groundwater. Therefore, in this paper a study of hydrogen-oxygen stable isotopes for six geotectonic units or the entire Guanzhong basin is coducted, with the intention of proposing the circulation and source models of the geothermal water in Guanzhong Basin, together with some insights for the future planning and development of geothermal water resources in the basin.

1 Tectonic background

Guanzhong Basin covers 20 000 km^2 in areal size with the Cenozoic deposit of more than 7 000 m in thickness. As a fault-block basin active during the Cenozoic era, this basin has the main topographic features like rivers, Tertiary eolian sedimentation and Quaternary loess. Bedrocks are composed of Proterozoic schists and Cenozoic intrusive granite. Currently surrounded by mountains on three sides, the generation and evolution processes of the basin involved uplifting and depression in several tectonic stages. As influenced by Qilian-Lvliang-Helan epsilon-type tectonic system, New China tectonic system, Longxi rotating-rolling tectonic system and Qinling latitudinal tectonic system, many faulting structures extending in different directions has been developed in the fault-depression basin, from which the Guanzhong basin was identified as a complex graben basin. Previous studies (Yao et al. 2001; Yan et al. 2012; Singh et al. 2019; Jiao et al. 2019) with a lot of detailed discussions on the tectonic systems show that the Guanzhong basin can be divided into six geotectonic units including Baoji bulging, Xianli fault-step zone, Xi’an depression, Linlan bulging, Gusi depression and Pucheng bulging. The demarcation of the tectonic units was conducted on the basis of analyses of fault scale and activity, thickness of sedimentary construction, bedrock facies structure, landform type, earthquake distribution and settlement rate. Large numbers of faults offer the paths for the migration, storage and discharge of heat and substances in the basin (Fig. 1).

As a typical distribution area of medium-low temperature geothermal system in China, Guanzhong Basin is famous for its’ abundant geothermal resources. The main thermal reservoir in the Guanzhong basin is divided into three types, namely, Cenozoic sandstone pore thermal reservoir, structural fracture and fissure thermal reservoir, and carbonate thermal reservoir. The Quaternary and Neogene strata act as the caprocks of the thermal reservoirs. Guanzhong Basin has sufficient water circulates to an allowable depth. The underground flow can “collect” heat and useful elements that are scattered in the rocks. It took a long time to

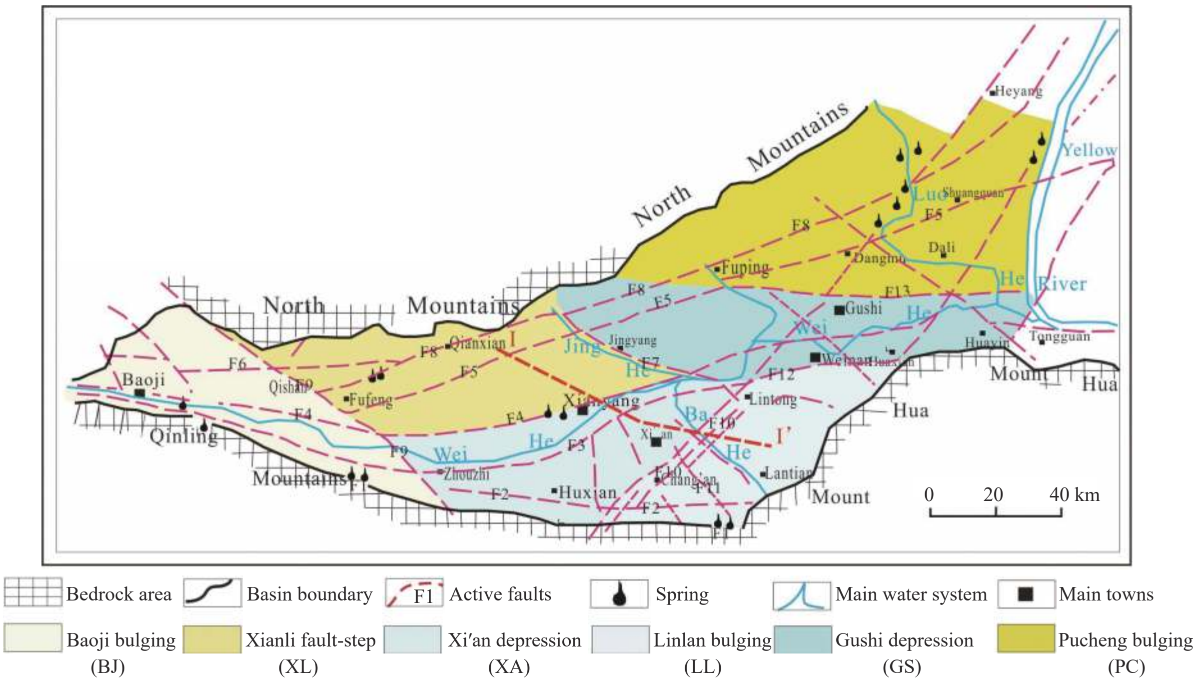

Fig. 1 Main fracture distributions and tectonic zoning of the Guanzhong Basin

form and build these geothermal systems. In addition, these geothermal systems are mostly found in the fault-fractured zone or at the intersection of two fault systems in different directions (Ma et al. 2016), the temperature of geothermal reservoir is usually lower than 140℃ and the circulation depth is less than 4.0 km (Craig, 1961; 1966).

2 Sampling and testing methods

This study was conducted, based on the analysis of water quality with samples collected from geothermal wells in the six geotectonic units and surface water bodies in the Guanzhong Basin, and main focus on hydrogen-oxygen isotopes. The sampling points for this study are shown in Fig. 2, where the typical geothermal wells in the regions (such as Xi'an and Xianyang) with dense distribution of geothermal wells were also sampled. As a result, there were in total 121 sets of isotopic data were acquired, including 90 sets from the sample analysis and 31 sets from related literature survey (Liu et al. 2009).

In the sampling process, each groundwater sample was leached through 0.45 μm micro filtration membrane to remove the suspended solids in water, and then moisturized twice by deionized water and put into the dry polyethylene bottle (100 mL). The measurement instrument is MAT-253 isotope mass spectrum. The hydrogen and oxygen isotopes were measured through zinc reaction method and CO_2-H_2O balance method, respectively, with the measurement precision (mass fraction) of ±2.0‰ and ±0.2‰ (Table 1).

3 Results and analysis

3.1 Characteristics of spatial distribution

The hydrogen-oxygen stable isotope samples collected from the geothermal water wells and cold water from Qinling Mountains and river in six tectonic units within the study area were analyzed. The result shows that δD value of geothermal water ranges from –90.0‰ to –54.5‰, with an average value of –77.1‰. The maximum and minimum δD values are found in samples from Gushi depression zone and Xi'an depression zone separately. The $\delta^{18}O$ value of geothermal water ranges from –12.8‰ to –1.7‰, with an average value of –8.82‰; and the maximum and minimum $\delta^{18}O$ values are found in samples from Gushi depression zone and Baoji bulging zone separately. It is noted that the maximum δD value and the maximum $\delta^{18}O$ value are both found in the Gushi depression zone. In terms of isotope signature in source water, the δD and $\delta^{18}O$ values of piedmont surface water of Qinling Mountains range from –81‰ to –71‰, and from –11.4‰ to –9.9‰ separately, while δD and $\delta^{18}O$ values of river water range from –68.4‰ to –57.1‰ and from –9.28‰ to –8.29‰ respectively. In other words, these δD and $\delta^{18}O$ values all fall within the range of geothermal water.

As indicated in Fig. 3, the δD contours of geothermal water in Xi'an depression zone form a low-value cone, showing that the geothermal water has perhaps been recharged by low temperature water or water at the high latitude regar-

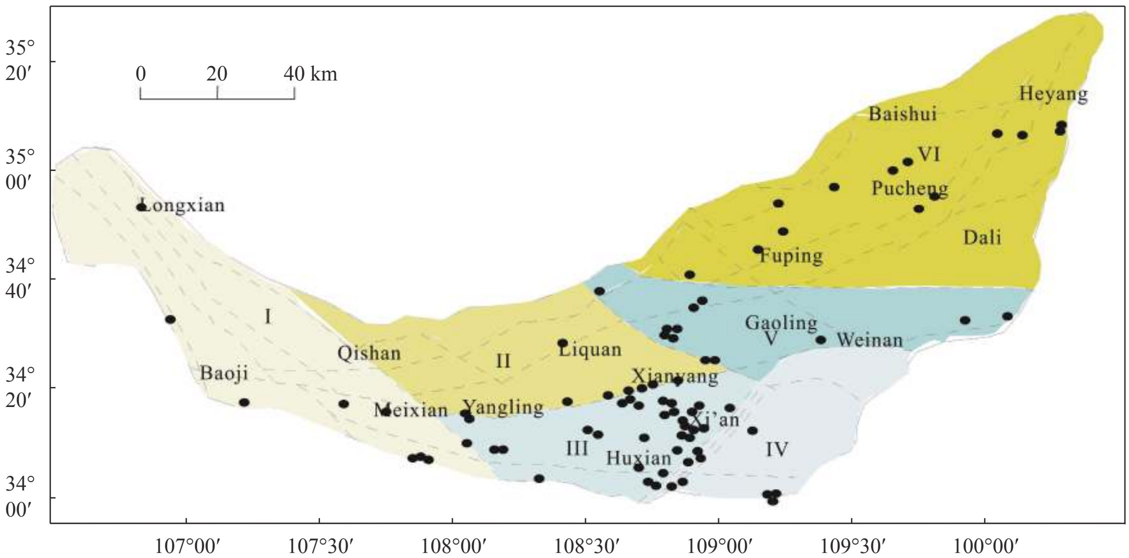

Fig. 2 Distribution of sampling points of hydrogen-oxygen stable isotopes in study area

Table 1 The result of hydrogen-oxygen stable isotopes in study area

Sample NO.	Depth	Temperature	pH	δD/‰	$\delta^{18}O$/‰	Sample NO.	Depth	Temperature	pH	δD/‰	$\delta^{18}O$/‰
Surface water						q014	1 672.08	66	8.57	–79.42	–11.25
R001	-	17.5	7.63	–61.24	–8.87	q031	2 850	88	8.22	–84.63	–9.17
R005	-	17.5	7.38	–57.1	–8.28	q035	496.8	68.3	8.76	–84.93	–12.52
R007	-	17.5	7.83	–66.92	–9.14	q036	573	49.6	8.66	–82.57	–11.43
R008	-	17.5	7.53	–68.4	–9.28	q037	1 360	57	8.32	–80.02	–11.18
R009	-	17.5	7.47	–65.1	–9.05	q039	1 500	54	8.86	–84.01	–11.4
Outside basin						q043	2 402	23.5	8.35	–87.71	–4.73
q008	580	45	8.23	–86.51	–12.9	q045	2 700	96	8.32	–83.28	–5.12
q041	250.27	58.2	8.02	–73.51	–10.61	q046	3 000	91	8.36	–78.1	–8.72
q042	530	43	8.31	–78.92	–11.38	q048	1 750	69	8.15	–82.36	–7.27
q056	648.08	33.7	8.34	–78.44	–11.51	q057	2 685.3	80	7.9	–79.57	–9.44
Baoji bulging（BJ）						q058	2 905.3	86	7.88	–81.62	–9.84
q006		28.9	7.55	–71.46	–10.62	q060	1 450	55	7.94	–83.89	–11.46
q009	1 462	46	8.39	–82.24	–11.9	q075	1 650	85	8.88	–85.02	–11.92
q015	2 470	53	7.85	–85.23	–11.47	q077	2 000.2	65	8.26	–84.48	–9.34
q028	1 602.6	51.2	8.56	–85.54	–11.65	q078	2 731.86	80	8.11	–84.74	–6.85
q029	350.5	72	8.39	–86.34	–12.06	q079	3 479.35	112	8.39	–85.29	–3.48
q033	450.5	64	8.87	–86.2	–12.65	q083	3 000	93	8.58	–85.64	–5.89
q034	282	68	8.77	–88.06	–12.82	q084	3 015.9	98	8.68	–83.19	–8.05
q071	-	29	8.27	–81.88	–11.85	q090	1 601.9	65	7.77	–84.38	–7.22
S001	1 450	29	8.32	–70.4	–8.1	q091	1 958	69.5	8.41	–77.24	–8.81
S002	1 114.35	39.2	8.27	–76.8	–11.5	q092	3 558	94	7.65	–84.07	–2.3
S003	400.18	41.5	8.16	–81.8	–11.1	q094	3 355	102	7.81	–87.3	–3.48
S004	400	41.5	8.32	–72.3	–10.6	q095	2 658	92	8.3	–81.41	–8.56
S005	Spring	30	8.36	–69	–9.6	q096	2 003.17	52	8.64	–83.5	–11.44
S015	1 253	47	8.25	–70.8	–9.2	q097	2 211.8	81	8.15	–84.45	–10.22
Xianli fault-step（XL）						q098	2 651.7	99	8.46	–85.17	–3.65
q030	3 050	90	7.98	–82.6	–8.08	q099	2 500		8.47	–83.5	–9.18
q080	2 700	70	7.83	–85	–7.8	S014	1 450	40	8.23	–76.6	–11.611
q086	2 800	90	8.28	–85.95	–10.41	**Pucheng bulging（PC）**					
q087	2 105.8	65	7.96	–85.07	–10.3	q016	169	29.5	8.2	–74.92	–9.79
q088	1 901.68	53	7.65	–76.45	–10.24	q017	160	27.5	8.17	–73.22	–9.72
q093	2 975	90	7.71	–83.9	–2.85	q018	150	27.8	8.08	–73.16	–9.77
S008	2 787	71	8.03	–68.1	–6.7	q019	210	28.6	8.16	–72.66	–10
S020	1 751	72	8.14	–71.6	–6	q020	300	41	7.79	–75.6	–10.25
S022	2 471	90	7.95	–66.3	–3.8	q021	520	27	8.1	–74.16	–10.01
S023	3 553	94	7.89	–70.6	–4.5	q022	2 000	63	8.23	–87.78	–9.87
S024	2 000	74	8.31	–69.3	–4.4	q023	651.8	25.5	8.33	–69.47	–9.37
S025	2 818	89	8.03	–66	–3.7	q024	270	26	8.32	–69.12	–9.72
S028	3 500.3	120	7.96	–71	–5.3	q025	430	28	7.68	–73.06	–10.14
S029	2 905.3	86	7.88	–71.5	–9.34	q026	2 452	75	8.16	–83.59	–7.98
S030	2 013	80	8.15	–70.8	–9.07	q049	651.5	28	8.22	–74.11	–10.23
Linlan bulging（LL）						q050	1 050	33	8.13	–77.17	–11.26
q027	2 625.5	63	8.34	–81.22	–9.75	q051	778.3	42	8.16	–75.99	–10.86
q032	1 500	56	8.81	–85.01	–12.03	q073	2 600	105	7.3	–68.23	–3.69

continued Table1

Sample NO.	Depth	Temperature	pH	δD/‰	$\delta^{18}O$/‰	Sample NO.	Depth	Temperature	pH	δD/‰	$\delta^{18}O$/‰
q038	1 772	56	8.78	–84.58	–11.61	q085	2 857.8	96	8.64	–84.09	–9.36
q040	2 060	79	8.41	–85.85	–11.6	q089	800	35	7.74	–76.81	–10.2
q052	854.3	49	8.68	–78.74	–11.36	**Gushi depression（GS）**					
q053	10.7	44.6	8.33	–72.36	–10.46	q001	2 470	71	8.41	–85.23	–7.23
q055	2 136.9	52	8.34	–81.48	–10.54	q002	2 403	78	7.98	–85.93	–7.32
q061	455.9	54.5	8.76	–76.4	–10.94	q003	2 341	68	8.13	–85.4	–7.67
q062	652.8	58	8.92	–82.27	–11.74	q004	2 790	80	7.31	–72.37	–7.25
q072	1 012.6	53	8.73	–83.25	–11.99	q007		22.1	8.16	–69.68	–10
q076	1 985	55	8.56	–81.65	–11.34	q044	2 870	100	8	–75.41	–3.96
q100	3 230	81	8.05	–85.14	–5.53	q059	1 669.7	61.5	8.76	–87.02	–11.92
S006	Spring	11	-	–71.3	–10.1	q069	3 258.7	63	7.94	–85.06	–7.66
S007	Spring	43	-	–69.1	–9.8	q070	3 200	101	7.5	–84.45	–2.3
S018	460	55	-	–72.9	–10.8	S009	3 008.9	100	-	–54.5	–1.7
S019	1 550	50	-	–76.2	–11	S010	2 451	92	-	–56.4	–2.7
Xi'an Depression（XA）						S011	2 600	105	-	–61.1	–3.21
q005	2 100	35.2	8.83	–85.01	–11.68	S012	854	49.5	-	–71.9	–10.4
q010	3 258.7	92	8.63	–85.37	–8.41	S013	1 500.3	55	-	–68.9	–9.5
q011	2 096	81.5	8	–85.43	–10.99	**Qinling（QL）**					
q012	2 436.5	52	8.6	–84.32	–10.94	S041	0	16	7.83	–71	–9.9
q013	3 005	80	8.53	–83.08	–9.4	S042	0	16	7.52	–81	–11.4

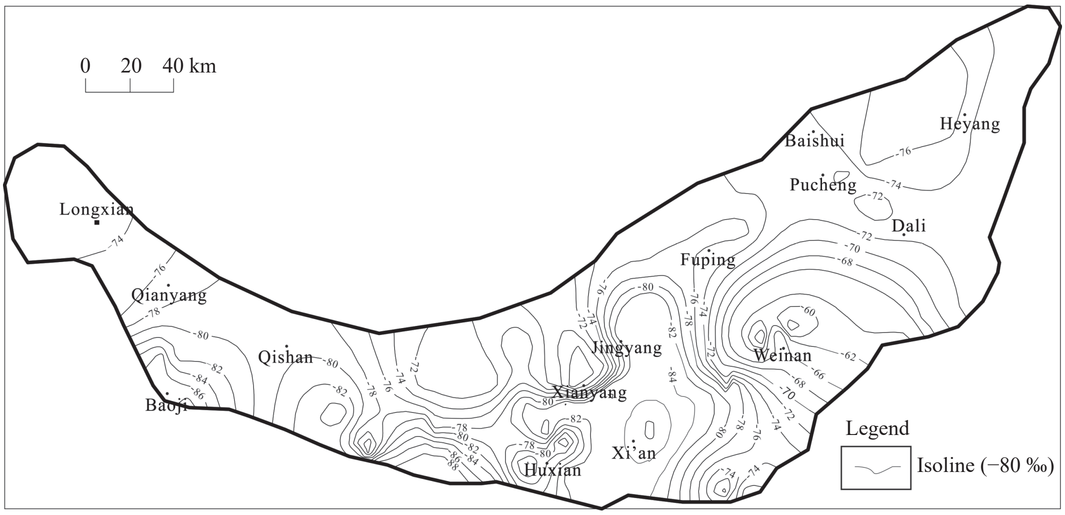

Fig. 3 The isoline map of δD value of geothermal water in Guanzhong Basin

dless the influence of climatic condition. The δD value of geothermal water along Weinan-Huayin belt in Gushi depression zone forms a δD dome, with the maximum δD value of –54.5‰ in the basin. The depletion of ^{2}H shows that the geothermal water may be recharged by low-temperature or high latitude water. For the ^{18}O isotope (Fig. 4), the $\delta^{18}O$ value of the geothermal water shows a gradual increase from the areas around the basin boundary to the basin hinterland. The maximum $\delta^{18}O$ values in Weinan-Huayin belt and Xianyang-Xi'an belt are –1.7‰ and –2.3‰, respectively, showing that the ^{18}O might have experienced a drifting process. The most noticeable drifting happens along Weinan-Huayin belt with the largest drifting range; and the second one is in Xianyang-Xi'an area.

3.2 Analysis of geothermal water recharge

3.2.1 Recharge sources

Based on the data of hydrogen-oxygen stable isotopes of meteoric water obtained from IAEA/WMO

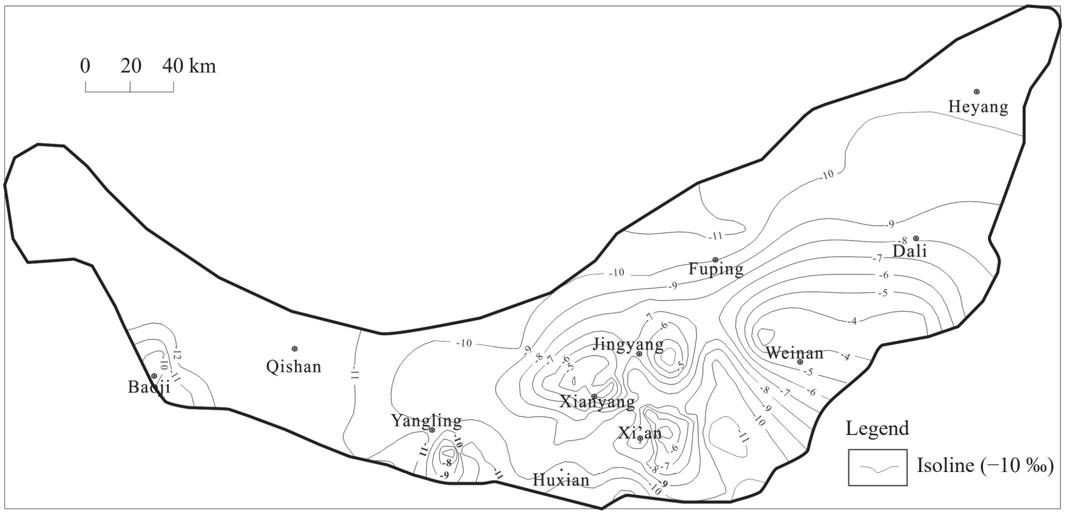

Fig. 4 The isoline map of $\delta^{18}O$ value of geothermal water in Guanzhong Basin

Xi' an Station, the linear regression method was used to build the relationship between δD and $\delta^{18}O$ based on the precipitation in Xi' an area, which is $\delta D=7.49\delta^{18}O+6.12$. Because the study area is located in China' s landlocked arid and semi-arid area with limited precipitation and high evaporation, the meteoric water is strongly affected by evaporation. Compared to the $\delta D/\delta^{18}O$ equations of both global meteoric water and that of China, the $\delta D/\delta^{18}O$ equation of the Guanzhong area has a smaller intercept and a lower gradient. The relation between δD and $\delta^{18}O$ in the study area is shown in Fig. 5.

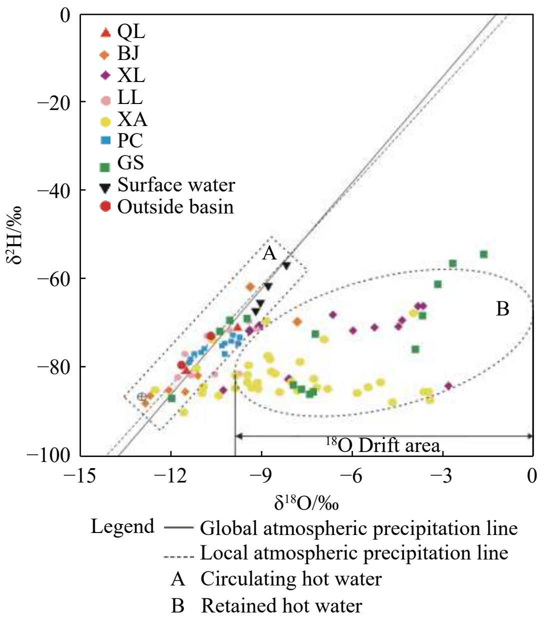

Fig. 5 δ^2H versus $\delta^{18}O$ plot of geothermal water in Guanzhong Basin

As can be seen from Fig. 5, the $\delta D/\delta^{18}O$ plot for surface water in Qinling Mountains and the river water in study area both fall below the meteoric water line; and the isotopic signatures of most geothermal water in Baoji (BJ), Linlan (LL) and Pucheng (PC) bulgings distribute near the rainwater line, showing that there is a frequent renewal of the geothermal water by the surface water in the bulging areas, which also suggests that the modern meteoric water and river seepage are the main source of recharge. The signatures of some piedmont geothermal water of Qinling Mountains in Xi' an and the geothermal water along the North Mountains of Xianli and Gushi distribute along the rainwater line. Moreover, the geothermal water in Xi'an and Xianyang has the similar δD value to the piedmont geothermal water of Qinling Mountains, and the geothermal water in Gushi has the similar δD value to the piedmont geothermal water of the North Mountains, showing that they are located in different hydrogeological units. Taking Weihe Fault as a boundary, the area to the south is Qinling piedmont geothermal water system, which is mainly recharged by meteoric water and surface water of Qinling Mountains, while the area to the north is piedmont geothermal water system of North Mountains, which is mainly recharged by meteoric water and surface water of North Mountains.

The considerable $\delta^{18}O$ drifting quantity also reveals that there is the strong water-rock interaction in Huayin section of the Gushi depression zone. Because of the enclosed geological environment, the geothermal water is recharged by the sources at a low temperature. At the same time, the depletion of ^2H and ^{18}O happens in a few thermal water sampling points. The variance of ^2H is 17.4‰, which is the largest in Weinan-Huayin section of the Gushi depression zone, showing that the geothermal water in this area might migrate in a reduction-type enclosed geological environment. In addition, δD-$\delta^{18}O$ points of the geothermal water in Xi' an, Xianyang and Gushi depression areas overlap or intersect each other, showing that the mutual mixing or recharge may exist among the geothermal water of different regions.

3.2.2 Recharge water temperature

It is acknowledged that the difference in the temperature of recharge meteoric water is one of the important factors that influence the drifting of oxygen isotope. The relational expression between the $\delta^{18}O$ of meteoric water and the annual average temperature in Xi' an Meteorological Station is $\delta^{18}O$=0.47T-12.24, with a correlation coefficient of 0.976. This expression shows that the annual average $\delta^{18}O$ value may drop by 0.47‰, if the annual average temperature falls by 1℃. The average $\delta^{18}O$ value of meteoric water in the study area is –7.38‰, and major $\delta^{18}O$ drifting occurs in Xianyang-Xi' an and Weinna-Huayin sections in the basin. Furthermore, calculated results reveal that the two sections are actually the center of $\delta^{18}O$ high value. The calculated results also show that the atmospheric temperatures for current geothermal recharge water are 10.8℃ and 12.7℃, respectively, in the two sections, which are lower than modern atmospheric temperature as 12°C-13.6°C in average in Shaanxi province. However, in the recharge source area, the atmospheric temperature is about 0.2℃-1.8℃ in the study area. The difference in atmospheric temperature between that at the moment of the geothermal water recharge and the modern atmospheric temperature is consistent with the ground temperature change since the last glacial period. This was confirmed by the record of plant pollen analysis performed in the north of China (Yao et al. 2001), showing that the geothermal water in the areas with major $\delta^{18}O$ drifting occurs in the Xianyang-Xi'an and Weinan-Huayin in sections was recharged by meteoric water during the last glacial period.

3.3 Analysis of influencing factors of $\delta^{18}O$ drifting

As stated above, there are quite a few factors that influence the $\delta^{18}O$ content and migration in the geothermal water, which will be discussed below. Once the recharge source water of different periods of time and at different altitude spenetrates into the geothermal reservoir through various infiltration paths, the $\delta^{18}O$ drifting will be related to such factors as the geothermal water storage environment, flow retardance coefficient, lithologies and water-rock interaction. Specifically, because of the $\delta^{18}O$ richness in rock minerals, it is often used to measure the strength of water-rock interaction.

3.3.1 Depth of geothermal reservoir

As indicated in Fig. 6a, the $\delta^{18}O$ value of geothermal water in the Guanzhong basin seems to have a positive correlation to the depth of the geothermal reservoir, with the correlation coefficient described as r^2=0.53. And this type of correlation is more obvious in the deep geothermal wells than that of the shallower ones. It can also be seen from Fig. 6a that the distribution of $\delta^{18}O$ from the geothermal water of less than 1 000 m deep is near the local precipitation line, implying that there is a more frequent interaction between the shallow geothermal reservoir and meteoric water than that of water-rock interaction. On the other hand, more $\delta^{18}O$ is accumulated in a relatively closed deep geothermal reservoir than that of shallower one. However, the $\delta^{18}O$ value does not change much at depth with the involvement of active fault where the reservoir is in a relatively open condition due to being well connected with the ground surface. This is the case in the geothermal monitoring points near the big fault zone of Qinling Mountains to the south of Xi'an depression zone.

3.3.2 Temperature of geothermal reservoir

Because of the difficulty in reaching the temperature of thermal reservoir, wellhead temperature is often used to characterize the temperature of thermal reservoir to a certain extent. As the sampling temperature of geothermal water increases, $\delta^{18}O$ drifting quantity grows gradually (Fig. 7b). The positive correlation coefficient is described as: r^2=0.68. Correlation rises with the increasing temperature at well heads, showing that high temperature of the thermal reservoir is more conducive to the positive drifting of $\delta^{18}O$. Under the same condition, the water-rock interaction is very likely to happen in the high temperature groundwater. Besides, the temperature of geothermal water depends on such factors as the proportion of cold surface water, the depth of geothermal water and availability of favorable geological condition.

3.3.3 Water-rock equilibrium

Water-rock equilibrium is an important factor that affects the $\delta^{18}O$. Fig. 7a indicates the relationship between total dissolved solids (TDS) and $\delta^{18}O$, showing that the $\delta^{18}O$ content increases along with the increasing TDS in the geothermal water system. Without the foreign TDS sources, TDS can usually reflect the strength of water-rock equilibrium. The larger TDS, the more frequent exchange of $\delta^{18}O$ and the larger drifting scope are. As

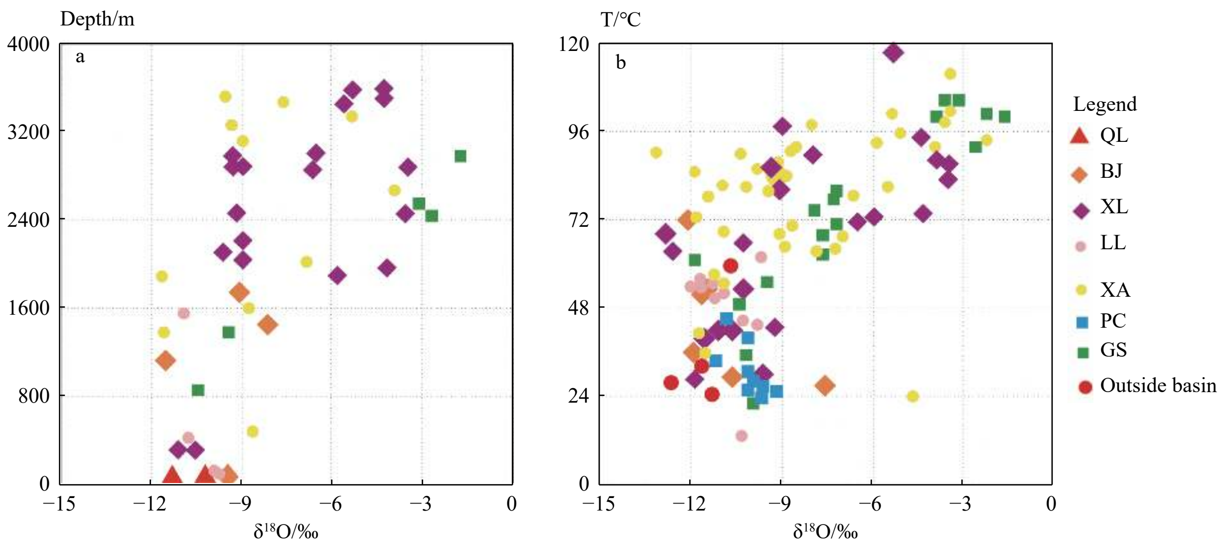

Fig. 6 Plots of $\delta^{18}O$ value versus depth (a) and temperature(b) of geothermal water in Guanzhong Basin

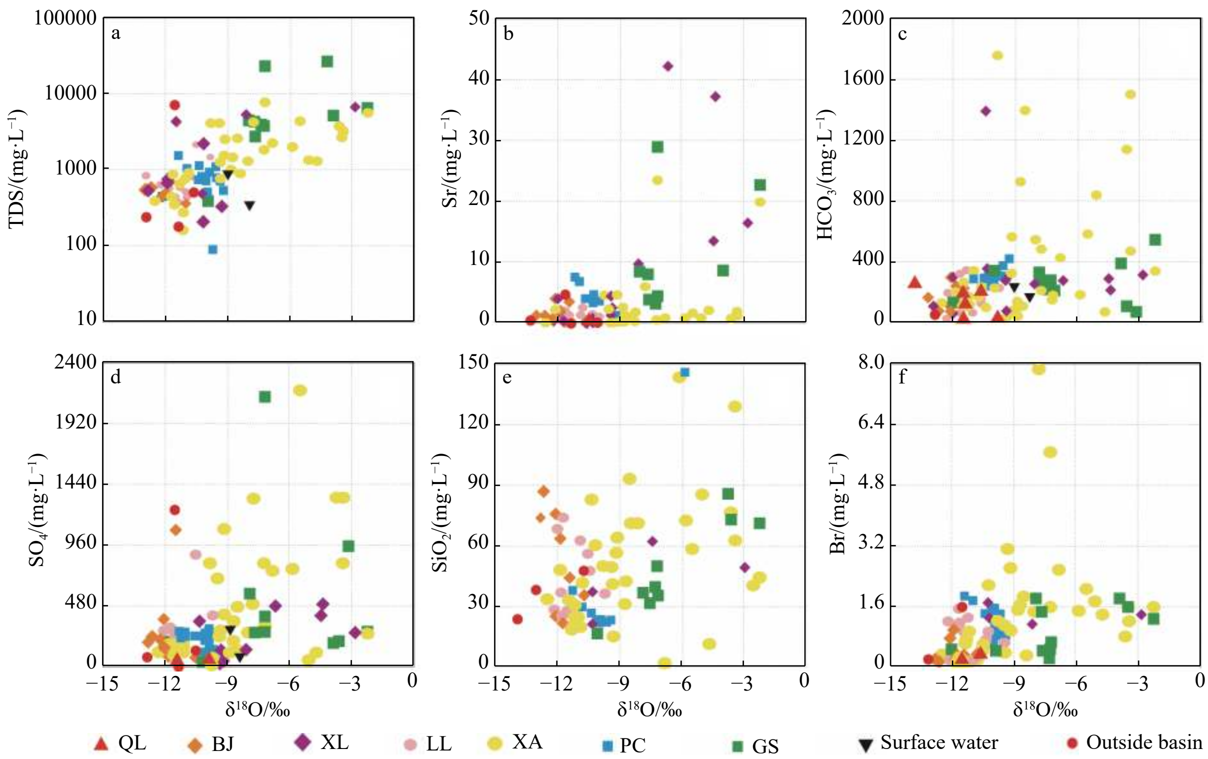

Fig. 7 Diagrams of $\delta^{18}O$ value versus TDS, Sr, HCO_3^-, SO_4^{2-}, SiO_2 and Br of geothermal water in Guanzhong Basin

indicated in Fig. 7b, the abundance of $\delta^{18}O$ value happens along with the increasing strontium (as Sr) contents in geothermal water system. The positive correlation coefficient is described as: r^2=0.48, showing that $\delta^{18}O$ drifting quantity of the geothermal water is related to the water-rock equilibrium. The stronger water-rock reaction, the larger $\delta^{18}O$ drifting quantity is. The strong water-rock reaction is an important factor that affects $\delta^{18}O$ drifting quantity.

Rock type is also a key factor that enables the $\delta^{18}O$ migration in groundwater. Fig.7c-e shows the relationship between anions from different types of rock and the $\delta^{18}O$ value of geothermal water. As indicated in Fig. 7c, the abundance of $\delta^{18}O$ value happens along with the increase in HCO_3^- contents, which are in a weakly positive correlation (coefficient: r^2=0.32). On the basis of regional tectonic analysis, in the study area the water-rock interaction with the involvement carbonate rocks frequently takes place in the vicinity of fault and fault transitional zones. Similarly, Fig. 7d reveals that $\delta^{18}O$ drifting quantity of geothermal water increases along with the rise in SO_4^{2-} contents, with a positive correlation coefficient of r^2=0.38. The chemical exchange between the minerals with sulfate constituent such as gypsum, and the geothermal water, causes the SO_4^{2-} increase and considerable $\delta^{18}O$ content in the geothermal water. Similar trend occurs in the geothermal water system with the minerals of silicate rock involved, where the higher SiO_2 contents, the more considerable the $\delta^{18}O$ drifting quantity is.

3.3.4 Geothermal reservoir environment

Geothermal reservoir environment is another factor that affects the $\delta^{18}O$ in geothermal water. In the case of an accessible geothermal reservoir environment, the circulation of the geothermal water can cause the reservoir effectively updated, and the depleted $\delta^{18}O$ of meteoric water constantly gets supplemented and $\delta^{18}O$ hardly experiences any drifting. Under a closed geothermal reservoir environment, the long-term water-rock interaction contributes much to the abundance of $\delta^{18}O$.

Brominate (as Br^-) in a geothermal reservoir is usually the biochemical indicator for organic decomposition. The higher Br^- contents reflect a strong biochemical reaction and the reduction environment, namely a closed system in the geothermal reservoir. Fig.7 indicates the weakly positive correlation between Br^- contents and $\delta^{18}O$ value in the geothermal water of Guanzhong Basin, and the correlation coefficient is 0.33. Specifically, in the closed environment, $\delta^{18}O$ tends to get concentrated.

3.3.5 Lithological characteristics

The initial isotopic difference between host rocks of geothermal reservoir and recharge water is also one of important factors that affect the $\delta^{18}O$ value. Different rock minerals may yield different $\delta^{18}O$ values. The $\delta^{18}O$ differences between carbonate minerals and meteoric water is as much as 36‰ (Yan et al. 2012). As $\delta^{18}O$ gradient difference is rather high, the $\delta^{18}O$ in geothermal reservoir of carbonate rocks is more likely to get concentrated in depleted ^{18}O-type water body. As a result, the geothermal water witnesses a considerable $\delta^{18}O$ drifting under the same condition, as indicated in Fig. 7C, i with a positive correlation between carbonate content and $\delta^{18}O$ exchange.

Moreover, Fig. 8a indicates the positive correlation between $\delta^{18}O$ and $\delta^{13}C$ values in geothermal water (coefficient r^2=0.54). The abundance of $\delta^{18}O$ values happens along with an increase in $\delta^{13}C$ values, showing that the stronger reaction between geothermal water and carbonate salt in the water, i.e. the stronger water-rock equilibrium and the larger ^{18}O drifting is.

3.3.6 Residence time

The residence time of groundwater can be indicated by identifying the water age. As indicated in Fig. 8b, the $\delta^{18}O$ values in geothermal water gradually increases along with the increase of the water residence time. In other words, the longer residence time of geothermal water in geothermal reservoir, the larger drifting of the $\delta^{18}O$ isotopic signature is. The residence time of geothermal water is one of the main factors that affect $\delta^{18}O$ drifting. The higher residence time, the stronger $\delta^{18}O$ exchange between geothermal water and reservoir rocks.

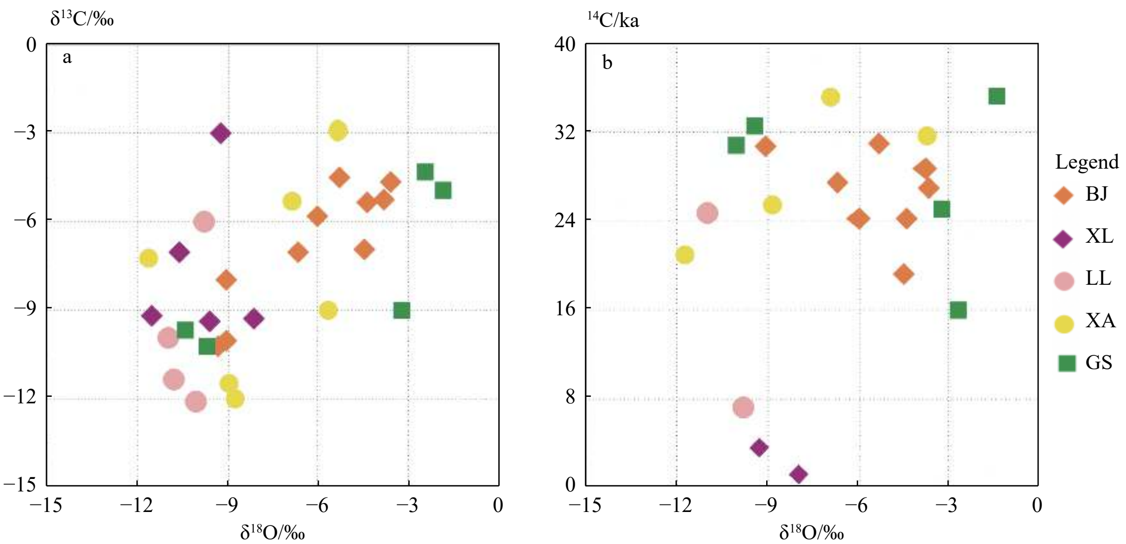

Fig. 8 Relation between $\delta^{18}O$ value of geothermal water in Guanzhong Basin and $\delta^{13}C$ and ^{14}C

3.4 Deuterium excess (d-excess) characteristics

From the definition of d-excess (Deuterium excess, parameter d=δD-8δ^{18}O (Dansgaard,1964)), it was reported that factors affecting the change of δD were the same as the δ^{18}O. The d-excess of the geothermal water in Guanzhong Basin ranges from −66.3‰ to 16.3‰, with a wide δD range of 82.6‰ (Fig. 9). The minimum and maximum points of the d-excess parameter are located near the Gushi depression along Jinghe fault zone and Longxian-Qianshan-Yabo fault zone separately. The evolution characteristics of d-excess parameter can be used to reveal the recharge, runoff and discharge characteristics of the groundwater in the area. Fig. 10 shows the distribution and contours of the d-excess parameter over the basin.

As indicated in Fig. 10, the d-excess parameter (d) of geothermal water in the study area, unlike the abundance trend of δ^{18}O, gradually declines from the edge of basin to the basin center, where the d lows extend over the area with δ^{18}O highs. For example, in the centeral areas of d low confined by Xianyang-Xi' an-Gaoling and Weinan-Huayin, the d values reach their lowest as −65.7‰ and −44.1‰, respectively, while the highest values occurs on the basin edges along piedmont areas such as the Qinling mountains in particular. This shows that the geothermal water along the piedmont has the considerable d value, depleted δ^{18}O and small δ^{18}O drifting scope. The isotopic signatures of both ^{2}H and ^{18}O with sampling points along the North Mountains and the piedmont of Qinling are roughly closed to the local meteoric water line. As regard to the d-excess parameter, the d isoline map shows the same pattern as that of the meteoric water (6.12‰), which suggests that frequent exchange between the geothermal water and meteoric water, limited water-rock interaction and almost no identifiable δ^{18}O drifting occur in the piedmont area; thus the area can be identified as direct recharge area of the geothermal water. Because the strength of water-rock interaction and the length of residence time can affect the δ^{18}O drifting quantity, which even affect d-excess (d) value, the δ^{18}O drifting in geothermal water from recharge area to discharge area increases, while the d value decreases. The distribution characteristics of the d value show that the flow directions of geothermal water in study area are generally from the basin edges to basin center. They can be identified as: 1)

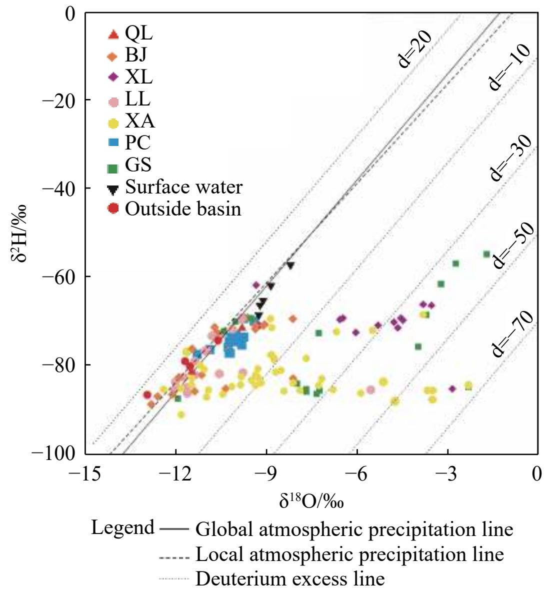

Fig. 9 Underground d-excess parameter (d) characteristic lines of Guanzhong Basin

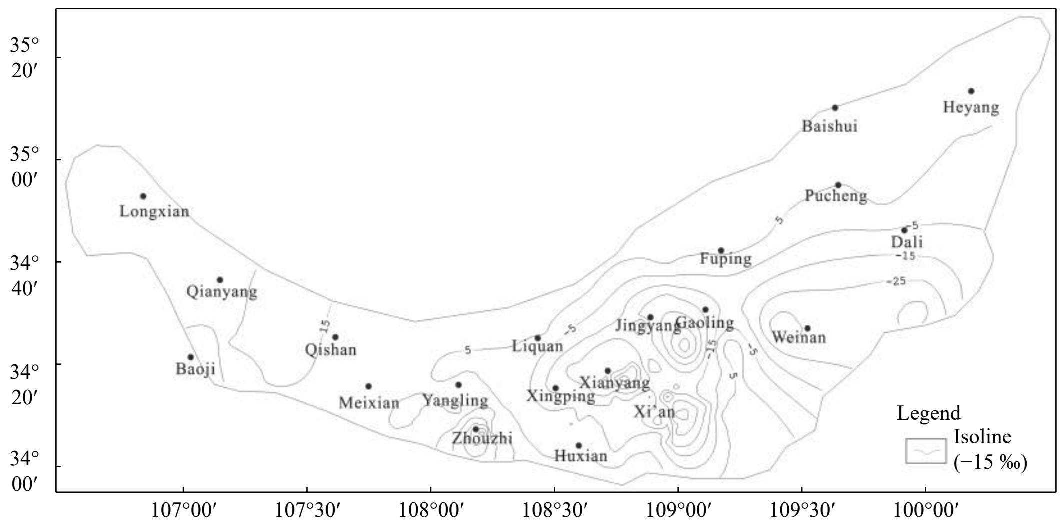

Fig. 10 Underground d-excess parameter (d) isoline of Guanzhong Basin

the geothermal water flows from the northeast to the southwest, and then to the north of Weihe River; 2) it flows from the southwest to the northeast, and to the south of Weihe River. In other word, these flows go together the basin center area with the confluence zone at theXianyang-Xi' an-Weinan.

4 Formation mechanism and circulation model of geothermal water

4.1 Formation mechanism

The geothermal water of the Guanzhong Basin is likely to have ancient water of sedimentation genesis. Fig. 11 shows the $\delta^{18}O$-δD relation of different genesis types, which suggests that the geothermal water in the study area is almost unlikely to have magmatic and mantle origins. The metamorphic water at the temperature of 300℃-600℃ is either unlikely to recharge the geothermal reservoir in this study area. The $\delta^{18}O$-δD values in the geothermal water in the Gushi depression, Xianli fault-step and Xi'an depression all fall in the range of sedimentation water which was recharged by ancient surface water. This is consistent with the conclusion drawn from the fact that $\rho(Cl^-)/\rho(Br^-)$ ratio is larger than 293. Thus, it further reveals the genetic characteristics of sedimentary geothermal water in Gushi depression and the features of residual sedimentation water near Weihe fault of Xi'an fault and Xianli fault-step.

According to the relationship between $\delta^{18}O$ value and Cl^- contents, the geothermal water in the basin can be classified as follows. As indicated in Fig. 12, point A represents the source value of modern circulating geothermal water that is quite active and well-connected to the shallow surface or ground surface of the basin; and point B represents the source value of circulating geothermal water on the basin edge. The typical zones are geothermal wells in tectonic uplift area and geothermal wells along Qinling Mountains in Xi'an depression zone. Point C represents the source value of closed geothermal water in the basin hinterland. The typical zones are geothermal wells in Gushi depression, Xi'an depression and the part of Xianli fault-step. From an entire basin perspective, the $\delta^{18}O$ value and Cl^- content varies from the shallow surface on basin edge, through the areas surrounding the basin, to the basin center, experiencing an evolution from Source A to Source B, and finally to Source C. During the evolution from Source A to Source B, the recharge proportion of modern meteoric water decreases, and the geothermal water residence time gets longer and results in a less strong circulation and renewal ability. In the evolution from Source B to Source C, the geothermal water sees a growing $\delta^{18}O$ value, stronger water-rock equilibrium, weak circulation and renewal ability, low degree of hydraulic connections, and more closed geothermal reservoir. According to Fig. 12, the geothermal water in the Gushi depression zone has a potential of very weak renewal and low hydraulic exchange, the most

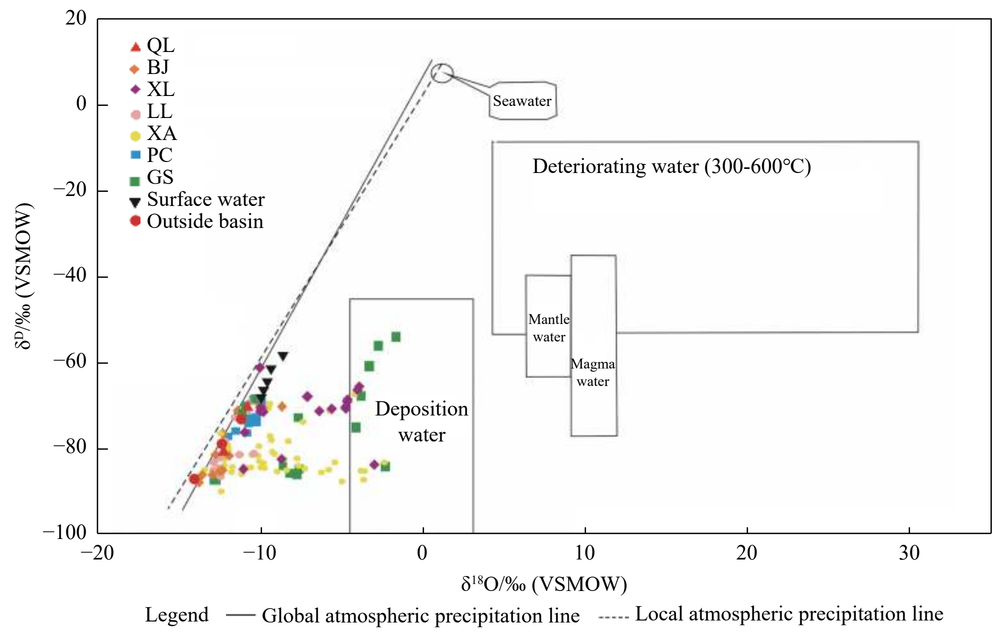

Fig. 11 Hydrogen-oxygen isotope relation of geothermal water of different genetic types

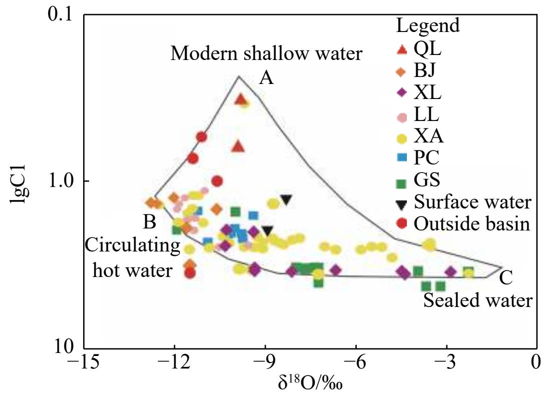

Fig. 12 Triangular chart of geothermal water in Guanzhong Basin

closed geothermal reservoir, and then comes the geothermal water in the Xianli fault-steps and Xi'an depression zone.

4.2 Circulation model

Based on the above discussions, the geothermal reservoirs of the Guanzhong Basin can be divided into four types, i.e. open circulation, semi-open, closed and sedimentary environments (Fig. 13).

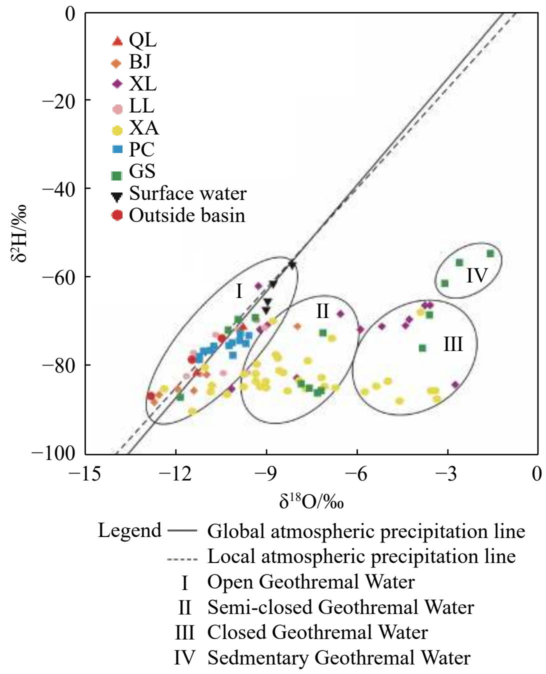

Fig. 13 Classification of geothermal water storage environments in Guanzhong Basin

Finally Fig. 14 gives four geothermal types, corresponding to the I-I profile in Fig. 1.

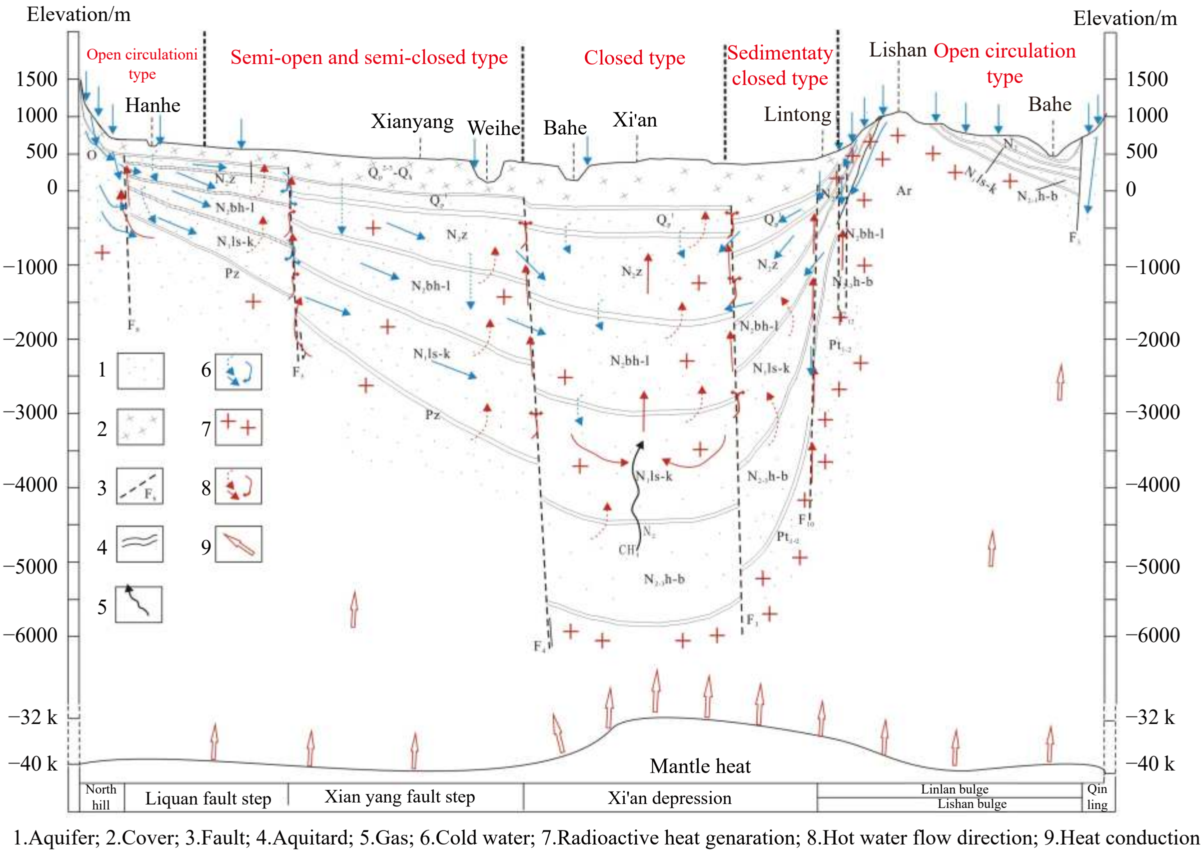

Fig. 14 Four types of geothermal water storage environments in Guanzhong Basin

(1) Open circulation type. This type of geothermal reservoir refers to as the geothermal environment within uplifting areas with the shallow geothermal water along the southern foot of North Mountains and the piedmont of northern foot of Qinling Mountains within the depression area. Typical feature of the thermal water is characterized by low concentrations of major ions and TDS, with the δD-δ^{18}O values mainly distribute along the local meteoric water line and the δ^{18}O drifting that rarely happens. The geothermal water is closely related to surface water and local meteoric water, and the modern meteoric water accounts for a considerable proportion of recharge source. The geothermal water has the sufficient exchange and renewal potential, which is favorable for sustainable development.

(2) Semi-open or semi-closed type. This type of geothermal reservoir refers to as the tectonic depressions, with some of deep geothermal water that moves toward the basin hinterland within the Xianli fault-step, the Gushi and Xi'an depressions. Its typical feature is characterized by gradual rise in major ions and TDS contents along their flow paths, with the δD-δ^{18}O value that is mainly distributed away below the meteoric water line. There is the moderate oxygen drifting of δ^{18}O and the geothermal reservoir is mainly restricted to the reduction environment. The hydraulic connection between geothermal water, local meteoric water and surface water gradually declines. The modern meteoric water contributes to a smaller portion of recharge, with low exchange and renewal potential between the thermal water and surface water. It is suggested that the geothermal water should be properly developed in the recharge process.

(3) Closed type. This type mainly refers to as the storage environment where the deep geothermal water that is stored in the basin hinterland, and as Xianli fault-step and both sides of the Weihe fault in the Xi'an depression as well. Typical features of the thermal water include the high concentrations of major ions and TDS, with a type of Na-Cl geothermal water and the δD-δ^{18}O values that distribute considerably away from the meteoric water line. There is a noticeable ^{18}O drifting and a center of δ^{18}O high can clearly be identified. The geothermal reservoir is basically located in a reduction environment with very limited ^{16}O replenishment. There is a weakly hydraulic connection between geothermal water, local meteoric water and surface water in the closed storage environment. The geothermal water may be the mixing of ancient meteoric water and the gradual recharge at the later stages. It is suggested that the water can be used as the regional strategy water source for heating and health improvement.

(4) Sedimentary closed type. This type refers to as the geothermal water that is distributed in Gushi depression and Huxia-Huayin area. Typical features of the thermal water are the extremely high concentration of major ions and TDS, with water type of highly mineralized Na-Cl geothermal brine and the δD-δ^{18}O values is distributed extremely away from the meteoric water line. With the δ^{18}O drifting as high as 8.7‰, the geothermal reservoir is located in a strong reduction environment. There is almost no hydraulic connection between geothermal water and local meteoric water, surface water and other aquifers. The local geothermal water sees no recharge from modern meteoric water, with a very low exchange and renewal potential. The hydrochemical and isotopic analyses collectively show that the localized geothermal water has distinct features of sedimentary water, recharged through the ancient meteoric water. If its recharge assessment can't be guaranteed, it is suggested that the geothermal water should not be exploited.

5 Conclusions

(1) The Guanzhong Basin is a giant fault-controlled sedimentary basin that formed during the Himalaya period in western China. This paper systematically analyzes the hydrogen and oxygen isotope characteristics of various tectonic areas from the perspective of geothermal research, which is of great significance for studying basin-scale hydrothermal activities. The isotope technique is an effective way to study the circulation and storage of midium-low temperature geothermal system dominated by the geothermal gradient in relation to geo-pressure. The analyses of environmental isotope components can provide direct evidence for assessing the recharge source, mixing, circulation and water-rock interaction of the geothermal water in the Guanzhong Basin; and the results are expected to provide a theoretical basis for the scientific exploitation, use and management of the geothermal resources.

(2) In current study, the systematic analysis of stable isotopes in the whole basin is conducted. The result shows that the geothermal water in the basin is mainly recharged by meteoric water. The plot of δ^{18}O-δD shows that on the basin edge and in the uplifting areas the δ^{18}O-δD points are distributed along the precipitation lines, which suggests that the geothermal water in the areas gets an acute

recharge with sources from modern meteoric water and surface water. However, in the basin hinterland such as Xianyang, Xi'an and Huayin areas, the geothermal water was recharged by ancient meteoric water of the last glacial period. The change of δD value indicates that, with Weihe Fault as a border, the area to the north belongs to North Mountains groundwater system, which is mainly recharged by piedmont surface water from the North mountains, while the area to the south is Qinling groundwater system which is mainly recharged by meteoric water and surface water from the Qinling mountains.

(3) The factors that affect $\delta^{18}O$ drifting in Guanzhong Basin include depth of geothermal reservoir, temperature of the thermal reservoir, water-rock equilibrium, geothermal reservoir environment, lithological characteristics and residence time. The d-excess influencing factors are almost the same as the factors those of the $\delta^{18}O$ drifting. The distribution characteristics of d value show that the flow of geothermal water is in the direction from the basin edge to the basin center.

(4) It is of great significance to analyze the geothermal occurrence from the perspective of groundwater flow systems. The circulation and origin models of geothermal water in the basin are built. Based on the hydrogen-oxygen isotope characteristics, the storage environment of geothermal water is divided into four types, including open circulation, half-open and half-closed, closed and sedimentary closed types. The open circulation type refers to the geothermal water within bulging areas and the shallow geothermal water along the southern foot of North Mountains and the piedmont of northern foot of Qinling Mountains within the depression area. The half-open and half-closed type refers to the geothermal water in depression, including some of deep geothermal water that moves toward the basin hinterland within Xianli fault-step, Gushi depression and Xi'an depression. The closed type refers to the deep geothermal water that is distributed in the hinterland of Guanzhong Basin and Xianli fault-step, and on the two sides of Weihe fault in Xi'an depression. The sedimentary closed type refers to the geothermal water that is distributed in Gushi depression and Huxia-Huayin area.

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