# Isotope Constraint for Genetic Types of Geothermal Water in the Center Part of Guanzhong Basin, NW China

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**Abstract**: The study area is the centre part of Guanzhong basin, which is located in the middle of Shanxi Province NW China and mainly consists of Xianli terrace, Xi 'an depression and Gushi depression. The main geothermal aquifer in the basin is Lantian-Bahe Group ($N_2l$+b). The method of environmental isotope and hydrogeochemistry are used to study the genetic types of deep geothermal water, in order to deepen and enrich the understanding of the genetic types of geothermal water in sedimentary basin in China. The results show that δD and $\delta^{18}O$ of Huayin 051 in the Gushi depression have significant drift; *d* value is as low as -41‰, which significantly deviates from the local meteoric water line and is the result of an extreme isotope hydrogeochemistry evolution process in closed environment. In addition, rNa/rCl<0.85, Cl /Br>293, $rSO_4^{2-}$ /rCl=1.09 and rCa/rMg=12.26, which meets the characteristics of sedimentary water. Therefore, the genetic type of geothermal water of Huayin 051 is residual continental sedimentary water. The δD and $\delta^{18}O$ of geothermal water of Weinan City in Gushi depression and the Eastern Xianli terrace fall within the range of δ values of sedimentary water. And the storage environment is relatively closed, so the genetic types are ancient infiltrating water mixed with a small amount of continental sedimentary water. The genetic types of geothermal water in the Xi'an depression and Western Xianli terrace are ancient infiltrating water mixed with modern meteoric water. In addition, the sedimentary evolution history of basin in the study area also supports the above conclusion.
**Keywords:** Isotope Constraint**;** Geothermal water; Genetic types; Guanzhong Basin.

## 1. Introduction

The study on genetic type of deep geothermal water is a major subject of contemporary earth science and is also very important for sustainable development and utilization of geothermal water. For a long time, there are many contradictory views on the genetic type of deep geothermal water. Professor Zhan-xue Sun[1] believed the geothermal water in Jiangxi Province was recharged by the deep cycle of meteoric water; Professor Hong-bing Tan[2] speculated that the fluid below 1500m in Qaidam Basin was the deep cycle of mixed water from the mantle and crust; Professor Run-san Wang[3] thought that geothermal water system of Guanzhong Basin was in a closed environment; Da-jun Qin[4] considered that geothermal water's recharge area of Xi'an was mainly located in high elevation place in the south and the west part of Xi'an; In addition, Ma[5], Qin and Tao[6]thought that the meteoric water formed at the last glacial period in Late Quaternary in Northern Qinling mountain was the source of geothermal water in Xi'an. So far, academic members generally believe that there are 4 genetic types of geothermal water: infiltrating genesis (ancient, modern), sedimentary genesis, magmatic genesis and metamorphic genesis [7]. At present, the main exploration of geothermal water's genetic type in China is infiltrating type, which verifies the Precipitation View of the traditional groundwater theory. The traditional research of the genetic type of groundwater is based on the understanding of the shallow hydrosphere; as a result, infiltrating type became the dominant source of geothermal water. However, in recent decades, the exploiting depth of geothermal water reaches thousands of meters; for example, the exploiting depth of geothermal water in the center part of Guanzhong basin was more than 4000 meters. The research object has already transferred from the water-rock system with clear source and stable chemical reaction to the water-rock system with diverse genetic types and all kinds of chemical reaction which formed in high temperature and high pressure environment [8]. More interesting, all the δD values of geothermal water of Lantian-Bahe Group in the center part of Guanzhong basin between 1600m and 4000m are lower than the δD value of seawater, and they are not constant compared with the δD value of geothermal water in normal pressure [9]. In addition, the δD and $\delta^{18}O$ values of geothermal water have significant drift, d values are as low as -41‰, $rSO_4^{2-}$/rCl values decrease rapidly, rNa/rCl<0.85. These characteristics indicate that the water was in the closed state and that there are other genetic types present in addition to infiltrating type. Environmental isotope hydrogeochemistry method is one of the new methods to research the geothermal water and is also the key point in the research of geothermal water [9]. This paper uses environmental isotope hydrogeochemistry method to study the genetic types of deep geothermal water in sedimentary basin, in order to deepen and enrich the understanding of the genetic types of geothermal water in sedimentary basin in China, and to provide theoretical basis for sustainable development of water resource.

## 2. Geology Background

The study area is in the center part of Guanzhong Basin (coordinates between 33°00'-35°20'N and 106°30'-110°30'E), located in the middle of Shanxi Province, NW China (Fig.1) [10]. The study area is north of Weihe fault, south of sub- Qinling fault, east of Chang 'an-Lintong fault, west of Yabo-Qishan fault. Its main tectonic units are Xianli terrace (Xianyang-Liquan terrace), Xi'an depression and Gushi depression (Fig.2) [11]. The difference in movement of fault blocks led to the different fault blocks with different sedimentary thickness, landforms and characteristics of sedimentary facies [12]. In order to carry on the comparative study, the study area was extended to the whole Guanzhong basin. The Guanzhong basin is located in the semi-arid temperate continental monsoon climate zone, and annual average rainfall is 550 ~ 750 mm. In the basin, precipitation in the south and west is greater than those in the north and east [10].

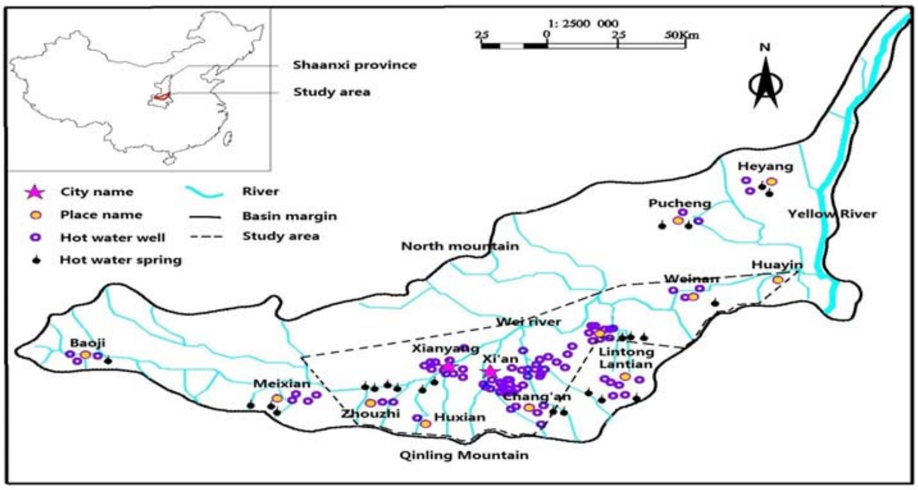


**Fig.1 Location map of Guanzhong basin**

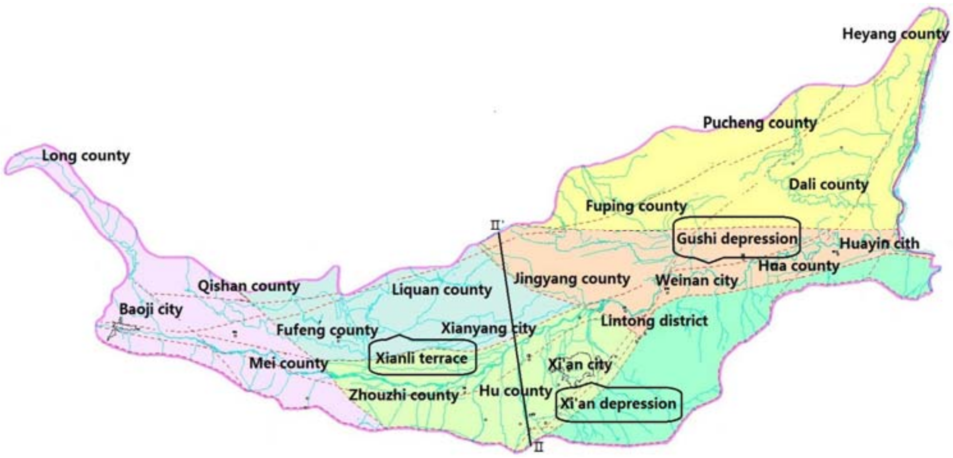


**Fig.2 Plate tectonic map of Guanzhong basin**

The Guanzhong basin is one of the important depositional basins with rapid sedimentary characteristics in China. It is surrounded by mountains except for the east. The topography from the mountain to the center of basin are proluvial fan, loess table land and valley terrace, in order. And the elevation gradually reduces. According to "Investigation of geothermal resource in Guanzhong basin of Shaanxi Province" [11], the thermal reservoir system is divided into 5 groups (Table 1), and the main thermal reservoir in Guanzhong basin is Lantian-Bahe group because of its optimal storage condition. Therefore Lantian-Bahe group ($N_2$l+b) is regarded as the main research object of deep geothermal water in the study area in this article.

**Table1 The main features of the thermal reservoir section**

| Thermal reservoir section | Mean temperature/℃ | Depth/m | Hydrochemical type |
|---|---|---|---|
| ①（$Q_1^s$）Sanmen Group | 30～50 | 300～700 | $HCO_3\cdot SO_4$–Na |
| ②（$N_2^z$）Zhangjiapo Group | 40～70 | 500～1300 | $SO_4\cdot HCO_3$–Na |
| ③（$N_2^{l+b}$）Lantian-Bahe Group | 50～90 | 900～1800 | $SO_4\cdot$Cl–Na |
| ④（$N_1^g$）Gaolingqun Group | 80～120 | 1500～2400 | Cl$\cdot SO_4$–Na |
| ⑤（$E_3^b$）Bailuyuan Group | 130～150 | 2900～3100 | $SO_4$–Na |

## 3. Sampling and Testing

47 water samples were collected in this study. Among them 16 samples were from Xi'an depression, 19 samples were from Xianli terrace, 6 samples were from Gushi depression, 2 samples were from the shallow geothermal water in front of mountain, and 4 samples were from Northern Qinling Mountain. Isotope including δD and $\delta^{18}O_{H2O}$ (37 groups), $^{34}S$ and $\delta^{18}O_{SO4}$ (21 groups), $^{14}C$ (15 groups), $^{13}C$ (16 groups) and $^3He/^4He$ (14 groups) were examined from the water samples. Hydrogen and oxygen isotope samples were tested in the Environmental Geology and Hydrogeology Institute of Chinese Academy of Sciences (CAS) from 2012 to 2013 using MAT253 mass spectrometer and measurement accuracy was 0.2‰. $^{34}S$ of sulfate in geothermal water were tested in the Stable Isotope Laboratory of the Geology and Geophysics Institute of CAS and measurement accuracy was 0.2‰. $^{14}C$ and $^{13}C$ samples were tested in the Cenozoic Geology and Environment Laboratory of the Geology and Geophysics Institute of CAS in November 2008. Helium isotope samples were tested in the Geochemical Testing Department of Lanzhou Research Center of Oil and Gas Resources of the Geology and Geophysics Institute of CAS using VG-5400 mass spectrometer, and measurement accuracy was 1%. Hydrochemistry samples (24 groups) were tested in the Zhongnan Testing Center of Metallurgical and Geological from 2008 to 2012 and the main instrument was AA-100 atomic absorption spectrometer.

## 4. Environmental Isotope Constraint

### 4.1Constraints of Hydrogen and Oxygen Stable Isotopes

The distribution characteristics of δD and $\delta^{18}O$ of geothermal water can be used to record the origin, formation, evolution and hydrogeochemical reaction process once deep geothermal water accepted recharge. More importantly, the comparison of environmental signals among modern precipitation, magmatic water and metamorphic water, which shown by δ D-$\delta^{18}O$ global meteoric water line equation, provided signals to identify different genetic types of geothermal water and their degree of mixing[13,14]. According to previous research results[5,15], the research team realized that the enrichment degree of $\delta^{18}O$ of geothermal water in the study area is closely related to the rock type of thermal reservoir, the temperature of thermal reservoir, water-rock interaction, the buried depth of thermal reservoir and the retention time of geothermal water.

The comparison of hydrogen and oxygen stable isotopes between the geothermal water in the study area and different genetic types of groundwater [16] (including seawater, metamorphic water, mantle water, magmatic water and sedimentary water) is shown in figure 3. In figure 3, δ value of all water samples from Northern Qinling Mountain and some samples' from Western Xianli terrace fall on meteoric water line, which indicates that they are closely related to modern precipitation. δ value of samples from Xi 'an depression are near meteoric water line, which indicates that it had mixed with modern precipitation and the thermal storage environment is open in some degree. δ value of parts of water samples from Easten Xianli terrace and all water samples from Gushi depression deviate from the meteoric water line and fall outside the area of δ value of seawater, metamorphic water, mantle water and primary magmatic water, which indicates that their origin and genesis do not belong to the above, that is to say there are almost no modern precipitation and endogenous water, while these water samples' δ value fall within the area of δ values of sedimentary water, whether or not they are sedimentary water and residual continental sedimentary water have become the focus. There are several basic characteristics of sedimentary water [14, 16, 17]: (1) sediment and sedimentary water deposit at the same time or sedimentary water are transformed from ancient surface water in later time. Sedimentary water is buried in a closed environment and rarely participates in the cycle of modern meteoric water. (2) The isotope characteristic line of hydrogen and oxygen of sedimentary water is an upward diagonal which is between meteoric water line and oxygen drift line ($^{18}O$ isotope in geothermal water is highly enriched in contrast to that of the local rainfall, while $^2H$ in the same samples remains basically constant, this phenomenon is called oxygen drift.). (3) Sedimentary water has a remarkable $^{18}O$ enrichment and drift, which $\delta^{18}O$ values (-4.5‰~3.0‰) [17] are smaller than the $\delta^{18}O$ value of seawater in general. At present, the exact range of δ D value of sedimentary water varies from place to place and this needs further refinement. For the Guanzhong basin, we conclude that the range -100‰~-45‰ is reasonable after taking into account of the δ D value of typical sedimentary basin from various parts of the world [15, 16].

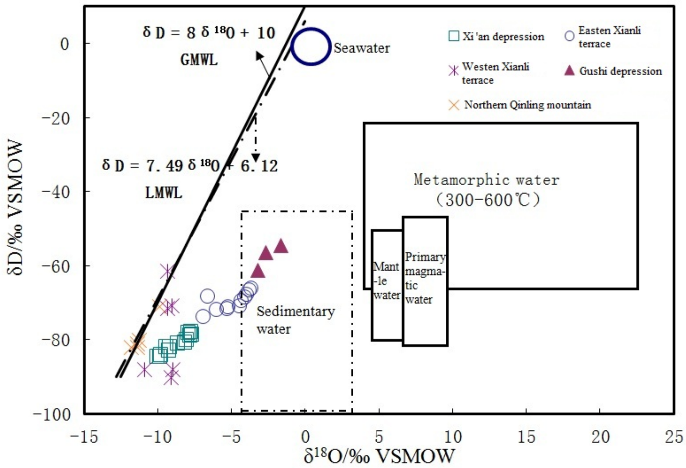


**Fig.3 The distribution of δ values of different origins water**

The relationship between δD and $\delta^{18}O$ of geothermal water in typical sedimentary basin from various parts of the world is shown in Figure 4 (4a. global sedimentary basin [16]; 4b. Tarim Basin [18]). In figure 4, we can see the hydrogen and oxygen isotope trend line's slope of deep geothermal water in study area is similar to the slope of sedimentary water of Tarim Basin, Michigan basin etc. In addition, the geothermal water has the characteristics of remarkable $^{18}O$ drift and lower δD value. All these factors suggest that the environment temperature was low, the storage condition was closed and water-rock reaction was intense when geothermal water accepted recharge. And these are coincidence with the characteristics of geothermal water which belong to sedimentary genesis or infiltrating genesis.

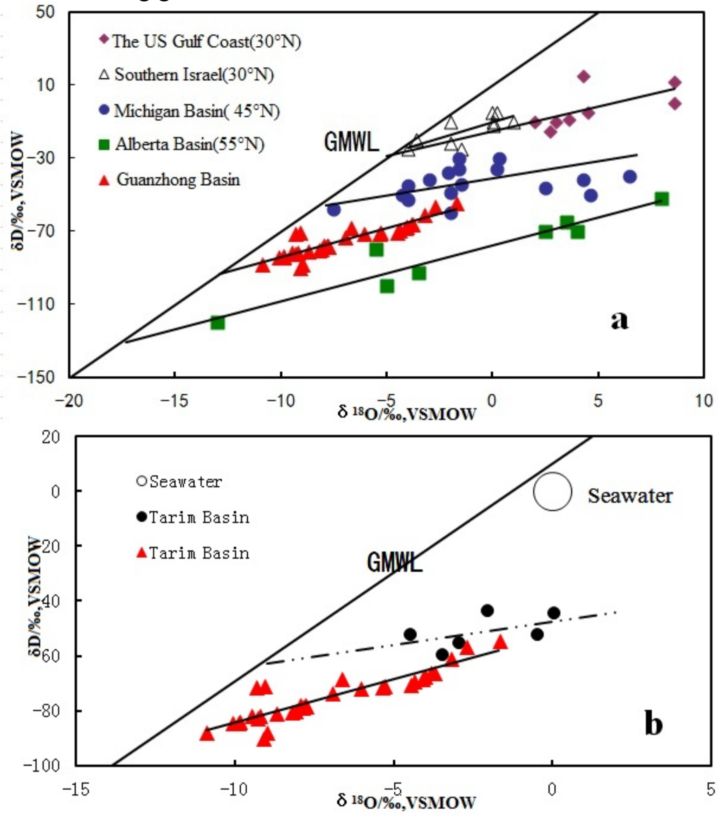


**Fig.4 The relationship between δD and $\delta^{18}O$ of typical sedimentary basin geothermal water from various parts of the world (4a. Global sedimentary basin [16]; 4b. Tarim Basin [18])**

In order to further explain the genetic type of the geothermal water, we use deuterium excess (d-excess) to analyze. D-excess can be used to indicate oxygen exchange degree of water-rock reaction, and $\delta^{18}O$ can be used to indicate the degree of water-rock reaction. The combination of d-excess and $\delta^{18}O$ can be a complete description of water-rock reaction and the basis of classification of geothermal water in the study area. In Figure 5, samples of group A are mainly geothermal water from Gushi depression, which have the richest δ values, and lower d-excess (-30‰~-41‰). Among these samples, the δ values of Huayin 051 (Table 2) have a remarkable drift and d-excess is as low as -41‰. The high δD value shows that there is reducibility gas such as $H_2S$ and $CH_4$. These factors indicate that geothermal water of Gushi depression is in closed environment, water-rock reaction is sufficient, and geothermal water is stagnant. Combined with hydrogeochemical constraint, we conclude that its genetic type is ancient infiltrating water mixed with a small amount of sedimentary water. Samples of group B are mainly geothermal water from the Easten Xianli terrace, whose hydrogen and oxygen isotope drift are just less than group A's and the range of d value is from -10‰ to -40‰. These statistics also indicate that geothermal water of Easten Xianli terrace is in closed thermal storage environment and water-rock reaction is intense. Combined with hydrogeochemical constraint, we conclude that its genetic type is ancient infiltrating water mixed with a small amount of continental sedimentary water. Samples of group C are mainly geothermal water from Xi'an depression and the Westen Xianli terrace. These samples have moderate δD values, richer $\delta^{18}O$ and higher d value (0~-20‰). Modern infiltrating water flows into hot water well near the fault zone along the fissures and the thermal storage environment is improving in the direction from edge to centre of the basin. The genetic type for this group is ancient infiltrating water mixed with modern meteoric water. Samples of group D are from the front of Qinglin Mountain. The δ values of these samples are near the meteoric water line, the range of tritium value is from 2TU to 15TU, which indicates that geothermal water in front of Qinglin Mountain is associated with meteoric water, so its genetic type is modern infiltrating water.

**Table2 Isotope measurements of samples in the study area**

| Location | Sample point | X※ | Y※ | δD(‰) VSMOW | $\delta^{18}O_{H2O}$ (‰) VSMOW | $\delta^{34}S$(‰) CDT | $\delta^{18}O_{SO4}$ (‰) VSMOW | $^{14}C$ (a) | $\delta^{13}C$(‰) VPDB |
|---|---|---|---|---|---|---|---|---|---|
| Western Xianli terrace | GZ36 | 19244001 | 3796599 | -88 | -9 | 8.31 | 2.27 | | |
| | GZ38 | 19242190 | 3796482 | -90 | -9.1 | 8.14 | 2.22 | | |
| | GT6 | 19214300 | 3816563 | -88 | -10.9 | | | | |
| | XY22 | 19263898 | 3800990 | | | 11.05 | 2.23 | 25911 | -8.01 |
| | XY20 | 19229650 | 3794420 | -89 | -9 | 10.06 | 2.088 | | -10.23 |
| Eastern Xianli terrace | XY17 | 19289825 | 3801100 | | | 12.3 | 3.37 | | |
| | XY14 | 19291085 | 3806733 | -69.3 | -4.37 | 13.69 | 4.755 | 20251 | -5.4 |
| | GZ57 | 19290614.37 | 3801195.2 | -68.38 | -4.12 | | | | |
| | GZ58 | 19293008 | 3805314 | -73.49 | -6.5 | | | | |
| | GZ56 | 19364624.73 | 3823072.26 | -71.7 | -6.12 | | | | |
| | GZ23 | 19280492.69 | 3801674.08 | -69.61 | -6.82 | | | | |
| | GZ22 | 19281869 | 3802993 | | | 13.12 | 4.26 | | |
| | XY07 | 19289884 | 3799546 | | | 13.95 | 4.93 | | |
| | R4 | 19290404 | 3810510 | -68.08 | -6.66 | | | 22717 | -7.11 |
| | XY15 | 19288979 | 3804863 | -66.02 | -3.75 | 14.68 | 5.09 | 22263 | -4.59 |
| | XY03 | 19286504 | 3804057 | -71.61 | -6.04 | 12.63 | 3.86 | 20219 | -5.83 |
| | XY18 | 19289307 | 3799013 | -70.97 | -5.3 | 13.12 | 4.26 | 26290 | -4.5 |
| | XY13 | 19292136 | 3805490 | -70.64 | -4.48 | 13.8 | 4.7 | 15788 | -6.97 |
| | XY10 | 19290299 | 3805379 | | | 14.54 | 5.037 | 23652 | -5.12 |
| Xi 'an depression | XR022 | 19309596.02 | 3792156.07 | -85 | -7.8 | | | | |
| | GZ60 | 19309596.02 | 3792156.07 | -83 | -8.9 | | | | |
| | GZ61 | 19356915.89 | 3819488.83 | -87 | -8.3 | | | | |
| | XR036 | 19314531 | 3777628 | | | | | 12270 | -8.58 |
| | XR041 | 19309690 | 3790970 | | | 11 | 2.823 | 18513 | -8.82 |
| | GZ50 | 19253463.12 | 3775141.25 | -89 | -9.4 | | | | |
| | GZ54 | 19333793.18 | 3805325.37 | -73 | -9.9 | | | | |
| | XR059 | 19310311 | 3802424 | -89 | -9.2 | 10.49 | 1.795 | | |
| | GZ53 | 19335104.34 | 3805450.09 | -76 | -10 | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | GZ62 | 19295114.85 | 3770506.24 | -90 | -11.3 | | | | |
| | GZ47 | 19295114.85 | 3770506.24 | -86 | -11.8 | | | | |
| | XR033 | 19314642 | 3793658 | | | 12.06 | 2.752 | 23274 | -8.46 |
| | XR169 | 19308655 | 3782793 | -86 | -11.9 | | | 13585 | -7.88 |
| | XR058 | 19305009 | 3788304 | | | 10.59 | 2.008 | | |
| | GZ55 | 19334677.8 | 3806194.45 | -84 | -9.7 | | | | |
| | XR035 | 19329364 | 3789849 | | | 11.63 | 2.918 | | |
| Gushi depression | WR01 | 19359530 | 3821884 | -85 | -0.7 | | | | |
| | WR02 | 19359507 | 3820004 | -88 | -2.1 | | | | |
| | WR04 | 19311878 | 3831670 | -80 | -3 | | | | |
| | 51 | 19403781 | 3827040 | -61.13 | -3.21 | 15.51 | 5.38 | 20048 | -8.84 |
| | GZ50 | 19253463.12 | 3775141.25 | -54.55 | -1.68 | 13.92 | 6.199 | 29983 | -5.18 |
| | GZ51 | 19280680.07 | 3778015.76 | -56.38 | -2.7 | 12.09 | 5.049 | 13323 | -4.08 |
| Front of mountain | XR102 | 19293750 | 3771113 | -80.85 | -8.71 | | | | |
| | GZ10 | 19292813 | 3770123 | -90 | -11.3 | | | | |
| Northern of Qinling mountain | GZ01 | 19296972 | 3763605 | -71 | -9.9 | | | | |
| | GZ03 | 19280894 | 3753787 | -81 | -11.4 | | | | |
| | GZ04 | 19279879 | 3753922 | -80 | -11.3 | | | | |
| | GZ06 | 19280864 | 3755580 | -82 | -11.8 | | | | |

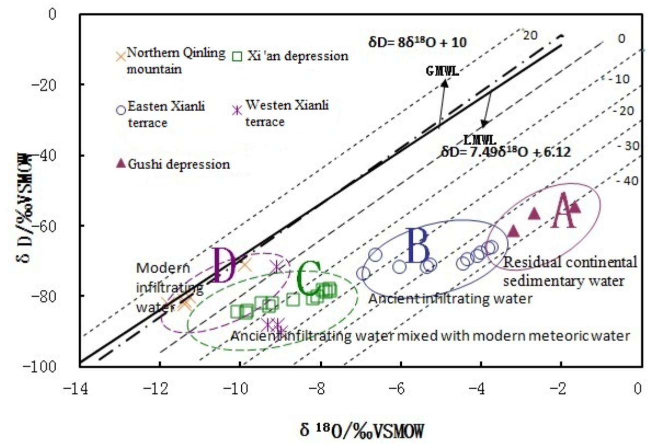


**Fig.5 The δD-δ$^{18}$O relationship of geothermal water in the study area**

## 4.2 Constraint of Carbon Isotope

The purpose of $^{14}$C dating is to identify the formation of geothermal water of different geological time and to provide constraints for genetic type of geothermal water [14, 19]. The $^{14}$C age in this article is the correction result of δ$^{13}$C [20].

The results of $^{14}$C dating show that the $^{14}$C ages of geothermal water in Guanzhong basin are more than 10 ka, which indicates that they accepted the ancient precipitation before Holocene recharge. The order of $^{14}$C age from the oldest to the newest are Gushi depression, Xianli terrace and Xi'an depression. The maximum$^{14}$C ages of geothermal water of Gushi depression and Xianli terrace are 30 ka and 26 ka (Table2), respectively, which confirmed the existence of ancient infiltration water, in view of the limitation of $^{14}$C dating, the actual age of geothermal water may be older. In order to verify the existence of residual sedimentary water, some samples have been sent to $^{36}$Cl laboratory to test.

The comparison of δ$^{13}$C and δ$^{18}$O between marine carbonate and secondary continental carbonate [14] is shown in Figure 6. The range of δ$^{13}$C and δ$^{18}$O value of deep geothermal water in Guanzhong Basin and that of hydrothermal calcite overlap, which indicates that the main source of inorganic carbon of geothermal water in the study area is the dissolution of secondary hydrothermal carbonate. The dissolution process influenced by tectonic factor should be the result of pressure reduction and degasification of thermal reservoir in the geological time. The accumulation and diagenetic process of deposits can keep a certain amount of water, that is, water and rock are formed in the same time or water is later, which indicates that geothermal water in the study area may be formed in a long geological time.

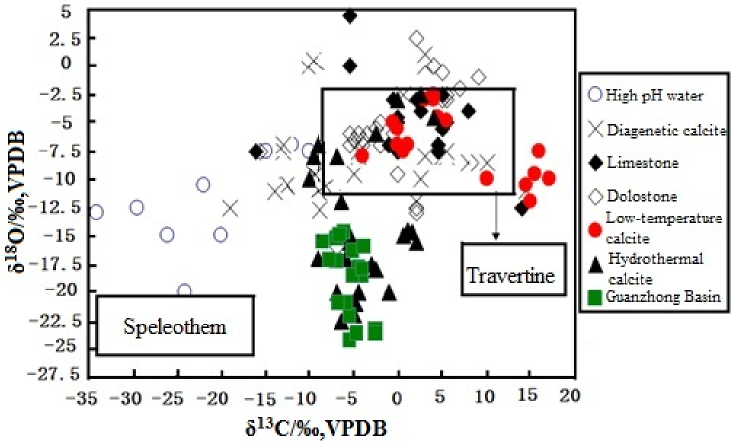


**Fig.6 Composition of $\delta^{13}C$ and $\delta^{18}O$ in marine and secondary continental carbonate**

## 4.3 Constraint of Sulfur Isotope

The $\delta^{34}S$ of sulfate can be used to indicate the recharge sources and thermal storage environment of geothermal water [21]. The comparison of $\delta^{34}S$ and $\delta^{18}O$ among the continental, seawater and atmospheric sulfate [16] is shown in Figure 7. According to the distribution range of geothermal water samples in the study area, we can eliminate such possibility that atmosphere and seawater sulfate are the main source of the $SO_4^{2-}$ in geothermal water. The $\delta^{34}S$ and $\delta^{18}O$ of sulfate of Xi'an depression and Western Xianli terrace are near that of terrestrial evaporate. Because the tectonization of Xi'an depression is frequent, and the fault is open, and thus part of deep geothermal water travel up along the fracture and the $H_2S$ in geothermal water forms terrestrial evaporite after reoxidation. It is therefore concluded that deep geothermal water of Xi'an depression experiences the transition from sedimentary closed state to infiltration open state. The $\delta^{34}S$ and $\delta^{18}O$ of sulfate of Eastern Xianli terrace and Gushi depression are richer as a result of sulfate reduction and isotopic exchange, with the latter being more significant. The closed geological environment combined with the hydrochemistry characteristic, lead to the conclusion that Eastern Xianli terrace and Gushi depression exhibit residual continental sedimentary water. Among them, the Huayin 051sample in the Gushi depression is the most typical (Tab.2).

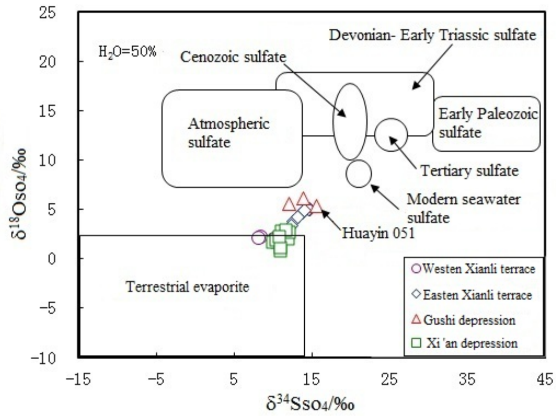


**Fig.7 Composition contrast figure of $\delta^{34}S$ and $\delta^{18}O$ among the continental, seawater and atmospheric sulfate**

## 4.4 Constraint of Helium Isotope

Helium isotope is very sensitive to the mantle composition in the fluid [22], so it can be used to identify whether geothermal water is mantle-derived water or not. If we set meteoric $^3He/^4He$ ratio ($1.4\times10^{-6}$) as Ra, set ratio of the sample as R, then $R/Ra<1$ is the characteristic of crust-derived helium, $R/Ra>1$ is the characteristic of exiting mantle-derived helium and $R/Ra=1$ is the characteristic of meteoric-derived helium[18]. The relationship between helium and neon isotope can be used to identify the degree that geothermal water is influenced by the atmosphere. The bigger the $^4He/^{20}Ne$ of geothermal water is, the lesser degree geothermal water is influenced by the atmosphere [23].

As shown in table 3(part samples quoted from Xianping Chai[23]): the R/Ra values of all samples in the study area are significantly less than 1,which indicates that geothermal water comes from crust. The $^4He/^{20}Ne$ of all samples are greater than the atmosphere's (0.318), so the degree of influence by the atmosphere is small.

**Table 3 Helium neon isotope analysis results in the study area**

| Location | Sample point | $R={}^3He/{}^4He$ | R/Ra | $^4He/^{20}Ne$ |
|---|---|---|---|---|
| | Lintong711 | $2.92\times10^{-7}$ | 0.209 | 439 |
| | Lantian valley hot spring | $7.8\times10^{-7}$ | 0.557 | 1500 |
| Xi 'an depression | Xidian University | $5.02\times10^{-8}$ | 0.036 | 1011 |
| | Lingshan temple | $6.05\times10^{-8}$ | 0.043 | 226 |
| | Qinbao casino | $4.7\times10^{-8}$ | 0.034 | 357 |
| | Northwest supply and marketing corporation of airline | $5.56\times10^{-8}$ | 0.04 | 163 |
| | The east of Tangyu | $1.26\times10^{-7}$ | 0.09 | 132 |
| | Xi 'an cable factory | $5.07\times10^{-8}$ | 0.036 | 1010 |
| Eastern Xianli terrace | WR1 | $9.54\times10^{-8}$ | 0.068 | 2114 |
| | WR2 | $9.98\times10^{-8}$ | 0.071 | 1590 |
| | WR9 | $8.68\times10^{-8}$ | 0.062 | 1110 |
| Gushi depression | Weinan school of traditional Chinese medicine | $1.49\times10^{-7}$ | 0.106 | 1987 |
| | Weire1 | $1.27\times10^{-7}$ | 0.091 | 3212 |
| | 51 | $1.00\times10^{-7}$ | 0.071 | 2562 |

All isotope constraints show that the thermal storage environment of Gushi depression in the study area is the most enclosed. The genetic type of geothermal water of Weinan city of Gushi depression is ancient infiltrating genesis, and the geothermal water of Huayin 051 in Gushi depression has the characteristics of residual continental sedimentary water; The geothermal water in front of Qinling mountain is modern infiltrating water; The geothermal water of Xi'an depression is ancient infiltrating water mixed with modern meteoric water; The geothermal water of Eastern Xianli terrace is ancient infiltrating mixed with litter residual continental sedimentary water.

## 5. Hydrogeochemical Constraint

In order to further verify research results of various isotopes and to provide hydrogeochemical constraints of the origin of geothermal water, the ratio coefficient of element is used here. The ratio coefficient of element [17, 24] is significant in the research of genetic type and formation process of geothermal water. At present, the widely applied of ratio coefficients of element are: rNa/rCl, rCa/rMg rCl/rBr,and $rSO_4$/ rCl.

### 5.1 rNa/rCl Characteristic

rNa/rCl can be used to indicate the genesis and degree of metamorphism of geothermal water[17]. The rNa/rCl value is about 0.85 for normal seawater, below 0.85 for marine sedimentary water, and close to 1 for infiltrating water. When the infiltrating water mixed with geothermal water, the rNa/rCl tends to be bigger than 0.85[17]. The relationship between rNa/rCl and Cl is shown in Figure 8. We can see the rNa/rCl of Huayin 051(0.7) and Huayin farm(0.58) in Gushi depression are smaller than normal seawater's (0.85), which indicates that they are in closed thermal storage environment, water-rock reaction is intense, and exchange adsorption of cations (exchange between $Na^+$ and $Ca^{2+}$) is intense in geological time. Thus the rNa/rCl value is as low as 0.58~0.7 and it reaches medium metamorphic grade (rNa/rCl is 0.6~0.8[24]). The exchange adsorption of cations led to calcium ions enrich, and increased rCa/rCl and rCa/rMg (12.26), and that is larger than rCa/rCl(0.004) and rCa/rMg (0.19) of normal seawater, which is similar to the rCa/rCl and greater than the rCa/rMg(2.1~6.5) of

Sinian sedimentary water of Weiyuan gas field in Sichuan[25]. The sedimentary environment of Lantian-Bahe Group of Huayin region is typical fluviolacustrine facies[8], while rNa/rCl of geothermal water reaches the standard of marine sedimentary water, it is concluded that geothermal water of Huayin 051 is buried in the closed environment in geological time like marine sedimentary water. The rNa/rCl of Xianli terrace are slightly greater than 0.85. It is speculated that it is the result influenced by infiltrating water and ancient infiltrating water gradually replaced the sedimentary water. The rNa/rCl of Xi'an depression and Gushi depression are greater than that of seawater, and Cl had low concentration, which indicates that they experience the reverse metamorphism and infiltrating water mix into sedimentary water in later period.

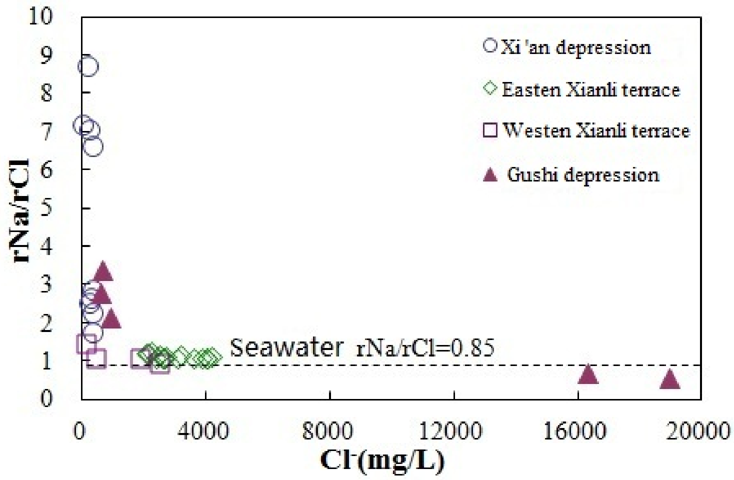


**Fig.8 The Cl- rNa/rCl relationship of geothermal water in the study area**

## 5.2 rCl/rBr Characteristic

The rCl/rBr can be used to indicate the characteristics of the sedimentary water[17, 25]. The rCl/rBr of seawater is 293 and rCl/rBr >293 is the characteristic of continental sedimentary water[17]. The relationship between rCl/rBr and Cl is shown in Figure 9. We can see the rCl/rBr (424.66) of Huayin 051 in Gushi depression is significantly higher than that of seawater (293). These results are in conformity with the characteristics of continental sedimentary water, so it is speculated that the thermal storage environment of Huayin region is very isolated. The dissolution of halite makes the enrichment rate of $Cl^-$ greater than that of $Br^-$. So geothermal water of Huayin 051 is continental sedimentary water. The rCl/rBr of Xianli terrace is below and close to that of normal seawater (293)[17]. The recharge source of Xianli terrace is Ordovician Limestone water, and it is in conformity with the characteristics of the marine sedimentary water. The structure of Xi'an depression is open and the rCl/rBr is relatively low. It is possible that infiltrating water mix into continental sedimentary water in later period in Xi'an depression.

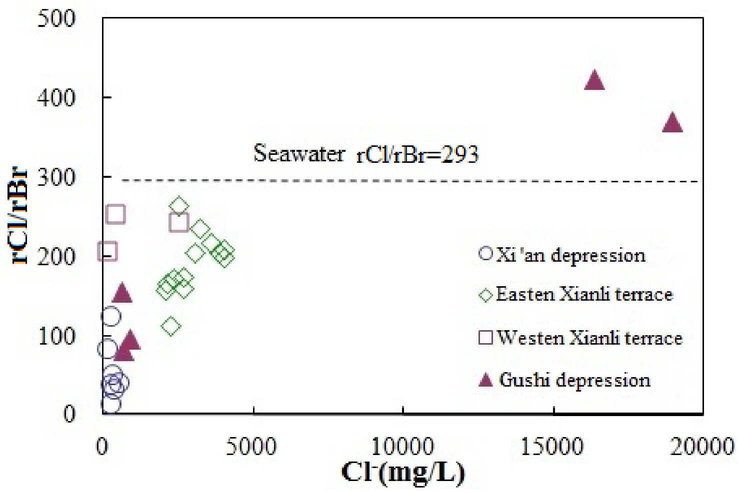


**Fig.9 The rCl/rBr-Cl relationship of geothermal water in the study area**

## 5.3 $rSO_4$/rCl Characteristic

The coefficient of desulfurization ($rSO_4^{2-}$/rCl) can be used to indicate the degree of desulfurization and the isolation of thermal storage environment. The less the coefficient is, the more closed thermal storage environment is [25, 26]. The 100×r$SO_4^{2-}$/rCl of normal seawater is 10.26[17]. The 100×r$SO_4$/rCl of Huayin 051 and Huayin farm in Gushi depression are 1.09 and 0.47 respectively, which indicates that the degree of desulfurization is high and thermal storage environment is closed. The 100×r$SO_4$/rCl average value of Xi'an depression, Weinan City of Gushi depression, Huayin of Gushi depression and Xianli terrace are 124.6, 22.94, 0.78 and 3.04, respectively. The comparison results show that the closed degrees of thermal storage environment of geothermal water are as follows: Huayin of Gushi depression> Xianli terrace >Weinan City of Gushi depression > Xi 'an depression (Table 4). The 100×r$SO_4$/rCl average value of Huayin of Gushi depression and Xianli terrace are far less than that of seawater (10.26), which indicates that they experience long–term desulfurization in a closed environment.

The above analysis shows that geothermal water of Xi'an depression has the biggest rNa/rCl, the biggest 100×r$SO_4$/rCl and the smallest rCl/rBr, which indicates that the structure of Xi 'an depression is open, reductive degree is small and that geothermal water mixes with modern infiltrating water. Combined with isotope constraints, we can conclude that the genetic type of geothermal water of Xi'an depression is ancient infiltrating water mixed with modern meteoric water. Geothermal water of Xianli terrace and Weinan City of Gushi depression have bigger rNa/rCl and bigger 100×r$SO_4$/rCl, which indicates that the thermal storage environment is closed. Combined with isotope constraints, we can conclude that their genetic types are ancient infiltrating water mixed with a small amount of continental sedimentary water. Geothermal water of Huayin 051in Gushi depression has the smallest rNa/rCl, the smallest 100×r$SO_4$/rCl and the biggest rCl/rBr, which indicates that the thermal storage environment is much closed and the degree of desulfurization is large. Combined with isotope constraints, we can conclude that the genetic type is residual continental sedimentary water. The sedimentary evolution history of basin in the study area [11] also supports the above conclusion.

## 6. Constraint of Sedimentary Evolution

According to previous studies, the Guanzhong basin is a composite and continental rift sedimentary basin based on different structures. The basin was in a state of uplift and erosion during the late Cretaceous and Paleocene period. Since the Eocene, the basin began to sink and water was gradually accumulated into a lake. Then in the Pliocene, the rifting speed of Weihe fault was increasing. In the Quaternary, the speed of subsidence of Weihe fault was faster than that of deposition, so it forms a broad “Sanmen lake”. Weihe fault continues to sink in the late Pleistocene and it is characterized by extensive fluvial facies. The Weihe fault experiences many peroids of subsidence and accumulation since the middle Pleistocene, thus it formed multi-level alluvial terrace. The evolution of Weihe fault is characterized by subsidence and accumulation from Eocene to Holocene.

In other words, the sedimentary environment of Guanzhong basin is fluviolacustrine facies. The rapid accumulation of Guanzhong basin not only can seal groundwater formed in the early time in loose formation, but also can make geothermal water stored in deep porous medium into the aquifer. Therefore the groundwater is stagnant. The shallow fluid could drain until Wei river formed, while the geothermal water 1500m below ground is rare to participate in the water cycle. Due to the continuous water-rock reaction and concentration caused by evaporation, the groundwater has oxygen isotope drift and forms the high salinity water. The formation of deep faults or other open structures meant that the fluids have more opportunities to accept infiltrating water and surface water. The original saline fluids are gradually diluted, or transform into infiltrating water and ancient infiltrating water. Some fluids retain the features of original sedimentary water, namely residual sedimentary water.

## 7. Conclusions

1) The δ values(δD and $\delta^{18}O$)of geothermal water of Huayin 051 in Gushi depression have a remarkable drift, d-excess is as low as -41‰ and the degree of the deviation from meteoric line is large, which indicates that it exhibits an extreme isotope hydrogeochemical evolution process in a closed environment. The hydrogen and oxygen stable isotopic trend line of Gushi depression is similar to typical sedimentary basin around the world, the δ values of all samples fall within the range of δ values of sedimentary water, in addition, $\delta^{13}C$ and $\delta^{34}S$ values are rich, which indicates that the thermal storage environment is closed reducibility environment and geothermal water forms in the long geologic time. The $^3He/^4He$ value shows that the geothermal water of Gushi depression is mainly from crust.

**Table 4 The comparison of hydrogeochemical parameters among study area samples, seawater and the deep water of Sichuan Weiyuan gas field**

| Location | Sample point | rCa/rMg | rNa/rCl | 100×$rSO_4$/rCl | rCl/rBr | Location | Sample point | rCa/rMg | rNa/rCl | 100×$rSO_4$/rCl | rCl/rBr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Normal seawater | | 0.19 | 0.85 | 10.26 | 293 | Xianli terrace | GT5 | 1.37 | 1.44 | 6.47 | 207.45 |
| The deep water of Sichuan Weiyuan gas field | | 2.1~6.5 | 0.85~0.92 | 0 | 128~240 | | XY22 | 3.14 | 1.08 | 1.48 | - |
| Xi 'an depression | XR184 | 7 | 3.72 | 38.98 | - | | XY20 | 38.28 | 0.92 | 0.36 | 243.28 |
| | XR185 | 3 | 5.75 | 71.16 | 265.83 | | GT6 | 2.11 | 1.05 | 2.89 | 254.46 |
| | XR102 | - | 7.17 | 89.96 | 140.42 | | XY133 | 3.24 | 1.09 | 2.79 | 6.47 |
| | XR059 | 5 | 6.62 | 47.34 | - | | XY10 | 2.93 | 1.07 | 3.44 | 1.48 |
| | XR003 | 1.97 | 6.02 | 67.52 | - | | XY14 | 2.29 | 1.07 | 2.42 | 0.36 |
| | XR005 | 5.01 | 3.59 | 32.76 | 100.77 | | XY11 | 3.45 | 1.28 | 3.8 | 2.89 |
| | XR006 | 5.71 | 8.48 | 164.47 | 185.81 | | WR4 | 2.88 | 1.2 | 3.75 | 204.08 |
| | XR009 | 3.91 | 14.35 | 357.2 | 22.57 | Gushi depression | WR01 | 2.82 | 2.14 | 11.42 | 96.3 |
| | XR169 | 2.97 | 11.09 | 252.3 | 27.83 | | WR02 | 10 | 3.4 | 33.08 | 81.69 |
| Gushi depression | 51 | 12.26 | 0.7 | 1.09 | 424.66 | | WN2 | 12.26 | 1.67 | 7.49 | - |
| | WR03 | - | 2.77 | 39.77 | 156.36 | | WR04 | 11.55 | 0.58 | 0.47 | 371.91 |

2) The sedimentary evolution history of the basin as well as the research results of hydrogeochemical in the study area supported the above conclusion. The geothermal water of Huayin 051 is high-salinity brine in the ancient salt lake sedimentary environment, rNa/rCl<0.85, rCl /rBr>293, $rSO_4$/rCl=1.09 and rCa/rMg=12.26, which coincides with the characteristics of sedimentary water. The above isotope and hydrogeochemical constraints show that geothermal water of Huayin 051 is residual evaporation lake water buried in geologic time and the genetic type is residual continental sedimentary water.

3) The δ values (δD and $\delta^{18}O$) of geothermal water of Weinan City of Gushi depression and Eastern Xianli terrace fall within the range of δ values of sedimentary water. The research results of $\delta^{13}C$, $\delta^{34}S$, $^3He/^4He$ and hydrogeochemical result show the storage environment is relatively closed, so we speculate that the geothermal water of Weinan City of Gushi depression and Eastern Xianli terrace is sedimentary water charged by ancient infiltrating water in later and their genetic types are ancient infiltrating water mixed with a small amount of residual continental sedimentary water.

4) The $\delta^{18}O$ values of geothermal water of Xi'an depression and Western Xianli terrace have a certain drift. In addition, fault along the Qinling Mountain are open, so a small amount of modern infiltrating water mixed with geothermal water, which indicates that the geothermal water of Xi 'an depression and Western Xianli terrace is early sedimentary water mixed with infiltrating water. So their genetic types are ancient infiltrating water mixed with modern meteoric water.

5) In conclusion, most deep geothermal water in the study area is ancient infiltrating water flowed into thermal reservoir in the geologic time. Part of the fluid with isotope and hydrogeochemical characteristic of sedimentary water is a precious nonrenewable resource. To ensure the sustainable development and utilization of geothermal water in the study area, it is recommended that we must stick to reinjection when the deep geothermal water is exploited.

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