

Hydrochemical and Geochemical Characteristics of Geothermal Water in Gedong Area of Guizhou Province

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Abstract

Geothermal energy is a green and renewable energy source. There are abundant geothermal resources in Gedong area of Guizhou Province, China. The Geothermal resources are controlled by regional structure. The shape of heat storage is zonal distribution. In order to know more about the characteristics of banded thermal reservoirs and provide reference for the development and utilization of banded thermal reservoirs in Qiandongnan area of Guizhou, on the basis of fully understanding the geothermal geological conditions in the Gedong area of Guizhou, the samples of geothermal fluid were collected and the hydrochemistry, hydrogen and oxygen isotopes of regional geothermal water were analyzed. The result shows that regional geothermal water circulation is very deep. The circulation depth of geothermal water is at least 1330 m. Ground water is heated continuously by large geothermal flow during circulation and finally becomes geothermal water. The source of geothermal water supply is meteoric water and its lower limit of recharge height is 926 m. The characteristics of hydrogen and oxygen isotopes of geothermal water in different geothermal wells (Springs) are different, and the main factor is elevation. The chemical composition of geothermal water is controlled by the surrounding rock of geothermal water, the dissolved specific mineral of geothermal water and the circulation of geothermal water are difference. Geothermal water in different geothermal wells (Springs) can be divided into two groups. The division is based on whether geothermal water reaches mineral equilibrium and whether it is mixed with shallow ground water.

Keywords: Hydrochemical type; Hydrogen-oxygen isotope analysis; Geothermal water; Circulation depth; China

Introduction

At present, energy shortage and environmental pollution have become one of the important problems that restrict the sustainable development of the whole world. Geothermal energy is a green, low-carbon and recyclable renewable energy source [1]. The geothermal resources in Guizhou province are rich, but the exploration and exploitation level are low [2,3]. The Gedong area of Gui Zhou generally includes Taijiang, Jianhe, Leishan, Cengong and Sansui areas. Today, there are 2 natural hot springs and 6 geothermal wells in this area (Figure 1). Since the 80s of last century, the Guizhou Institute of Geology and the Guizhou Institute of environmental science, respectively, the hot springs in Jianhe were investigated and studied. In 2009, the Guizhou Provincial Department of land and resources submitted the research manual on the exploration, exploitation and utilization of geothermal water resources in Jianhe, and planned the geothermal resources of Jianhe County. Although predecessors carried out some explorations and researches to the region of Jianhe, Leishan geothermal resources [1,4-6], it has not systematically studied the hydrogeochemistry and thermal storage temperature in the whole of Gedong area, and this researches in this area has played an important role in dividing the geothermal system types and evaluating the potential of geothermal resources [1,7-9]. Therefore, this paper takes geothermal water as an object of study. Based on the principal analytic hierarchy process, the hydrochemical test data of hot water in inland area were analyzed. And based on geochemical theory, the characteristics of H and O isotopic compositions of fluids are analyzed. Geochemical characteristics and evolutive characteristics of thermal fluids in the interior of the area are discussed. The water rock equilibrium state of the thermal anomaly points in the Gedong area is determined by using the Na-K-Mg triangle diagram and the multi mineral equilibrium method. To select a reasonable calculation of geothermometer heat reservoir temperature in Gedong area, the purpose is to understand

the formation mechanism of geothermal resources in the Gedong area and to provide a new reference for the exploitation and utilization of geothermal resources in this area.

General Situation of the Study Area

Located in the east slope of Guizhou plateau, the Gedong area is adjacent to the fold belt of the southwest and the north to the Yangtze quasi platform [10]. The terrain is high in the southeast and low in the north and West. The landforms are erosion and peak cluster depressions. The direction of the mountain stretch is basically the same as that of the structure, and most of them are NNE trending. In the region, the strata of Jianhe, Taijiang and Leishan regions are mainly blastopsammite of Qingshuijiang group (Qbq), Wuye group (Qbw), Fanzhao (Qbf) group and Jalu group (Qbj) of Qingbaikouan system. The upper part of the regional stratigraphic Cengong is the Cambrian Shilengshui group dolomite (ϵ_2s), Qingxudong group limestone (ϵ_1q). The underpart of regional strata is the Cambrian Palang group blastopsammite (ϵ_1p) and Qingshuijiang group (Qbq) of Qingbaikouan. The structures in the area are mainly NNE trending folds and faults, respectively Sansui syncline, Donglong syncline, Leishan syncline, Chong Suoxi anticline, Gedong fault, Shidongkou fault and Wen Shao fault (Figure 1).

The fault of Gedong, Shidongkou and Wen Shao is neoid active faults. The geothermal wells and hot spring of Jianhe and Taijiang,

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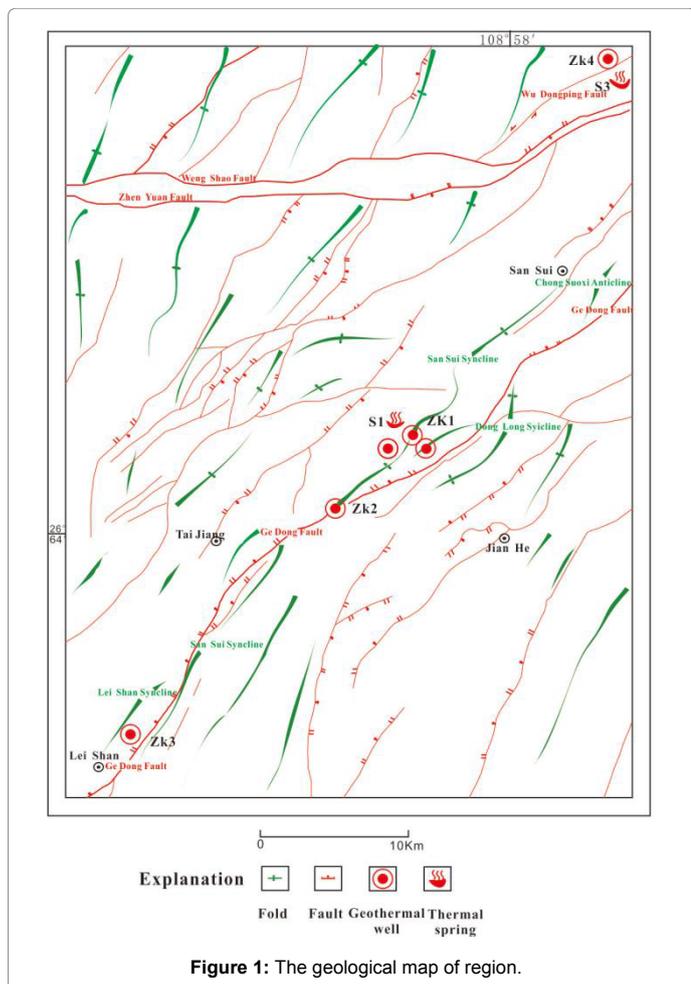


Figure 1: The geological map of region.

Leishan area is located in between the Gedong fault and its secondary faults and folds. They are controlled by the Gedong fault and the shape of the thermal reservoirs is zonal distribution. The geothermal wells and hot spring of Cengcong are controlled by Wudongping fault, WenShao fault and Shidongkou fault. The shape of the thermal reservoirs in this area is zonal distribution (Table 1).

The regional geothermal wells and hot springs are located in the upper wall of the neoid active faults. The neoid active faults and their secondary faults are the main runoff paths of geothermal water. The cyclic geothermal water moves upward along the upper wall of the fault. The relative thermal conductivity between strata and strata forms a relative heat insulating layer.

Sampling and Testing

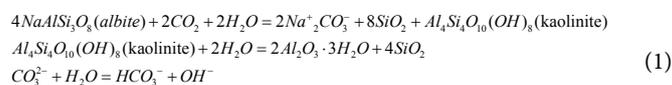
Sampling of water chemistry and isotope samples was carried out in the region in May 2014. The samples of water quality analysis are collected with 2.5 L plastic bottle. Samples of hydrogen and oxygen isotopes were collected in 500 mL plastic bottles. Before collecting, clean the bottle of sample 3 times with distilled water and fill the sample bottle with water and then seal the bottle with wax. Finally, the bottles are attached to labels. And the sample will be sent to the Guizhou geological and mineral Center Laboratory for testing immediately. The delivery time of sample is not more than 48 hours. The accuracy of analysis of hydrogen and oxygen isotopes is $\pm 1.0\%$ and $\pm 0.2\%$.

Interpretation of Results and Discussion

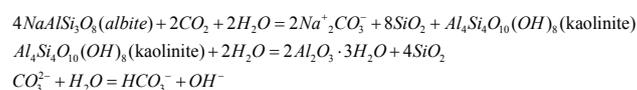
Hydrochemical characteristics

According to the analysis results of regional water samples, Piper diagram is made (Figure 2). As you can see in Figure 2, the data points are all concentrated in the same range. The chemical type of regional geothermal water is $\text{HCO}_3^- \text{Na}^+$. Its TDS is less than 1 g/L, belong to fresh water. Combined with regional hydrogeological conditions, chemical characteristics of geothermal water were analyzed based on principal component analysis. Principal component analysis is different from correlation analysis [2]. The correlation analysis considers only the correlation between the two variables. However principal component analysis takes into account the relationship among all the original variables, the independent factors of principal component can be extracted after transformation, and the main influencing factors can be analyzed according to the principal component factor.

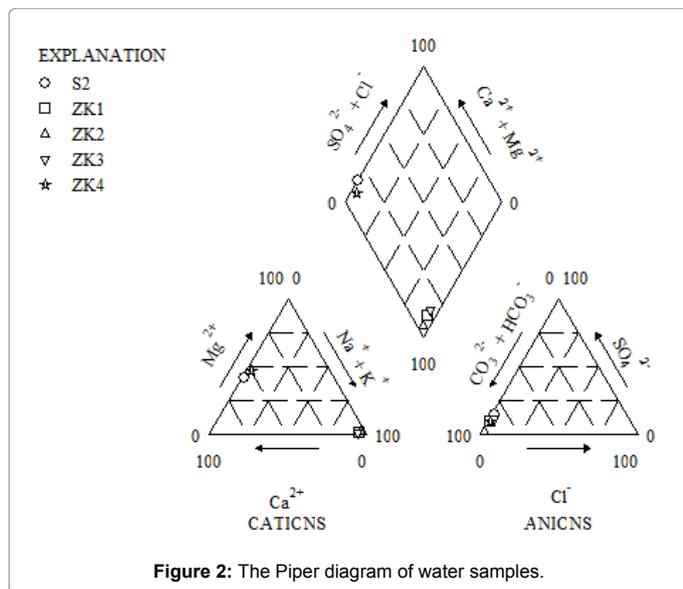
According to principal component analysis, regional geothermal water is mainly affected by 3 factors, the main components of F1, F2, F3 of the contribution rate were 53.76%, 23.93%, 18.52%, and the cumulative contribution rate was 96.22%. That shows that the first, the second and the third principal component represents the amount of information provided by the original 96.22% (Table 2). The principal component analysis of the 11 variables in the region is shown in Table 3. The principal component analysis diagram, consisting of F1, F2 and F3, is shown in Figure 3. By the load graph of each variable on the principal component axis (Figure 3), the K^+ , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- and SiO_2 can be found to have higher load on the F1, and the absolute value range is 0.72-0.95. Taking into account the regional stratigraphic lithology, mainly for the Qingbakou system's blastosammite and Cambrian sandstone, its main components are feldspar and quartz. When the system contains a certain amount of CO_2 , the water reacts with feldspar minerals (type 1 is albite, potash feldspar and anorthite are similar to albite), and then the $\text{HCO}_3^- \text{Na}^+$ type of water is formed. The first principal component F1 reflects the close relationship between the chemical composition of geothermal water and the surrounding rocks in this area. F1 accounted for 53.76% of the contribution, and the occurrence of geothermal water in sandstone and blastosammite plays an important role in hydrochemical composition of geothermal water. The Na^+ content in geothermal water is high, which is presumed to be rich in albite minerals in the geothermal water filter. The solubility of this mineral is low, so the content of Na^+ in geothermal water is high, but the salinity is not high.



In Figure 3, F, SO_4^{2-} and pH have higher loads on the F2, and their absolute range is 0.6-0.86. The F in geothermal water is mainly derived from the dissolved fluorine minerals (such as fluorite). The SO_4^{2-} is mainly derived from dissolved sulfate minerals (such as anhydrite). The second principal component F2 reflects the influence of specific mineral leaching by geothermal water on the chemical composition of geothermal water.

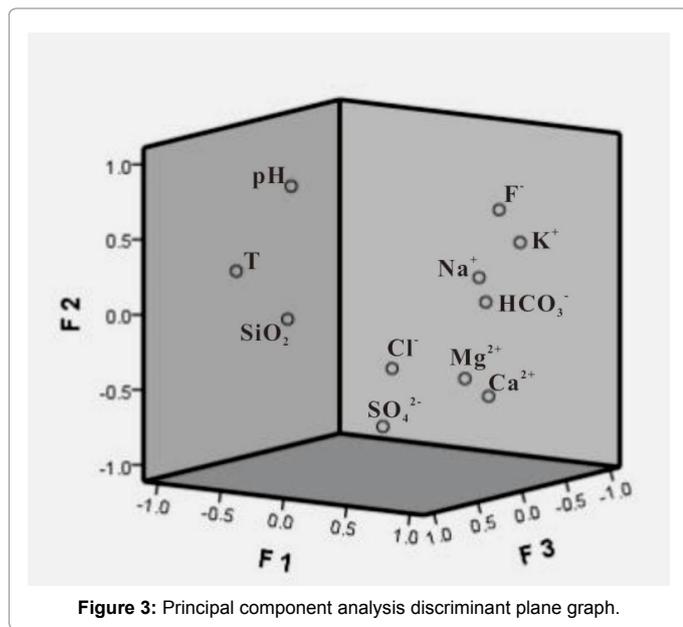


As shown in Figure 3, Cl^- and water temperature T have higher load



on F3, the range of absolute value is 0.63-0.75, and the K^+ has moderate load on F3, and the absolute value is 0.53. The consideration is mainly due to geothermal water leaching of chloride from rocks (such as potassium salts). Because of the natural water chloride dissolved easily, the formation of a stable Cl^- , Cl^- easy transfer, so only the hot water into the deep water stagnant zone, possible leaching of chloride. The F3 of principal components reflects the influence of regional geothermal water cycle on the chemical composition of geothermal water.

Due to the regional geothermal water, chemical types are HCO_3^- -Na, in order to better distinguish between different wells (Springs) the chemical characteristics of water, here using the method of cluster analysis to divide the area of geothermal water, the results shown in Figure 4. As you can see from Figure 4, when the samples are divided into two classes, one is ZK1, ZK3 and ZK4, and the other is ZK2 and S2. The difference between these two categories is mainly to consider whether geothermal water is chemically balanced and mixed with shallow subsurface water. From the Na-K-Mg triangle diagram (Figure 5), the ZK2 and S2 samples are in a partial equilibrium area, which indicates that some of these water samples may have partial chemical equilibrium and may be affected by mixing of shallow groundwater. The samples of ZK1, ZK3 and ZK4 are in immature water areas, indicating that such water samples may not yet reach chemical equilibrium. The SiO_2 content of ZK2 and S2 water samples is lower than that of ZK1, ZK3 and ZK4 water samples. The possible explanation is that ZK2 and S2 water samples are mixed by shallow groundwater.



As you can see from Figure 5, the water sample is in partially balanced area and immature area, and that means not using cationic scale, but the use of SiO_2 scale [8]. Phreeqc software is used to calculate the saturation index of heat storage minerals at different temperatures, and to estimate the thermal storage temperature by using multi mineral balance method [11]. Regional lithology is mainly blastopsammite and sandstone, consisting chiefly of feldspar and quartz, change in hydrothermal alteration, occurrence of chalcedony. Therefore, the calculation of selected quartz, chalcedony, feldspar, fluorite and anhydrite minerals as reference, simulation results shown in Figure 6 (listed only ZK1, the rest does the same treatment). After calculation, regional water saturation index of quartz, chalcedony closest to 0 (Table 4), the content of SiO_2 is mainly controlled by quartz and chalcedony, so using quartz and chalcedony is estimated heat storage temperature range (Table 4). The differences between the calculated temperature and geothermometer multi mineral equilibrium temperature is mainly owing to the mixing water and the groundwater. The actual logging

Number	Tectonic position	Well depth/m	Water temperature of Wellhead/°C	Flow/m ³ ·d ⁻¹
Thermal spring S1 of Jianhe	Between Chongsuoxi anticline and Gedong fault	-	48	1797.75
Thermal spring S2 of Cengong	Among Wu Dongping fault, Wen Shaosfault and Shi Dongkou fault	-	28	1728.6
Geothermal well ZK1 of Janhe	Among Ge Dong fault, Chongsuoxi anticline and San Sui syncline	1750	38	1800.46
Geothermal well ZK2 of Taijiang	Between San Sui syncline and Gedong fault	1618	40	841.85
Geothermal well ZK3 of Leishan	Among Ge Dong fault, Leishan syncline and San Sui syncline	2300	45	1030.95
Geothermal well ZK4 of Cengong	Among Wu Dongping fault, Wen Shaos fault and Shi Dongkou fault	802	46	6998

Table 1: Geothermal well location information.

Number	pE/(mg/L)									Temperature of water/T/°C	pH	δD	δ ¹⁸ O
	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	F ⁻				
S2	4.61	211.06	5.73	1.74	2.65	12.05	610.81	20.10	7.64	28.00	8.09	-54.30	-8.19
ZK1	1.88	85.10	2.90	0.75	1.67	18.19	223.91	46.52	1.68	38.00	8.00	-59.70	-8.83
ZK2	2.21	239.40	5.32	2.73	7.14	12.89	708.54	19.99	1.28	40.00	8.07	-63.20	-9.26
ZK3	0.84	46.39	1.83	0.37	2.45	12.18	119.65	38.57	0.35	47.00	8.46	-69.20	-10.03
ZK4	3.18	200.09	0.0082	0.50	2.41	10.06	467.27	33.87	5.68	46.00	8.54	-57.50	-8.64

Table 2: Chemical and isotopic compositions of samples.

Principal component total variance interpretation				The loading of Variable			
Principal component	Characteristic value	Percentage variance	Cumulation %		F1	F2	F3
1	5.914	53.761	53.761	K ⁺	0.727	0.429	-0.53
2	2.632	23.931	77.693	Na ⁺	0.885	0.312	0.162
3	2.038	18.527	96.22	Ca ²⁺	0.788	-0.524	-0.086
4	0.416	3.78	100	Mg ²⁺	0.884	-0.339	0.321
5	3.90E-16	3.55E-15	100	Cl ⁻	0.61	-0.236	0.754
6	1.99E-16	1.81E-15	100	SO ₄ ²⁻	-0.234	-0.867	-0.348
7	-2.02E-17	-1.83E-16	100	HCO ₃ ⁻	0.951	0.158	0.18
8	-1.14E-16	-1.03E-15	100	F ⁻	0.518	0.618	-0.59
9	-3.53E-16	-3.21E-15	100	SiO ₂	-0.915	-0.206	-0.241
10	-6.53E-16	-5.93E-15	100	pH	-0.511	0.798	0.297
11	-1.23E-15	-1.12E-14	100	T	-0.708	0.262	0.636

Table 3: Principal component total variance interpretation and analysis result.

Number	Saturation index SI		Thermometric scale of quartz 1/°C	Thermometric scale of quartz 2/°C	Thermometric scale of Chalcedony/°C	Multi mineral balance method/°C	Wellhead fluid temperature/°C	Measured bottom hole temperature/°C
	quartz	Chalcedony						
ZK1	0.0041	0.0073	98.48	99.67	68.3	86	38	-
ZK2	0.0081	0.0074	63.42	68.93	31.35	89	40	62.4
ZK3	0.0059	0.0057	90.08	92.39	59.35	93	47	76.5
ZK4	0.0106	0.0046	84.48	87.50	53.41	85	46	65.2
S2	0.0081	0.0059	63.63	69.12	31.56	52	28	-

Table 4: The calculation result of Temperature scale and SI.

temperature is lower than the multi mineral equilibrium temperature, and the reason is that the actual geological conditions are very complex. The distribution of thermal reservoirs controlled by structure is more complex. When choosing drilling location, it often deviates from the thermal reservoir, so that the actual logging temperature is often lower than the actual heat storage temperature [8].

The equilibrium temperature is regarded as the heat storage temperature, and the geothermal water circulation depth is estimated according to formula 2. According to the ground temperature logging data, the average geothermal gradient of the region is 2.83°C/100 m, and the depth of the normal temperature is h, taking 30 m. The temperature at normal temperature of ZK1, ZK2, ZK3, ZK4 and S2 is 17.5, 16.8, 16.7, 15.9, 15.2, respectively. It is estimated that the depth of hot water circulation in ZK1, ZK2 and ZK3 reaches 2450 m, 2581 m, 2726 m, 2471 m and 1330 m.

$$H = (t_1 - t_2) / G + h \quad (2)$$

The H is the geothermal water circulation depth (m); t₁ is the heat storage temperature (m); t₂ is the temperature at normal temperature (°C); G is the geothermal gradient (°C/100 m); h is the depth of normal temperature (m).

Isotope geochemical characteristics

The regional hydrogen oxygen isotope is divided into δD-δ¹⁸O

(Figure 7). The point of projection is located on the Chinese meteoric water line [12], indicating that geothermal water comes from meteoric water supply. At the same time, to the right from the Guiyang meteoric water line [13] this may be due to the regional and Guiyang latitude, elevation, temperature and rainfall differences.

Because the content of H in most rock forming minerals is relatively low, the underground hot water is almost not exchanged with the H in the surrounding rock. When δ¹⁸O is defined as a measure of isotopic exchange, d-excess=δD-8δ¹⁸O is often chosen [14]. The results show that ZK1, ZK2, ZK3, ZK4 and S2 are 10.94%, 10.88% 11.04%, 11.62% and 11.22%. The global meteoric water line δ¹⁸O-δD, which was given by Craig in 1961 shows that the d-excess value of atmospheric precipitation is 10‰, and the regional geothermal water d-excess is near it. Therefore, the degree of isotopic exchange between regional geothermal water and surrounding rock is low, and the water rock interaction environment is not closed. This is because the fault zone is caused by many pores and fissures, and this is obviously different from the high temperature reservoir [15,16]. Therefore, geothermal water originates from meteoric water and is in the medium and low temperature thermal reservoir.

Due to the difference of latitude and longitude, temperature and rainfall between ZK1, ZK2, ZK3, ZK4 and S2, the elevation of hydrogen and oxygen isotopes in geothermal wells should be dominated by

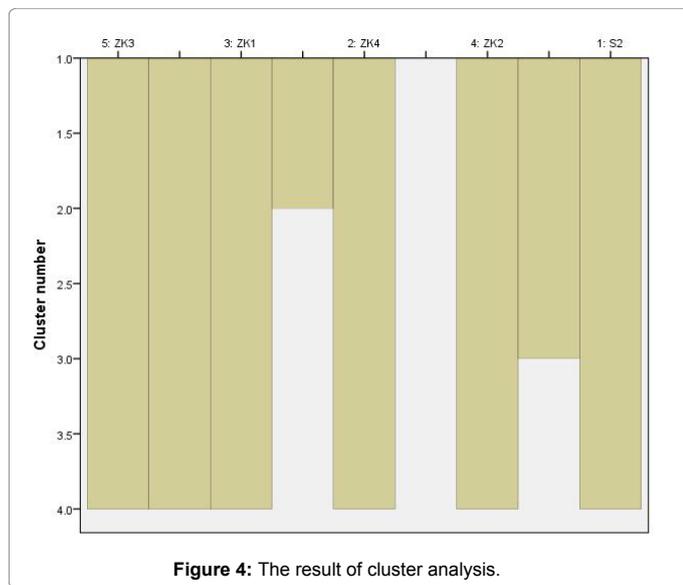


Figure 4: The result of cluster analysis.

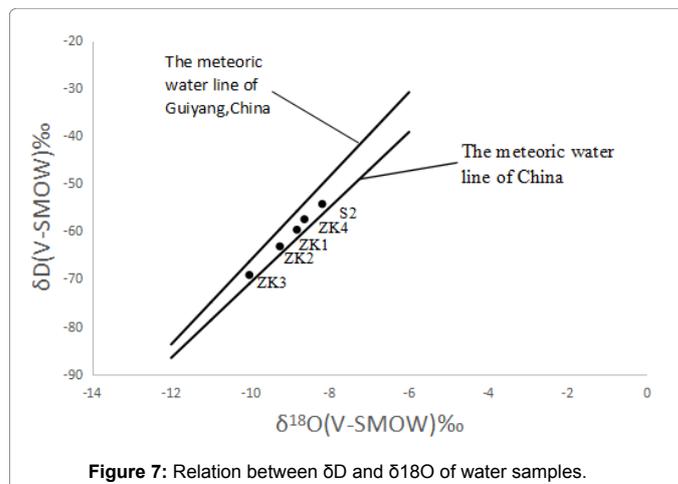


Figure 7: Relation between δD and $\delta^{18}O$ of water samples.

elevation effect. According to the estimation formula of elevation effect and Sichuan Tibet isotope elevation effect ($\delta D = -0.026H - 30.2$) in the study area [17], the supply elevation of ZK1, ZK2, ZK3, ZK4, S2 was estimated by 1134 m, 1269 m, 1500 m, 1050 m and 926 m respectively.

Heat source analysis

Since the Xuefeng movement, the region is in a stable land mass tectonic environment. Since the Cenozoic, there is no magmatic intrusion and volcanism. The heat reservoir temperature is lower than 100°C, a medium low temperature storage, the lack of regional water related to volcano, magmatism in a large number of CO₂, H₂S and other ingredients, also did not appear obvious drift of oxygen isotope, non-intrusive granite regional stratigraphic distribution, lack of material basis radioactive source. Therefore, the regional geothermal water does not have magmatic and radioactive heat source conditions.

Region is located in the Wuling Mountain and northeast of Guangxi SN to the gradient zone of gravity anomaly [3]. It is a primary fault (deep fracture) in the east of Guizhou. The value of geothermal flow is abnormally high, and the value distribution is mainly located in the suture boundary of the plate boundary and the deep fault active belt [18]. At the same time, the area is located in a relatively shallow location of Moho depth [19-21]. Geothermal water is formed in the process of deep circulation, under the larger value of terrestrial heat flow, which is heated by surrounding rock. Regional faults control the distribution of geothermal resources.

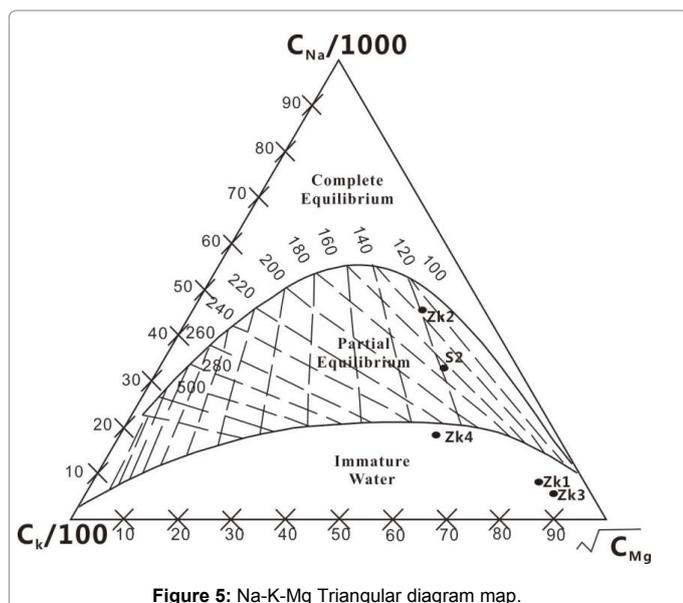


Figure 5: Na-K-Mg Triangular diagram map.

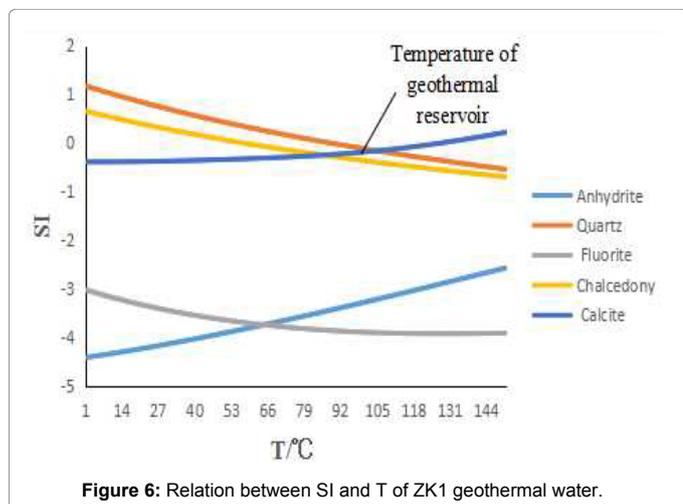


Figure 6: Relation between SI and T of ZK1 geothermal water.

Conclusions

The chemical type of regional geothermal water is HCO₃-Na, the chemical component of water is mainly affected by 3 factors. The first factor is the stratum of sandstone and blastopsammit; the second factor is the geothermal water leaching of certain minerals; the third factor is the deep circulation of geothermal water. Further, the division of regional geothermal water shows that regional geothermal water can be divided into two main types, whether or not the hot water in the main base has reached the balance of chemical reaction of some mineral and the mixture of shallow ground water and ground water. The heat storage temperature is about 52°C-93°C, and the geothermal water circulation depth is about 1330 m-2726 m. The supply of geothermal water is atmospheric water, the interaction between water and rock is weak, and the recharge elevation is about 926 m-1500 m. Geothermal energy in the region is not magmatic and radioactive heat sources, mainly by regional geothermal flow heating.

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