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Research Article

Hydrochemical Characteristics and Formation of the Madeng Hot Spring in Yunnan, China

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The Madeng hot spring emerges in the central river valley in the northeastern Lanping Basin in Jianchuan county of Yunnan Province in China. Quaternary sand and gravel occur in the valley which is underlain by the red beds consisting of sandstone and mudstone. The temperature of the hot spring is 42.1°C. The spring water has a pH value of 6.41, TDS of 3.98 g/L, F contents of 3.08 mg/L, and H_2SiO_3 of 35.6 mg/L. The hot water is of SO_4•Cl-Na•Ca type. There is a slight hydrogen sulfide odor in the spring water. Stable hydrogen and oxygen isotopes indicate that the hot water is of meteoric origin. It is estimated that the elevation of the recharge area of the hot spring is approximately 3800 m, the age of the hot water is some 140 years, the temperature of the geothermal reservoir is 75°C–80°C, the mixture ratio of cold water is approximately 80%, and the circulation depth of the thermal groundwater is 1870 m. After receiving recharge from infiltration of precipitation in the mountainous recharge areas, the groundwater undergoes a deep circulation, obtains heat from the heat flow, flows upward along the fractured zone, and emerges as an upflow spring through the Quaternary sand and gravel in the central low-lying river valley.

1. Introduction

Hot springs display the thermal energy in the internal earth, and they can provide us important information on groundwater circulation and hydrochemistry at depth [1]. There are about 2800 hot springs in China [2], and more than 1000 of them are discharging in the Yunnan region [3] where a significant geothermal anomaly is present in the collision zone between the Indian Ocean Plate and the Eurasian Plate. For this reason, Yunnan is called "the hometown of hot springs" [4]. The Madeng hot spring in Jianchuan country of Yunnan is located in a river valley in the Yunnan-Tibet geothermal zone and is rich in several trace elements critical to the human body [5]. Hot springs such as the Madeng hot spring which discharges thermal groundwater from deep geothermal reservoirs and emerges through a shallow aquifer of unconsolidated sediments are seldom encountered in Western Yunnan. The present work focuses on the hydrochemical aspects and formation of the hot spring.

Hydrogeochemical studies of hot springs were carried out by many researchers. For example, Ellis and Mahon [6] considered that most of the dissolved constituents of thermal water are from the reactions between surrounding rocks and water and elaborated the origins of hot water, thermal water isotope physicochemical characteristics, mineral precipitation in thermal water, and so on. Favara et al. [7] studied the chemical characteristics of thermal groundwater of the Sicily region in Italy and found that the geothermal water in this area is a mixture of two kinds of groundwater that one is rich in gypsum and the other is rich in carbonate. Cidu and Bahaj [8] examined the chemical characteristics of geothermal water in Morocco and reported that the thermal groundwater contains high concentrations of B, Li, and Sr and the hot water is of Na-Cl type. Frengstad et al. [9] carried out hydrochemical research on groundwater in Norway and revealed the elements in the groundwater as the root of the increased pH value. By studying the chemical characteristics of the geothermal water in Portuguese Azores, Cruz and Franca [10] found that the hot springs are affected by the local volcanism, and they used multivariate analysis to divide the hydrochemical type of the geothermal water in this area. Davraz [11] used the hydrogeochemical methods to analyze the local geothermal water in Turkey and found that the geothermal water was mixed with the surface water in this region.

Stable ^{2}H and ^{18}O isotopes are often used to examine the origin of groundwater since Craig [12] established the global meteoric water line between $\delta^{2}H$ and $\delta^{18}O$ of precipitation. Payne [13] pointed out that stable isotopes can also be used for groundwater recharge and age determination. Favara et al. [14] studied the stable isotopes $\delta^{2}H$, $\delta^{18}O$, and ^{13}C of hot and cold springs in the western Sicily and revealed that the groundwater in this region is a mixture of the groundwater and the sea water. Majumdar et al. [15] suggested that the hot springs in the eastern India were originated from meteoric precipitation, and the values of $\delta^{2}H$ and $\delta^{18}O$ of the geothermal water in this region would be increased during the winter. Radioactive isotopes are mainly used for estimating the residence time (age) of groundwater. Cherdyntsev [16] proposed a method of using ^{226}Ra and ^{222}Rn to estimate the residence time of thermal groundwater. Liu et al. [17] estimated the age of the Jifei hot spring in Western Yunnan by using contents of ^{226}Ra and ^{222}Rn.

Geothermometers are used to estimate temperature of deep geothermal reservoirs. In the 1970s–1980s, several geothermometers were established to estimate the temperature of geothermal reservoirs [18–22] which are widely used in the development and utilization of geothermal resources. From 1988 to 1992, a series of triangular figures were created for the study of the origin and formation mechanism of geothermal fluids [23–25].

In this paper, on the basis of field investigation and sample detection, we analyze the occurrence of the Madeng hot spring, examine the hydrochemical characteristics, and summarize the isotopic signature of the hot water. The origin of the geothermal water, residence time of the geothermal water, circulation depth, reservoir temperature, elevation and temperature of the recharge area, and mixture ratio of the hot water and cold water are also identified and estimated. The formation of the hot spring is further proposed.

2. Materials and Methods

2.1. Geological Setting. The Madeng hot spring is located at the southeast of the Houdian village in Jianchuan County of Yunnan (Figure 1). The hot spring emerges in the central river valley in the eastern Lanping Basin. The elevation of the valley ranges from 2350 m in the southeast to 2400 m in the northwest [26]. The Mishahe river and groundwater in the Quaternary sediment flow from northwest to southeast in the valley. The Madeng hot spring is located in the western flank of Mt. Xueban, whose peak is 4295 m high and almost permanently covered by a glacier.

The mean annual precipitation in Jianchuan county is 731.1 mm (1990–2010). The main outcropping formations in the study area are related to the Devonian dolomitic limestone and dolomite, Permian tuff, Triassic siltstone, basaltic sandstone, limestone sandstone and carbonaceous shale, Jurassic red mudstone, marl, siltstone and fine sandstone, Cretaceous amaranth mudstone and feldspar quartz sandstone, Paleogene amaranth mudstone, siltstone, sandstone and conglomerate, and Quaternary sandy clay, gravel and grit (Figure 1). In the surrounding areas of Madeng hot spring, red beds consisting of Jurassic, Cretaceous, and Paleogene sedimentary deposits occur [27]. The red beds exist in the western, southern, and central Yunnan, which mainly consist of the purple mudstone and small amounts of feldspar quartz sandstone, and occupy around one-third of the area of Yunnan Province [28].

Tectonically, Yunnan Province is located in the Indian Ocean Plate and Eurasian Plate collision zone and its affected area. From east to west, Yunnan and Tibet geothermal zone can be divided into the Ailaoshan anticlinorium, Lanping-Simao depression, Changning-Lancang anticlinorium, Baoshan synclinorium, and Tengchong-Gaoligong mountain anticlinorium [29]. The Jianchuan region is located in the composite part of the “Dai” type tectonic system consisting of the Qinghai-Tibet and Yunnan-Myanmar tectonic systems, which belongs to the Sanjiang fold belt in the conjunctive part of the Tangula-Changdu-Simao fold belt and the Yangtze Paraplatform. The deep and huge faults in the region trend nearly in NNW and NS directions, including from east to west the Jinshajiang fault, Weixi-Qiaohou fault, Duosong-Ludian fault, Lanping-Simao central fault, Jinshajiang-Ailaoshan fault, Zhongdian-Jianchuan fault, Annan-Jianchuan fault, Honghe fault, Heqing-Eryuan fault, and Jianchuan-Lijiang fault. The study area lies in a trigonal belt bounded by the nearly SN-trending Annan-Jianchuan fault in the east and the nearly NNW-trending Weixi-Qiaohou fault in the west. The Jinshajiang-Ailaoshan fault, Honghe fault, Duosong-Ludian fault, and Jianchuan-Lijiang fault occur in the study area, forming the main body of a regional complex tectonic framework consisting of NNW and SN-trending tectonic belts with frequent magmatic activities in the geological history (Figure 1) [27].

Special geological and geographical conditions make the Yunnan Province abundant in geothermal resources in China. There is a very close relationship between the formation of geothermal resources and the geological background. From the point of view of geothermal geology background, Yunnan Province can be divided into two areas by the Jinshajiang-Ailaoshan fault zone. The west is a high-temperature hydrothermal area where some boiling hot springs and hot springs of low to moderate temperature occur, and the east is a low-temperature hydrothermal area where boiling hot springs are seldom encountered. High-temperature hydrothermal activities in the Western Yunnan are in the south band of the Yunnan and Tibet geothermal band. The high-temperature geothermal systems in the region are obviously controlled by the distribution of the activity of the basement and depression layout and the tectonic uplift.

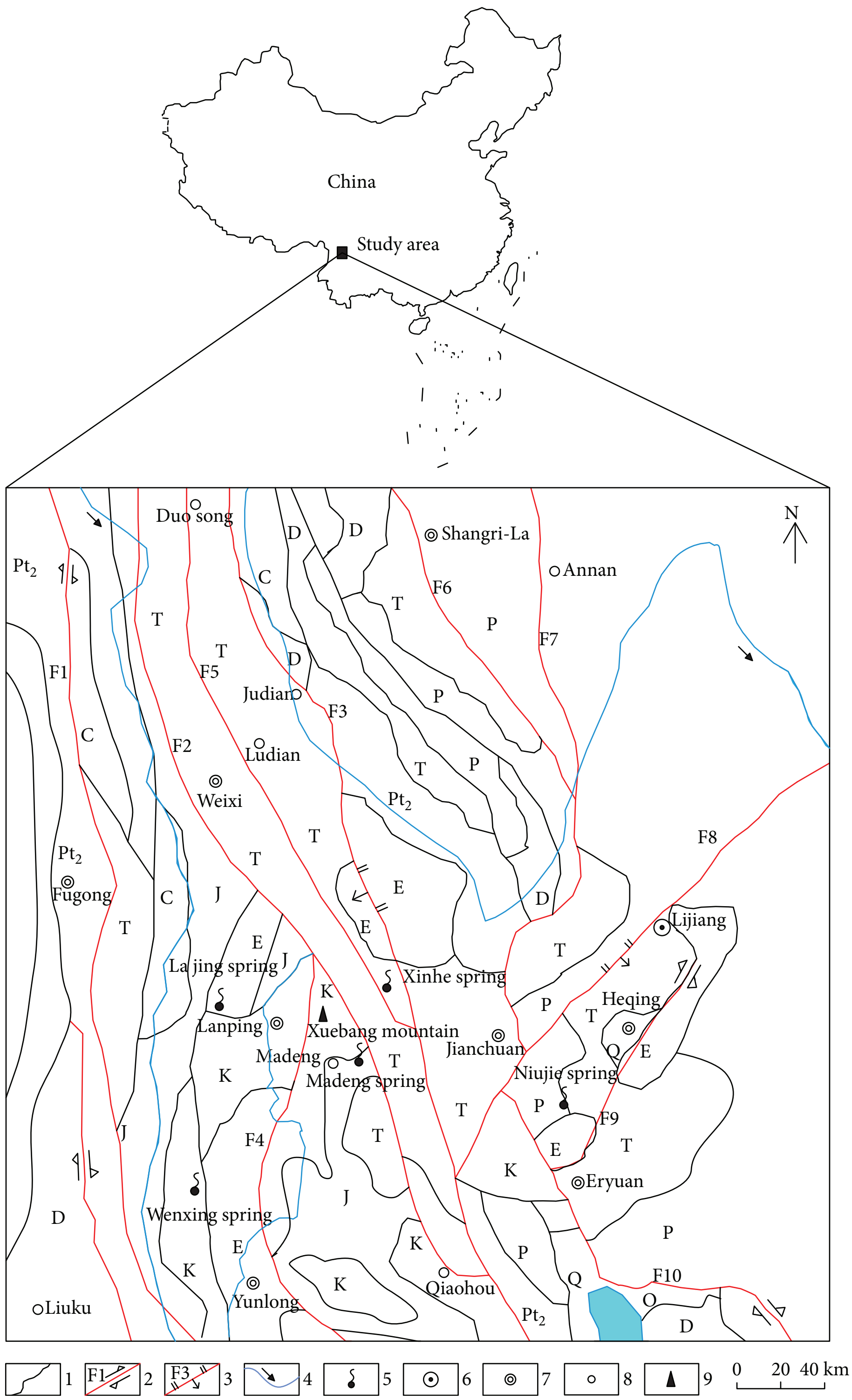

Figure 1: Geological sketch map near the Madeng hot spring in Jianchuan of Yunnan Q—Quaternary gravel and sand; E—Eogene purple mudstone, siltstone, sandstone, and conglomerate; K—Cretaceous fine-grained sandstone, amaranth mudstone, and feldspar quartz sandstone; J—Jurassic red mudstone, siltstone; T—Triassic limestone, siltstone; P—Permian basalt and tuff breccia; C—Carboniferous quartz sandstone, limestone; D—Devonian dolomitic limestone and dolomite; O—Ordovician quartz sandstone; Pt_2—Mesoproterozoic mica schist, dark cloud flash schist; F1—Lancangjiang river fault; F2—Weixi-Qiaohou fault; F3—Jinshajiang-Ailaoshan fault; F4—Lanping-Simao middle fault (Bijiang fault); F5—Duosong-Ludian fault; F6—Zhongdian-Jianchuan fault; F7—Annan-Jianchuan fault; F8—Jianchuan-Lijiang fault; F9—Heqing-Eryuan fault; F10—Honghe fault; 1—stratigraphic boundary; 2—strike-slip faults; 3—reverse fault; 4—rivers; 5—spring; 6—city; 7—county; 8—village and town; 9—mountain.

2.2. Brief Description of the Hot Spring. The Madeng hot spring (YJ2) is located in the west of Jianchuan county of Yunnan with an elevation of 2356 m. There are six vents in the hot spring, and the hot spring is an upflow spring. The upflow spring is a kind of genetic types of springs when the aquifer is covered by unconsolidated sediments of poor permeability or buried under an aquitard and when the hydraulic head in the aquifer is higher than the ground surface. Groundwater will flow through the upper unconsolidated sediments or aquitard and emerges on the land surface [30]. According to the "Hot Springs' Records in Yunnan Province' Records," the discharge of the hot spring was approximately about 10 L/s, the water temperature is 42°C, and TDS of hot water is 2.82 g/L [5]. According to the measurements by Yu [26], the discharge of the spring was 3.24 L/s with the water temperature of 43°C and TDS of 3.647 g/L. The hot spring is situated in the central river valley, and the vents occur on the northeastern side of the Mishahe river in a circular area with the diameter of about 50 m. There are a few bathhouses near the springs' vents. The water in the bottom pours with bubbles, and there is a slight hydrogen sulfide odor in the spring water. A shallow well and two drilling holes are located in three vents for pumping hot water for bathing, and the remaining three vents are still in a natural state. On August 19, 2014, the spring water temperature was measured as 42.1°C, pH as value 6.41, and TDS as 3.98 g/L and water samples were taken from the shallow well with the highest temperature of 42.1°C. The hot spring can also be regarded as a brackish spring according to TDS. In addition, there are 4 hot springs near the Madeng hot spring (Figure 1), including the Xinhe hot spring (Jianchuan county, 51.2°C), Wenxing hot spring (Yunlong county, 51.6°C), Lajing hot spring (Lanping county, 46.1°C), and Niujie hot spring (Eryuan county, 76.1°C).

2.3. Sampling and Chemical Analyses. Sampling was conducted for the Madeng hot spring in Jianchuan county of Yunnan on August 19, 2014. The chemical analyses were conducted at the laboratory of the Beijing Brigade of Hydrogeology and Engineering Geology, using the following methods: K, Na, Li, Sr, Zn, and Mn by the flame atomic absorption; Ba, Al, Pb, Cd, and Ag by the atomic absorption of the plumbago furnace; Cl, SO_4, and NO_3 by the ion chromatogram; NH_4, Fe^2, Fe^3, NO_2, F, Br, I, Cr(6), H_2SiO_3, HBO_2, and HPO_3 by the spectrophotometer; Hg, Se, and $HAsO_3$ by the atomic fluorescence; Ca, Mg, and hardness by the volumetric method (EDTA titration); HCO_3, CO_3, and total alkalinity by the volumetric method (HCl titration); total acidity by the volumetric method (NaOH titration); H_2S by the volumetric method (sodium hyposulfite titration); and ^{226}Ra and ^{222}Rn with the radioactive radon-thorium analyser. ^2H and ^{18}O were detected at the Analysis Center of the Beijing Research Institute of Uranium Geology by the zinc reduction method for hydrogen isotopes and the carbon dioxide—water equilibrium method for oxygen isotopes. The chemical constituents were tested for accuracy by calculating the normalized inorganic charge balance which was less than 2.22% for the YJ2 sample and 0.17% for the YJ2-A sample, respectively.

Table 1: Chemical analyses of the Madeng hot spring (mg/L).

Composition	YJ2	YJ2-A
K	11.4	17.9
Na	802	733
Ca	378	185
Mg	37.9	35.5
NH_4	<0.02	0.701
Fe	0.116	/
HCO_3	663	287
Cl	810	595
SO_4	1.24×10^3	1.05×10^3
F	3.08	2.32
NO_3	3.7	/
^{226}Ra (Bq/L)	0.420	/
^{222}Rn (Bq/L)	7.21	/
Ba	0.051	/
Cr (6)	<0.001	/
Pb	<0.0008	/
Mn	0.024	/
Al	0.060	/
Li	0.246	0.25
Sr	12.4	/
Br	0.17	/
I	<0.02	/
Zn	0.026	/
Se	0.0003	/
Ag	<0.0005	/
H_2SiO_3	35.6	/
$HAsO_3$	0.016	/
HBO_2	3.60	2.75
HPO_3	<0.01	/
NO_2	0.078	/
Free CO_2	91.5	/
TDS	3.98×10^3	2.82×10^3
Total alkalinity	543	/
Total acidity	104	/
Total hardness	1.10×10^3	/
H_2S	<0.05	/
pH	6.41	7.65
Temperature (°C)	42.1	42

YJ2 represents the sample collected in August 2014; YJ2-A represents the data recorded in the "Hot Springs' Records in Yunnan Province' Records" in 1999.

3. Results and Discussion

3.1. Hydrochemical Characteristics. The chemical analyses of the hot spring (YJ2) and those reported in the "Hot Springs' Records in Yunnan Province' Records" (YJ2-A) are listed in Table 1. The ion concentrations except K are higher in the year 2014 than in 1999. The minor ions in the water are predominated by NH_4, NO_3, and Fe, and their contents are less than 0.02 mg/L, 3.7 mg/L, and 0.116 mg/L, respectively. Trace

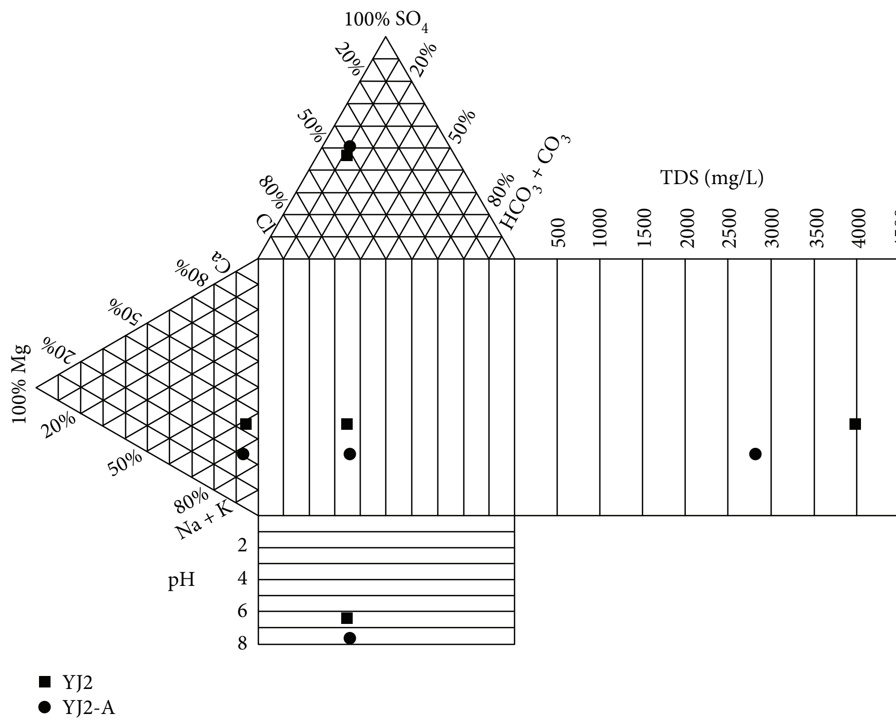

Figure 2: Durov diagram showing the Madeng hot spring water samples—YJ2: water sample of the hot spring taken in 2014; YJ2-A: water sample of the hot spring from Local Chronicles Compilation Committee of Yunnan Province [5].

elements mainly include I, Br, Sr, Li, Al, Zn, Ba, and Mn. The content of Sr in the hot spring water is 12.4 mg/L, and H_2SiO_3 is 35.6 mg/L, which means Sr water and H_2SiO_3 water, according to the Standards of "Chinese drinking natural mineral water" (GB8537-2008) ($Sr \geq 0.20$ mg/L for Sr water and $H_2SiO \geq 25.0$ mg/L for H_2SiO_3 water).

The content of F in the hot spring water is 3.08 mg/L, which is greater than that in the"Hot Springs' Records in Yunnan Province' Records" (2.23 mg/L) (Figure 2) and is beyond the standard of fluoride (<1.5 mg/L) in the Standards of "Chinese drinking natural mineral water" (GB8537-2008). The hot spring water always contains fluorine, and bathing with the hot water can be used to the treatment of skin disease and rheumatism. The H_2SiO_3 content of the Madeng hot spring water is greater than that of the standards of "Chinese drinking natural mineral water." The mineral water rich in H_2SiO_3 is useful for the treatment of nervous system disease and has certain effect on the disease of the heart, head, and blood vessel [31].

The pH of the hot spring water is 6.41, and the hot water is weakly acidic. As shown in Table 1, the Durov diagram is plotted in Figure 2. From the perspective of the data of 2014, we can see that the main cations are Na and Ca. Their corresponding milligram equivalent percentages are more than 60% and 35%, respectively. The main anions are SO_4 and Cl, and their corresponding milligram equivalent percentages are over 40%. The hot water is of SO_4•Cl-Na•Ca type. As described in the "Hot Springs' Records in Yunnan Province' Records," the hot spring water is of SO_4•Cl-Na type. Comparison shows that pH of the hot springs changes from 7.65 to 6.41, salinity increases from 2.82 g/L to 3.98 g/L, and the change of these two indicators results in the change in hydrochemical type from SO_4•Cl-Na type into SO_4•Cl-Na•Ca type. The source of the salinity of the hot water may be attributed to the subsurface incongruent dissolution of the red beds (containing salts to a larger or lesser degree) [28]. The pH of the hot spring water tends to reduce, causing the thermal groundwater to dissolve more Ca.

3.2. Isotopic Analysis

3.2.1. Recharge Source. Craig [32] summarized the values of δ^2H and δ^{18}O of the global meteoric water and established a linear relation between the values of δ^2H and δ^{18}O, which is called the Craig precipitation line (global meteoric water line):

$$\delta^2 H = 8\delta^{18} O + 10. \quad (1)$$

In order to examine the recharge source of the Madeng hot spring, we took the nearby hot springs (Xinhe, Wenxing, Lajing, and Niujie) into consideration. In August 2014, the five hot springs were analyzed for δ^2H and δ^{18}O (Table 2). We can see that the values of δ^2H and δ^{18}O of the hot springs in the region are mainly caused by the altitude effect. Figure 3 shows that the δ^2H and δ^{18}O data points of the water samples in the study area deviate slightly from the global meteoric water line, but overall fall near the line, indicating that the groundwater is of meteoric origin. At the same time, obvious ^{18}O shift cannot be found, reflecting that the deep thermal storage temperature is not high and the spring water belongs to geothermal water of low temperature [33]. On the contrary, slightly negative ^{18}O shift of the samples of Xinhe,

Table 2: Data of δ^2H and δ^{18}O of the hot spring water samples.

Name of hot spring	Madeng hot spring	Xinhe hot spring	Wenxing hot spring	Lajing hot spring	Niujie hot spring
Serial number	YJ2	YJ1	YY11	YLP1	YE1
T (°C)	42.1	42.7	40	46.1	76.1
δ^2H (‰)	−120.4	−128.6	−118	−112.4	−88.5
δ^{18}O (‰)	−18.5	−19.2	−19.1	−17.6	−11.4

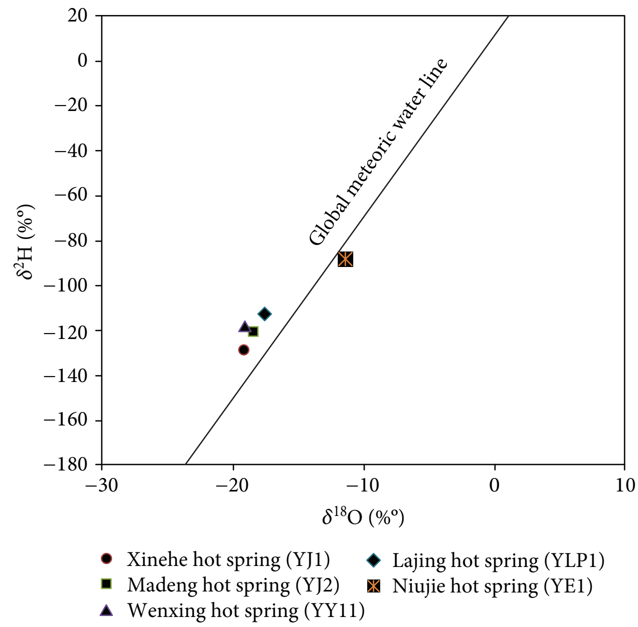

Figure 3: Plot of δ^2H-δ^{18}O of the hot water samples.

Madeng, Lajing, and Wenxing hot springs exists, which cannot be explained at present and will be a future subject of isotope studies.

3.2.2. Recharge Elevation. As mentioned previously, the geothermal water was originated from meteoric water in the study area. On the mainland, the δ^2H and δ^{18}O values of the precipitation increases with the increasing terrain elevation (i.e., altitude effect). Altitude effects of δ^2H and δ^{18}O values are the most important for the hot water samples [34–36]. When the elevation increases by every 100 m, the value of δ^2H reduces from −1‰ to −4‰ and the value of δ^{18}O from −0.15‰ to −0.5‰ [2]. Altitude effect can be used to roughly estimate the recharge elevation of geothermal water [2, 26, 36] through the following equations.

The relationship between the values of the isotope and the altitude in Sichuan, Guizhou, and Tibetan areas in China [26] is used.

$$\delta^{18}\mathrm{O} = -0.0031H - 6.19. \quad (2)$$

$$\delta^{2}\mathrm{H} = -0.026H - 30.2, \quad (3)$$

where H is the infiltration height of isotopes (m).

The equation describing the relationship between the values of δ^2H and δ^{18}O and the local elevation [36, 37] is used.

$$H = \frac{\delta G - \delta P}{K} + h, \quad (4)$$

where H is the infiltration height of isotopes (m), h is the elevation of the sampling point (m), δG is the value of δ^{18}O or δ^2H of the hot spring water, δP is the value of δ^{18}O or δ^2H of the precipitation, and K is the altitude gradient of isotopes (‰/100 m).

Yu [26] proposed that the average values of δ^{18}O and δ^2H about the rainwater of Tengchong of Yunnan Province in 1985 are −9.3‰ and −62.6‰. The values of δ^{18}O and δ^2H about the rainwater of Kunming are −10.13‰ and −76.1‰ in 1980. The precipitation in the study area of the elevation gradient (k) about δ^2H is 3.2‰/100 m, and the value of the δ^2H about the rainwater in the study area is −69.35‰. As we have known, the elevation of the Madeng hot spring is 2356 m, the value of the δ^2H is −120.4‰, and the value of the δ^{18}O is −18.5‰. Equations (2), (3), and (4) are used, and the recharge altitudes are 3971 m, 3469 m, and 3951 m, respectively. Thus, the average value of elevation of approximately 3800 m is reasonably obtained, which is close to that of the Xueban mountain to the west of the Madeng spring.

3.2.3. Temperature of the Recharge Area. The temperature effect of the values of δ^2H and δ^{18}O of meteoric water can be used to estimate the water temperature of the recharge area (or average temperature). According to the data in high latitudes in the northern hemisphere, Dansgaard [38] established the relationship between the annual average value of δ^{18}O and the annual average temperature.

$$\delta^{18}\mathrm{O} = 0.69t - 13.6, \quad (5)$$

where t is the monthly average temperature (°C). Yurtsever [39] summarized the relationship between the value of δ^{18}O and the average temperature of precipitation in the northern hemisphere.

$$\delta^{18}\mathrm{O} = (0.521 \pm 0.014)t - (14.96 \pm 0.21), \quad (6)$$

where t is the monthly average temperature (°C) and the correlation coefficient of the formula is 0.893.

According to (5) and (6), the temperature of the recharge area is estimated as −7.1°C and −6.2°C, respectively. In general, the temperature of the recharge area of most hot springs is above 0°C. However, the Xueban mountain covered with ice and snow is located to the northwest of the Madeng spring. This mountain could be the highest recharge area of the hot spring. The average temperature −6.6°C is thought to be the lowest air temperature of the recharge area of the hot spring.

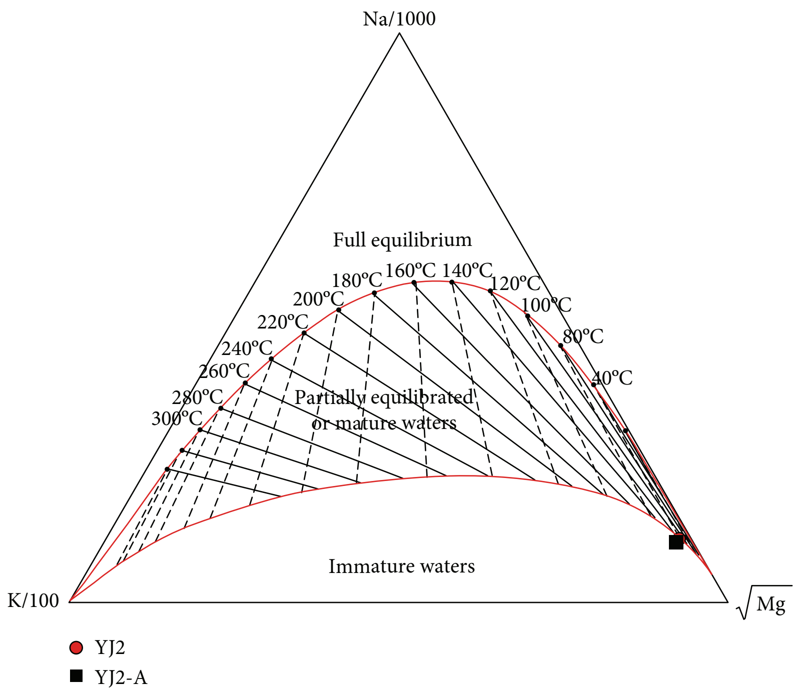

FIGURE 4: Triangular diagram of Na-K-$Mg^{1/2}$. YJ2: water sample of the hot spring taken in 2014; YJ2-A: water sample of the hot spring from Local Chronicles Compilation Committee of Yunnan Province [5].

3.2.4. Resident Time of the Thermal Groundwater. ^{226}Ra and ^{222}Rn are of uranium series isotopes. ^{226}Ra is formed after the decay of uranium, and it becomes ^{222}Rn after further decay of ^{226}Ra. According to the contents of ^{226}Ra and ^{222}Rn in the hot water, the resident time (age) of the thermal water can be estimated by using the following equation [16]:

$$t = -\frac{1}{\lambda_{Ra}} \ln\left(1 - \frac{N_{Ra}}{N_{Rn}}\right), \quad (7)$$

where λ_{Ra} is the decay constant of ^{226}Ra (0.00043) and N_{Ra} and N_{Rn} are contents of ^{226}Ra and ^{222}Rn (in Bq/L).

The contents of ^{226}Ra and ^{222}Rn of the hot water are 0.42 Bq/L and 7.21 Bq/L, respectively. According to (7), it is estimated that the age of the thermal water of the Madeng hot spring is approximately 140 years.

3.3. Genesis of the Thermal Groundwater

3.3.1. Estimation of the Reservoir Temperature. Surface temperature of hot water usually can be observed in the field, but the surface temperature does not stand for the reservoir temperature of the thermal water [40]. Silica geothermometers, cation ratio geothermometers and multimineral equilibrium geothermometers, and so on are widely used to estimate the temperature of a geothermal reservoir (Wang et al. 1993). The Na-K-$Mg^{1/2}$ diagram (Figure 4) shows that the hot water samples of the Madeng hot spring is in the area of immature water, that is, cation geothermometers are not suitable [25]. Therefore, the silica geothermometers are considered in the present work.

SiO_2 mineral is widespread in geothermal water. When the hot water temperature drops, the process of SiO_2 deposition is very slow. When the temperature is lower than 300°C, the pressure and salinity have little impact on the solubility of quartz and amorphous SiO_2, and the dissolved SiO_2 in the water is generally not affected by other ions. These characteristics of SiO_2 make it suitable as a geothermometer and extensive applications. There are five commonly used silica geothermometer equations as follows [18, 41]:

(1) Quartz geothermometer—without steam separation or mixing action:

$$t(^\circ\mathrm{C}) = -42.198 + 0.28831 SiO_2 - 3.6686 \times 10^{-4} (SiO_2)^2 + 3.1665 \times 10^{-7} (SiO_2)^3 + 77.0341 \lg SiO_2. \quad (8)$$

(2) Quartz geothermometer—without steam loss (0–250°C):

$$t(^\circ\mathrm{C}) = \frac{1309}{5.19 - \lg SiO_2} - 273.15. \quad (9)$$

(3) Quartz geothermometer—largest steam loss at 100°C (0–250°C):

$$t(^\circ\mathrm{C}) = \frac{1522}{5.75 - \lg SiO_2} - 273.15. \quad (10)$$

(4) α-christobalite geothermometer:

$$t(^\circ\mathrm{C}) = \frac{1000}{4.78 - \lg SiO_2} - 273.15. \quad (11)$$

Table 3: Relationship between the hot water temperature, enthalpy, SiO_2 content, and ratio of cold water (X).

T (°C)	S_h (×4.1868J/g)	SiO_{2h} (mg/L)	X1	X2
50	50	13.5	0.255	−3.966
75	75	26.6	0.588	−0.047
100	100.1	48	0.715	0.543
125	125.1	80	0.782	0.752
150	151	125	0.825	0.849
175	177	185	0.854	0.901
200	203.6	265	0.875	0.932
225	230.9	365	0.891	0.951
250	259.2	486	0.904	0.963
275	289	614	0.914	0.971
300	321	692	0.924	0.975

The relationship between the hot water temperature, enthalpy, and SiO_2 content is quoted from Fournier and Truesdell [44].

(5) Chalcedony geothermometer—without steam loss (0–250°C):

$$t(^\circ\mathrm{C}) = \frac{1032}{4.69 - \lg SiO_2} - 273.15. \tag{12}$$

The reservoir temperature is estimated as 76.2°C, 75.7°C, 79.8°C, 26°C, and 44.1°C by using (8), (9), (10), (11), and (12), respectively (content of H_2SiO_3 is approximately equal to 1.3 times that of SiO_2). The results show that the reservoir temperature by using quartz geothermometer is higher than that using christobalite geothermometer. The results with (11) and (12), which are lower than the temperature of the hot spring, are unreasonable and should be ignored. The result with the quartz geothermometer conforms to the actual situation. The reservoir temperature of the Madeng hot spring in Yunnan is in the range 75°C–80°C. The reason why this temperature is slightly lower than expected may be the mixture with the cold groundwater in the Quaternary sand and gravel in the valley, when the hot water rises to the land surface.

3.3.2. Circulation Depth. After receiving recharge from infiltration of precipitation, the groundwater is heated during a deep circulation, flows upward to the surface, and emerges in the form of the hot spring. The temperature of the geothermal water is mainly derived from geothermal heating in the process of deep circulation. The geothermal water often can reach as deep as thousands of meters [2]. If the temperature of the geothermal water relies on the deep circulation through normal geothermal heating, one can use the following equation to estimate the depth of geothermal water circulation [2, 33, 42]:

$$Z = G(T_z - T_0) + Z_0, \tag{13}$$

where Z is the depth of geothermal water circulation, G is the reciprocal of the geothermal gradient (m/°C), Tz is the geothermal reservoir temperature (°C), T_0 is the annual average temperature of the recharge area (°C), and Z_0 is the depth of the local constant-temperature zone (m).

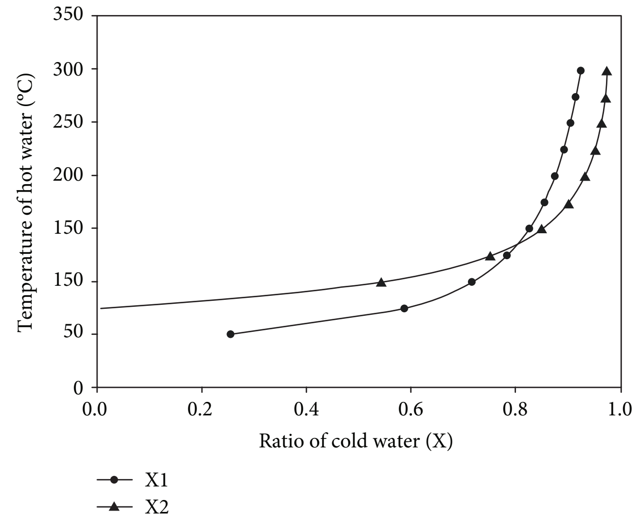

Figure 5: Relationship between temperature of hot water and ratio of cold water $X1 = (S_h - S_s)/(S_h - S_c)$; $X2 = (SiO_{2h} - SiO_{2S})/(SiO_{2h} - SiO_{2C})$.

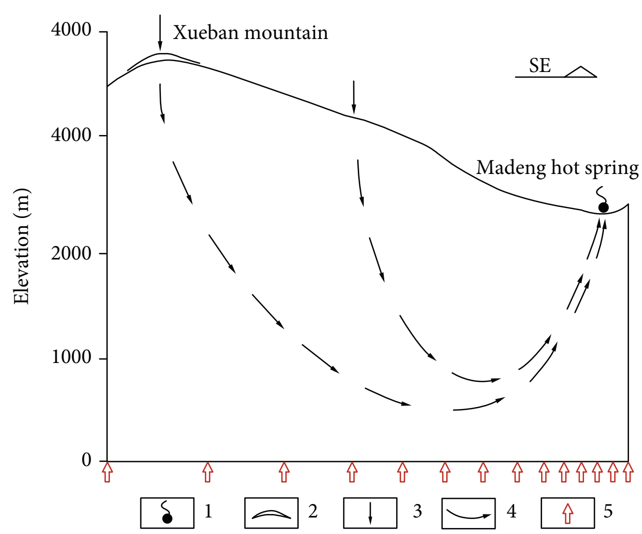

Figure 6: Schematic diagram showing the formation (a regional scale) of the Madeng hot spring in Jianchuan county, Yunnan. 1—hot spring; 2—snow and ice; 3—meteoric water; 4—flow line; 5—heat flow.

According to the "Jianchuan County Annals" published in 1999, we can obtain $G = 28.57$ m/°C, $T_0 = 12.3$°C, and $Z_0 = 20$ m and the estimated underground averaged reservoir temperature $Tz = 77.2$°C. Circulation depth of the thermal water in the research region is estimated as approximately 1870 m by using (13).

3.3.3. Mixture between the Hot Water and the Cold Water. The mixing between hot water and cold water in geothermal systems is very common, which may occur in the whole process of the geothermal fluid circulation. It is very important to recognize the formation conditions and the reservoir temperature of geothermal water by examining the mixing effect [43]. The exposed geologic background near the Madeng hot

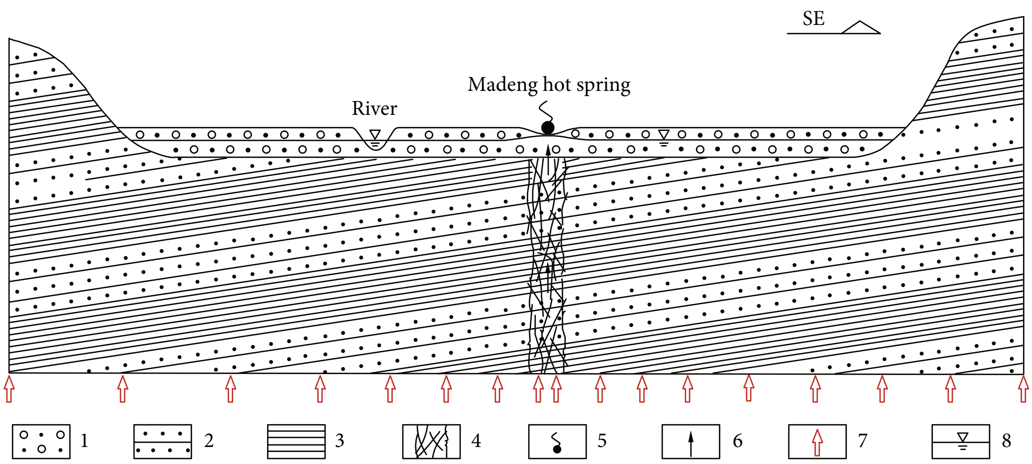

Figure 7: Schematic profile showing the formation (near the vent) of the Madeng hot spring in Jianchuan county, Yunnan. 1—sand and gravel; 2—sandstone; 3—mudstone; 4—fracture zone; 5—hot spring; 6—thermal ground water flow; 7—heat flow; 8—water table.

spring indicates that the geothermal water has the possibility of mixing with the shallow cold water in the sand and gravel while rising towards the ground.

Assuming that the dissolved SiO_2 of the deep geothermal water is in a saturated state, the initial enthalpy and SiO_2 content in the deep hot water at the beginning are inevitably converted into final enthalpy and SiO_2 content of hot spring water at last during the process of cold water and hot water mixing [17, 41, 44]. According to the law of conservation of mass, assuming that X is the cold water mixing ratio, then the relationship between the initial content of thermal groundwater SiO_2 and enthalpy and the final content of thermal groundwater SiO_2 and enthalpy can be expressed by the following equations [44]:

$$S_c X + S_h (1 - X) = S_s, \tag{14}$$

$$SiO_{2c} X + SiO_{2h} (1 - X) = SiO_{2s}, \tag{15}$$

where S_c is the enthalpy of the cold water, S_s is the final enthalpy of the spring water, S_h is the enthalpy of the deep thermal groundwater, SiO_{2c} is the SiO_2 concentration in the cold water, SiO_{2s} is the SiO_2 concentration in the spring hot water, and SiO_{2h} is the initial SiO_2 concentration in the deep thermal groundwater and is a function of S_h. The mixing ratio X of cold groundwater with deep thermal groundwater and the enthalpy of the deep thermal groundwater S_h are not known. The average temperature of the surface cold water in the Jianchuan area is 19°C, the corresponding content of SiO_2 is 10 mg/L, and the enthalpy is 79.55 J/g. The measured spring temperature is 42.1°C, SiO_2 content is 27.38 mg/L, and the corresponding heat enthalpy is 176.26 J/g.

Substituting the enthalpy of different temperatures and the content of SiO_2 (Table 3) into the (14) and (15), respectively, we can get a series value of X1 and X2 (Table 3), and the figure with the relationship between temperature of hot water and ratio of cold water in two curves can be drawn. The proportion corresponding to the intersection point is the required cold water ratio (Figure 5). The mixing ratio of the Madeng hot spring is approximately 80%, which indicates that the hot spring water is mixed with surface cold water. Since the selection of cold water enthalpy and SiO_2 content are empirically estimated and other factors are not considered, the mixing ratio may be higher than the actual result.

3.3.4. Formation of the Hot Spring. Tectonically, the Madeng area in Jianchuan county is located in the west of the Weixi-Qiaohou fault zone and in the east of the Lanping-Simao fracture (Bijiang fault), which formed an inverted triangle. Fractured zones are observed in the red beds in the western of Yunnan and could provide good circulation conditions for the formation of the hot spring. The Madeng hot spring emerges in the center of the river valley in the northeastern Lanping Basin. Quaternary sand and gravel occur in the valley, and the underlying strata are the red beds of sandstone and mudstone. After receiving recharge from infiltration of precipitation in the recharge area in the surrounding mountains (Figure 6), the groundwater undergoes a deep circulation and obtains heat from heat flow. The hot water flows upward along the fractured zone and through the Quaternary sand and gravel (Figure 7) and emerges in the central low-lying river valley. This kind of spring is called an upflow spring [30] for the hot spring does not issue directly from the bed rocks, that is, the red beds.

4. Summary

The Madeng hot spring emerges in the central river valley in the eastern Lanping Basin of Yunnan in China. Temperature of the hot spring water is 42.1°C, belonging to geothermal water of low temperature. The total hardness is 1100 mg/L belonging to the especially hard water according to the classification of hardness. The TDS is 3.98 g/L, indicating the brackish water. The hot water has a pH value of 6.41, belonging to weakly acidic water, which can express that the ability to neutralize the alkali is greater than the acid in the hot spring water in the study area.

The cations of the hot water are predominated by Na, K, Ca, and Mg and the anions of the hot water by SO_4, HCO_3, and Cl. The minor ions of the hot water include NH_4, NO_3, and Fe. H_2SiO_3 of the hot water is 35.6 mg/L and F content is 3.08 mg/L, which are greater than the drinking water standard of China and are not suitable for drinking. The hot water is of SO_4•Cl-Na•Ca type.

The values of the δ^2H and $\delta^{18}O$ are −120.4‰ and −18.5‰, indicating that the hot water is of meteoric origin. Obvious ^{18}O shift phenomenon is not observed, inflecting that the deep thermal reservoir temperature is not high, and the hot water belongs to thermal groundwater of low temperature. The recharge altitude of the hot water is estimated as approximately 3800 m, which may indicate the Xueban mountain. The lowest temperature of the recharge area, the Xueban mountain covered with ice and snow to the northwest of the Madeng spring, is estimated as −6.6°C. The values of the N_{Ra} and N_{Rn} are 0.042 Bq/L and 7.21 Bq/L. The age of the hot water is estimated with the Ra and Rn contents as approximately 140 years.

SiO_2 geothermometer is used to estimate the thermal reservoir temperature of the hot spring in the study area, and the temperature of the geothermal reservoir in the study area ranges from 75°C to 80°C. The mixing ratio of cold water is approximately 80%, and the circulation depth of the hot water, approximately 1870 m. After receiving recharge from infiltration of precipitation in the recharge area, the groundwater is heated during a deep circulation, flows upward along the fractured zone, and emerges as an upflow spring through the Quaternary sand and gravel in the central low-lying river valley.

Given the key information of hydrochemistry and formation hypothesis of the Madeng hot spring in this article, it could provide some insights into the potential and development of thermal groundwater resources in Western Yunnan. Future studies of further explanation of the solutes and isotopic features of the hot spring are required to better understand the substance migration of thermal groundwater occurring in red bed areas.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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