Research Article

Geothermometry and Circulation Behavior of the Hot Springs in Yunlong County of Yunnan in Southwest China

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Travertine and nontravertine thermal springs have been studied in Yunlong County in southwest China to determine the geothermal reservoir temperatures and to find the geochemical processes that affect the evolution of thermal groundwater constituents during subsurface circulation. Hydrochemical characteristics distinguish travertine from nontravertine types. Travertine springs show HCO₃·Cl-Na and SO₄·HCO₃-Ca-Na type, and a nontravertine spring presents Cl·HCO₃·SO₄-Na type. Log(Q/K) versus T diagrams show that reservoir temperatures can be expressed as intervals based on the equilibrium mineral assemblages coexisting in equilibrium and multiminerals in equilibrium with the aid of the PHREEQC and WATCH programs. The spring water mixing ratio with shallow water is between 59% and 82% with steam loss ranging from 12.1% to 27.8%. The Dalang Spring mixes with the highest proportion of cold water (76% to 82%) among the four hot springs and has the highest geothermal reservoir temperature (132°C to 176.9°C). The water-rock interaction during recharge from precipitation demonstrates that the minerals halite, kaolinite, chalcedony, plagioclase, and CO₂(g) play an important part in the evolution of the thermal groundwater. Four inverse modeling simulation paths between precipitation and spring discharge were established to calculate the mass flux of minerals by the PHREEQC program. Halite, kaolinite, chalcedony, plagioclase, and CO₂(g) participate in dissolution reactions in the thermal groundwater circulation, while gypsum, calcite, dolomite, biotite, and fluorite keep the geochemical processes in equilibrium.

1. Introduction

The hydrogeochemistry, geothermometry, and quantification of fluid-mineral reactions from four hot springs along the Bijiang River in Yunlong County of the Lanping basin in southwest China have been examined with respect to the major element compositions of the reservoir fluid discharging on the land surface. In the complex circulation processes, water-rock interactions play an important part in hydrogeochemical indicators of the waters in the geothermal systems which can be used to examine the properties of geothermal reservoirs and the mixing behavior of groundwater [1–4]. Shi et al. [2] studied the hydrochemical characteristics of thermal groundwater in the eastern Tibetan Plateau geothermal belt and found that the springs originated from snow melt in the mountains and surface water and that the groundwater was dominated by the hydrochemical interactions with host rocks. Mixing processes between thermal and nonthermal water can be enhanced by faults in a geothermal area [4]. Geothermometrical methods use mineral solubilities as a function of temperature and silica-enthalpy of liquid water in equilibrium with steam to indicate the reservoir temperature under certain circumstances with respect to the chemical characteristics of thermal groundwater during an ascent from an aquifer to the surface [5–10]. Wang et al. [8] documented the mixing processes with shallow waters and reservoir temperature estimated by chemical geothermometers and silica-enthalpy mixing models that
resulted in the hydrochemical characteristics in the Chabu geothermal system. Various geothermometrical approaches are applied to identify the origin of thermal fluids and to estimate the reservoir temperature at depth. Thermal groundwater with saturation indexes of minerals changing with temperature is in equilibrium in the reservoir. Ren et al. [9] estimated that the Madeng Spring in Yunnan province originated from meteoric water and recharged at 3800 m. Guler et al. [11] simulated water-rock interaction processes by PHREEQC inverse geochemical models and found the mineral phases participated in the hydrogeochmical evolution. Water-rock interaction processes take place in the thermal groundwater system, and fault zones provide highly conductive pathways for the hydrogeochmical evolution in reservoir [11–13]. Fractures play an important role in facilitating surrounding rock mineral dissolution and the sources of salinity in the thermal groundwater during the circulation and upwelling of deep thermal waters. The geochemical study of thermal groundwater, combined with geological and tectonic information, can explain the processes that occurred during the ascent of the fluid towards the surface and aid exploitation of thermal groundwater. Based on the geochemical data obtained from four hot springs along the Bijiang River, this study presents the distinctive hydrochemical characteristics, establishes the mineral equilibrium status, identifies the mixing behavior of geothermal fluids, and simulates the circulation of hot spring thermal groundwater.

2. Geological Setting

Four hot springs emerging near the Bijiang River in Yunlong County have been studied. Thermal groundwater circulation is accompanied by water-rock alteration, fluid mixing mechanisms during faulting activities, and water chemical reaction. The Dalang Hot Spring (altitude: 2,013 m), Dada Hot Spring (altitude: 2,040 m), Lianchangping Hot Spring (altitude: 2,046 m), and Hekou Hot Spring (altitude: 1,819 m) are located in Yunlong County of Yunnan province, one of the largest geothermal resources in China. In addition to the Hekou Spring, the other three hot springs are characterized by spectacular travertine landscapes. The thermal groundwater sampling points are along a N-S trending fracture zone between 26°00′N, 99°22′E and 26°11′N, 99°29′E which are shown in Figure 1. The study area is in the central of the Lanping basin which is on the boundary between the western Lancangjiang fracture and the eastern Jinshaijiang River-Ailao Mountain fracture that form a metamorphic belt composed of the Mesozoic red layers [14]. Meanwhile, this area is located about 135 km northeast of the Tengchong volcanic geothermal area near the large-scale tectonics of the continental collision of Asia and India-Eurasia [15]. The formation of the Yunlong geothermal field is attributed to the development of the fault system which is beneficial to the sedimentary process and the activity of geothermal fluids. About 50 km from the thermal spring area, there is a large gypsum deposit of gypsum ore that supports the Lanping-Jinding lead-zinc mine. Gypsum-bearing formations in the strata provided the source of minerals to the thermal water circulation along the fissures in the subsurface.

Bedrock units are mainly Jurassic and Cretaceous red beds in the area composed mainly of Cretaceous purple sandstone interbedded with purple and gray mudstone, Jurassic purple sandstone interbedded with mudstone and marls, and Triassic gray sandstone and brecciated limestone [16]. The faults in the Bijiang area (Figure 1) developed in the late Variscan and significantly controlled the nature, evolution, sedimentary facies, and magmatic metamorphic and hydrothermal activity of the Mesozoic-Cenozoic Lanping basin. The Mesozoic basin was deeply down dropped and accumulated very thick sedimentary sequence that is underlain by hot rocks. Subsequent deformation formed the Tertiary stretched basin. Despite the lack of magmatism and metamorphism in the basin from tectonism, there are small sporadic acidic intrusions of Himalayan alkaline porphyry and Quaternary volcanic rocks, as well as a discontinuous metamorphic belt. The concentrated zone of hot springs and seismic activities represent an abnormal area of modern hydrothermal activities [14, 16]. Thermal groundwater discharges along the fracture near the Bijiang River and other major fractures in the study area forming a strip zone at the surface before sedimentary mineralization (Figure 1). We hypothesize that there is a strong hydrothermal circulation and matter exchange in the subsurface from the thermal springs in the active hydrothermal area.

3. Material and Methods

Four typical hot spring samples are collected from the geothermal area along the Bijiang River. Major constituents are listed in Table 1, and the locations of sampling points are shown in Figure 1. Field work in Yunlong County, Yunnan province of China, was carried out on August 2013. The major elements K, Na, Li, Sr, Zn, and Mn were examined by flame atomic absorption. Ba, Al, Pb, Cd, and Ag were measured by atomic absorption using a plumbago furnace. Cl, SO₄, and NO₃ were determined by ion chromatography. NH₄, Fe, F, Br, I, H₂SiO₃, HBO₂, and HPO₃ were examined by a spectrophotometer. Ca, Mg, and total hardness were detected using the volumetric method (EDTA titration). HCO₃ and CO₃ were determined using the volumetric method (HCl titration). H₂S was analyzed using the volumetric method (sodium hyposulfite titration). Total acidity was determined by the volumetric method (NaOH titration). The chemical analyses (Table 1) were conducted at the laboratory of the Beijing Brigade of Hydrogeology and Engineering Geology based on methods for the examination of drinking natural mineral water (GB/T 8538-2008).

4. Results and Discussion

4.1. General Hydrogeochemical Characterization. The Hekou Spring is located on the west bank of the Bijiang River, and the other three hot springs are located on the east. The Bijiang area displays a range of spring temperatures between 43.8°C and 51.8°C, and pH values are from 6.89 to 7.9 (Table 1). The four hot spring waters were investigated in
Figure 1: Geological map of the Bijiang area and the location of sampling springs. (1) Upper Cretaceous, Nanxin group, purple sandstone clipping conglomerate, and mud; (2) lower Cretaceous, Jingxing group, and purple mudstone; (3) lower Cretaceous, Jingxing group, white sandstone clipping purple, and gray mudstone; (4) upper Jurassic, Bazhulu group, purple mudstone, and siltstone; (5) middle Jurassic, Huakaizuo group, gray-green and purple mudstone, and marls; (6) middle Jurassic, Huakaizuo group, and purple sandstone clipping mudstone; (7) upper Triassic, Maichujing group, gray sandstone, and black shale clipping coal; (8) upper Triassic, Sanhedong group, limestone, and brecciated limestone; (9) main E-verging normal fault or W-verging normal fault; (10) fault; (11) Bijiang River; (12) stratigraphic limit; (13) hot spring; (14) mountain peak with its elevation (m); (15) town and county; (16) latitude and longitude coordinates; (17) attitude of the strata.
Table 1: Physical and chemical properties of thermal springs from the Yunlong thermal area and of glacier water (mg/L).

| Samples          | Dalang | Dalang* | Dada* | Lianchangping | Lianchangping1 | Lianchangping2 | Lianchangping3* | Hekou | Hekou1* | Glacier water |
|------------------|--------|---------|-------|--------------|---------------|---------------|-----------------|-------|---------|---------------|
| pH               | 6.89   | 7.8     | 7.9   | 6.92         | 6.68          | 6.73          | 7.45            | 7.4   | 7.85    | 7.28          |
| T (°C)           | 43.8   | 43      | 48.5  | 51.8         | 51.7          | 46            | 53.2            | 51    | 54      | /             |
| TDS              | 31.10  | 2050    | 2070  | 42.32        | 4207          | 3569          | 3110            | 1844  | 1420    | 5.6           |
| Ca               | 162.9  | 4.52    | 3.72  | 721.4        | 720.4         | 570.1         | 385             | 83.6  | 68.2    | 1.96          |
| Mg               | 62     | 60      | 26.4  | 105.1        | 113           | 104.5         | 112             | 19.6  | 21      | 0.05          |
| Na               | 615    | 645     | 751   | 338          | 333           | 301           | 404             | 475   | 410     | 0.12          |
| K                | 106    | 63.5    | 77.1  | 40.1         | 48.3          | 35.7          | 46.7            | 12.7  | 15.2    | 0.07          |
| Al               | 0.051  | /       | /     | 0.069        | 0.052         | 0.115         | /               | 0.086 | /       | /             |
| NO₃              | 3.5    | /       | /     | 0.1          | 0.1           | 4.2           | /               | 0.1   | /       | 0.03          |
| Ba               | 0.113  | /       | /     | 0.077        | 0.114         | 0.083         | /               | 0.073 | /       | /             |
| Mn               | 0.416  | /       | /     | 0.137        | 0.162         | 0.052         | /               | 0.092 | /       | /             |
| Fe               | 0.366  | /       | /     | 0.538        | 0.276         | 0.404         | /               | 0.437 | /       | /             |
| Sr               | 1.86   | /       | /     | 6.44         | 7.09          | 8.01          | /               | 2.55  | /       | /             |
| SiO₂             | 36.4   | 40      | 42.8  | 27.6         | 28.1          | 24.7          | 36              | 42.9  | 50.8    | /             |
| Cl               | 438    | 454     | 402   | 350          | 345           | 339           | 320             | 380   | 360     | 0.05          |
| HCO₃             | 1526   | 1199    | 1294  | 1171.6       | 1149.6        | 743.2         | 539             | 476   | 390     | 6.45          |
| SO₄              | 159    | 75.1    | 86.1  | 1474         | 1466          | 1143          | 1510            | 352   | 294     | 0.09          |
| F                | 2.51   | 1.55    | 1.52  | 3.64         | 3.95          | 3.59          | 1.61            | 2.1   | 0.782   | /             |
| Li               | 2.31   | 2.19    | 2.94  | 1.45         | 1.52          | 1.42          | 1.88            | 0.226 | 0.31    | /             |
| HBO₂             | 15.8   | /       | /     | 18.8         | 20.5          | 17            | /               | 2.85  | /       | /             |
| CO₂              | 92.4   | /       | /     | 88           | 123           | 96.8          | /               | 13.2  | /       | /             |
| Water type       | HCO₃-Cl-Na | HCO₃-Cl-Na | HCO₃-Cl-Na | SO₄-HCO₃-CaNa | SO₄-HCO₃-CaNa | SO₄-HCO₃-CaNa | SO₄-Ca-Na | CHCO₃-SO₄-Na | CHCO₃-SO₄-Na | HCO₃-Ca |

*From the data recorded in the "Hot springs 'Records in Yunnan Province' Records" in 1999.
order to establish the chemical evolution of groundwater on the influence of local stratigraphic formation in the Bijiang area. The major physical and chemical parameters of the geo-
thermal waters are listed in Table 1.

The thermal groundwater has high total dissolved solids (TDS) ranging between 2,070 and 4,232 mg/L except the one hot spring that does not deposit travertine (the Hekou Spring) which has the lowest TDS (1,844 mg/L). The highest TDS levels are found in the hottest waters (the Lianchangping Spring). Based on the main ions (K, Na, Ca, Mg, Cl, SO4, and HCO3), the water types are HCO3-Ca-Na type (Dalang Spring), HCO3-Cl-Na type (Dada Spring), SO4-HCO3-Ca-Na type (Lianchangping Spring), and Cl-HCO3-SO4-Na type (Hekou Spring), respectively, as shown in Table 1.

The major ion components Ca, Mg, K+Na, Cl, SO4, and HCO3 in milligram equivalent percentage are 7.9%, 6.3%, 35.8%, 15.2%, 4.0%, and 30.8% in the Dalang Spring water; 0.2%, 3%, 46.8%, 16.5%, 2.6%, and 30.9% in the Dada Spring water; 27%, 8.2%, 14.8%, 8.3%, 25.7%, and 16% in the Lianchangping Spring; and 6.4%, 3.1%, 40.4%, 20.7%, 14.2%, and 15.1% in the Hekou Spring water. The milligram equivalent percentage of HCO3 and Ca in the Hekou Spring is significantly lower than those of the other three travertine-depositing hot springs. The percentage of chloride in milligram equivalent is consistently near 15% and is the dominant anion with concentrations between 350 mg/L (Lianchangping Spring) and 438 mg/L (Dalang Spring).

The water of the Dada Spring and Hekou Spring is brackish water (TDS, 1-3 g/L) which is an ephemeral spring and less chemically evolved, while the Dalang Spring and Lianchangping Spring are saline water (TDS, 3-10 g/L). Both springs are perennial springs and have longer residence time in the groundwater circulation. Considering the deep circulation in the major fault zone and the rock leaching and mixing processes, the geochemistry of the thermal groundwater is remarkably different [18]. The Na and HCO3 concentrations of the thermal groundwater have the highest mass concentrations among the analyzed ions. The high concentrations of HCO3 and Ca in the thermal groundwater are associated with the minerals of calcite and anhydrite. The major ions of Cl and Na in the thermal groundwater are related to the interaction with halite and sylvite and seem to be involved in the development of thermal groundwater circulation along the intense fracture networks at depth [19, 20]. The contents of the free CO3 in the four hot spring waters are 92.4 mg/L in the Dalang Spring, 90 mg/L in the Dada Spring, 88 mg/L in the Lianchangping Spring, and 13.2 mg/L in the Hekou Spring. These values are in disequilibrium with respect to the atmosphere (Log pCO3 = −3.5). The composition of the three travertine-depositing hot springs is obviously higher than that of nontravertine-depositing hot spring (Hekou Spring). The evolutionary conditions of the hot springs in the Bijiang area are different, involving circulation paths, circulation depth, rock matrix, physical conditions, and the associated chemical reactions. Despite the wide range of TDS, the lowest value of 1,844 mg/L still suggests that the thermal groundwater discharging at the surface is mixed with cold groundwater and intensive water-rock interactions occur as it rises from a region of high pressure at depth to the atmospheric pressure at the surface.

4.2. Statistical Analysis of Chemical Parameters. The statistical analysis method of hierarchical clustering, which is considered to be an unsupervised clustering method, was used to classify 13 chemical parameters of the four hot springs in order to group similar characteristics into clusters and to evaluate the relationships between variables and differences among the data sets [21, 22]. The hierarchical clustering method uses an algorithm that groups the most similar parameters into clusters by minimizing the squared Euclidean distance between water samples until all chemical parameters are combined [23].

The 13 chemical parameters of the four thermal groundwater split into three distinct parameter groups (Figure 2). By the statistical analysis, the three chemical parameter clusters can be expressed as group 1: {[TDS, Mg], {Ca, SO4}, F, T} consisting of five chemical parameters, group 2: {pH, SiO2} consisting of two chemical parameters, and group 3: {[K, HCO3], Li, [Na, Cl]} consisting of five chemical parameters. The three groups of water chemical parameters in the rescaled distance and ion concentration diagram indicate that waters with high concentrations of Ca, SO4, HCO3, Na, and Cl have a closer relationship (Figure 2). It is shown that thermal waters with high Ca, SO4, and HCO3 are correlated and Na and Cl show certain constraints.

The chemical parameter correlation matrix (Table 2) shows there is a highly significant positive correlation between K and HCO3, with a correlation coefficient of 0.94, and Ca and SO4, with a correlation coefficient of 0.88, while pH and SiO2 are independent of other major chemical parameters. Although the thermal groundwater has a wide range of concentrations of Na (338-751 mg/L) and SO4 (86.1-1,474 mg/L), the correlation coefficient between Na and SO4 is approximately 0.92 and has the strongest relationship between the anions and cations (Table 2). From the cluster dendrogram of the statistical analysis, it is of critical importance to determine the hydrochemical parameters which control the chemical classification of the hot spring waters.

4.3. Multimineral Geotemperature. The calculated results by chemical geothermometers are listed in Table 3. The reservoir temperature of a SiO2 geothermometer is lower than that of the cation geothermometer ranging from 22°C to 103°C. The cation geothermometers are more sensitive to the concentrations of cations, and the results by Na-K and Na-Li geothermometers are slightly higher than others. However, the formula calculation method of chemical compositions can determine the reservoir temperature intervals and the precise reservoir temperature is difficult to evaluate by chemical geothermometers owing to the hysteresis effect and ion mixing with shallow water.

The calculated mineral saturation index (SI) of the original thermal groundwater indicates that the initial conditions of some minerals are in dissolution and precipitation reactions. The calculated SI for 26 kinds of minerals and free
carbon dioxide is given in Table 4. Since the solubility of all minerals varies as temperature increases, the temperature under deep reservoir conditions may indicate the equilibrium condition as many oversaturated minerals are present in the thermal groundwater in the subsurface and stay in equilibrium. The assumption that thermal groundwater has reached the equilibrium with respect to the mineralogy of the matrix rock assuming multimineral solubility is applied to evaluate and estimate the thermal groundwater reservoir temperature by WATCH using the status of 26 kinds of mineral solubility and 65 kinds of chemical reactions related to 73 species of soluble constituents and 7 species of gas [33, 34]. The state of mineral equilibrium in a geothermal reservoir environment provides a method to determine the thermal reservoir temperature of water-rock equilibrium which considers a variety of mineral assemblages of multiminerals and avoids the errors of considering single material factors.

![Rescaled distance cluster combine](image)

**Figure 2:** The dendrogram showing three clusters of ingredient concentrations of four hot springs.

**Table 2:** Hydrochemical ingredient content proximity matrix of 4 hot spring waters calculated by SPSS.

| Correlation | pH   | T    | TDS  | Ca   | Mg   | Na   | K    | Li    | HCO₃⁻ | Cl   | F    | SO₄²⁻ | SiO₂ |
|-------------|------|------|------|------|------|------|------|-------|-------|------|------|-------|------|
| pH          | 1.00 |      |      |      |      |      |      |       |       |      |      |       |      |
| T           | 0.18 | 1.00 |      |      |      |      |      |       |       |      |      |       |      |
| TDS         | −0.77| 0.07 | 1.00 |      |      |      |      |       |       |      |      |       |      |
| Ca          | 0.26 | −0.58| 0.09 | 1.00 |      |      |      |       |       |      |      |       |      |
| Mg          | 0.65 | −0.62| −0.61| 0.72 | 1.00 |      |      |       |       |      |      |       |      |
| Na          | −0.10| −0.90| 0.14 | 0.86 | 0.65 | 1.00 |      |       |       |      |      |       |      |
| K           | −0.76| 0.11 | 1.00 | 0.06 | −0.63| 0.10 | 1.00 |       |       |      |      |       |      |
| Li          | −0.66| 0.44 | 0.92 | −0.20| −0.82| −0.24| 0.94 | 1.00  |       |      |      |       |      |
| HCO₃⁻       | −0.84| 0.29 | 0.93 | −0.28| −0.86| −0.18| 0.94 | 0.96  | 1.00  |      |      |       |      |
| Cl          | 0.04 | −0.96| −0.34| 0.52 | 0.75 | 0.81 | −0.38| −0.67 | −0.53 | −0.53| 1.00 |       |      |
| F           | −0.53| 0.63 | 0.81 | −0.33| −0.87| −0.44| 0.83 | 0.97  | 0.91  | −0.82| 1.00 |       |      |
| SO₄²⁻       | −0.23| −0.68| 0.46 | 0.88 | 0.41 | 0.92 | 0.44 | 0.12  | 0.12  | 0.52 | 0.52 | −0.07 | 1.00 |
| SiO₂        | 0.77 | −0.18| −0.99| 0.02 | 0.70 | −0.02| −1.00| −0.96 | −0.96 | 0.44 | −0.87| −0.36 | 1.00 |
Multimineral equilibrium geothermometers of four hot springs were performed in this study with the aid of the WATCH program with the assumption of conductive cooling and temperature change [8, 10, 34]. The saturation indexes of 23 kinds of minerals are calculated at the specified temperatures ranging between 20°C and 180°C to determine the temperature interval that the chemical ingredients are at equilibrium in the subsurface thermal fluid. The saturation index is calculated with a different temperature for each hot spring along the Bijiang River and interpreted. Figure 3 shows the results of minerals in the aqueous speciation for the four hot springs.

The Dalang Spring water minerals of adularia, Mg-chlorite, Ca-montmorillonite, Na-montmorillonite, albite, K-montmorillonite, analcime, Mg-montmorillonite, and quartz are close to reaching the equilibrium at the line of log (Q/K) = 0 (SI = 0) within the temperature range of 80°C-100°C (Figure 3(a)). The group of minerals is in balance with the subsurface thermal fluid, and the corresponding temperature 80-100°C is the deep geothermal reservoir temperature. Most minerals of the Dada Hot Spring reached the equilibrium state in the temperature interval of 65°C to 90°C, and the calculated circulation depth of the thermal groundwater is 2.1-3 km according to the average geothermal temperature gradient of 3°C/100 m. However, the interval of the Lianchangping Hot Spring reservoir temperature diverges in the range from 45°C to 120°C, probably due to the partial equilibration of the mixture of shallow water and deep groundwater during the upward migration to the surface. The geothermal reservoir fluids are reconstructed from data on hot springs, geothermometry, and fluid mineral equilibrium under reservoir conditions.

Figure 3(a) lists 23 kinds of minerals reacted in the thermal waters. The saturation indexes of anhydrite, aragonite, calcite, chalcedony, quartz, and fluorite converge in a temperature interval. The evaluated reservoir temperature is based on the assumption that the minerals from host rock reached equilibrium in thermal waters. The variations of the selected mineral saturation indexes with temperature are calculated by the WATCH program. The Dada Hot Spring multimineral geothermometry is 83°C, indicated by minerals of calcite, aragonite, quartz, and chalcedony (Figure 3(b)). The activity of aqueous ions and the solubility of minerals composed of the ions at the in situ temperatures must be determined to evaluate the chemical equilibrium between minerals and solutions in a thermal groundwater system. The status of minerals precipitating at the surface in thermal groundwater can qualitatively indicate the substances involved in reactions in deep circulation and indicate the reaction mechanisms in the subsurface. This can provide additional insight into the types of reactants necessary for the evolution of the travertine springs [20]. The minerals show that under the temperature at the spring orifices, the thermal groundwater is generally unsaturated with respect to gypsum (CaSO₄·2H₂O) and halite (NaCl). Both minerals actively participate in reactions during the groundwater circulation and indicate the mineralogy of the matrix rocks in the reservoir environment. The minerals of calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and kaolinite (Al₂Si₂O₅(OH)₄) are oversaturated at the spring orifices. These minerals are the main components of travertine and readily precipitate from the groundwater at high concentrations [35]. The mineral phases assumed to control the composition of geothermal waters provide a more comprehensive view on the mineral equilibrium assemblage and the chemical characteristics.

4.4. Estimation of Mixing Ratio and Subsurface Water Temperature. In the Na-K-Mg diagram (Figure 4), three travertine thermal groundwater is plotted in the immature water field, and the other is close to the partially equilibrated water field. Four hot spring waters are far from the full equilibrium line in the Giggenbach triangular plot [28], indicating that conductive cooling or mixing with other lower temperature groundwater is the main process responsible for the temperature decrease of the thermal groundwater discharging to the surface [7].
Table 4: Calculated saturation index (SI) for thermal spring water samples and thermodynamic calculations are based on PHREEQC computer code.

| Minerals/gas       | Chemical formula       | Dalang | Dalang1 | Dada | Lianchangping | Lianchangping1 | Lianchangping2 | Lianchangping3 | Hekou | Hekou1 |
|-------------------|------------------------|--------|---------|------|---------------|----------------|----------------|----------------|--------|--------|
| Albite            | NaAlSi3O8              | −0.6002 | /       |       | −1.5444       | −1.6896         | −1.2562        | /              | −0.636 | /      |
| Alunite           | KAl(SO4)2(OH)6         | −1.9434 | /       | /    | −1.79         | −0.7772         | 0.549          | /              | −5.3667 | /      |
| Anhydrite         | CaSO4                  | −1.5765 | −3.807  | −3.3453 | −0.12         | −0.1256         | −0.3192        | −0.2847        | −1.2868 | −1.389 |
| Anorthite         | CaAl2Si3O8             | −1.9301 | /       |       | −1.5808       | −1.8982         | −1.264         | /              | −1.6953 | /      |
| Aragonite         | CaCO3                  | 0.6491  | −0.0864 | 0.004 | 1.1539        | 0.9098          | 0.6538         | 1.1152         | 0.5148  | 0.8313 |
| Barite            | BaSO4                  | −0.0806 | /       | /    | 0.3009        | 0.4683          | 0.3679         | /              | 0.1149  | /      |
| Calcite           | CaCO3                  | 0.7802  | 0.0452  | 0.1321 | 1.2799        | 1.0359          | 0.7855         | 1.2404         | 0.6413  | 0.9561 |
| Ca-montmorillonite| Ca0.165Al2.33Si3.67O10(OH)2 | 2.4363 | /       | /    | 1.3406        | 1.4687          | 2.6201         | /              | 1.3395  | /      |
| Celestite         | SrSO4                  | −1.641  | /       | /    | −0.3534       | −0.3161         | −0.2953        | /              | −0.9558 | /      |
| Chalcedony        | SiO2                   | 0.0208  | 0.0611  | 0.031 | −0.1771       | −0.1677         | −0.1687        | −0.081         | 0.014   | 0.0494 |
| Chlorite (14A)    | Mg3Al2Si4O10(OH)8      | −1.7169 | /       | /    | −0.302        | −2.3746         | −2.1303        | /              | 1.5879  | /      |
| Chrysothile       | Mg5Si8O16(OH)4         | −4.3538 | 1.1533  | 1.2607 | −3.4818       | −4.81           | −5.1287        | 0.1094         | −1.9145 | 1.3709 |
| CO2(g)            | CO2                    | −0.6563 | −1.6708 | −1.7003 | −0.7841       | −0.5503         | −0.8209        | −1.6313        | −1.6064 | −2.1304 |
| Dolomite          | CaMg(CO3)2             | 1.6409  | 1.7269  | 1.6539 | 2.1611        | 1.7054          | 2.1735         | 2.3581         | 1.1232  | 1.8796 |
| Fluorite          | CaF2                   | −0.4171 | −2.3514 | −2.4909 | 0.3257        | 0.3918          | 0.3128         | −0.6414        | −0.7998 | −1.7511 |
| Gibbsite          | Al(OH)3                | 0.9894  | /       | /    | 0.7691        | 0.8431          | 1.3498         | /              | 0.4564  | /      |
| Goethite          | FeOOH                  | 7.4777  | /       | /    | 7.6917        | 7.1274          | 7.3194         | /              | 7.7689  | /      |
| Gypsum            | CaSO4.2H2O             | −1.4702 | −3.2661 | −3.2858 | −0.0932       | −0.0979         | −0.2347        | −0.2713        | −1.2516 | −1.383 |
| Halite            | NaCl                   | −5.2429 | −5.1908 | −5.1855 | −5.6249       | −5.6554         | −5.6862        | −5.592         | −5.3973 | −5.4795 |
| Illite            | K0.6Mg0.35Al2Si3O10(OH)2 | 2.2045 | /       | /    | 0.8589        | 0.8547          | 1.947          | /              | 0.9192  | /      |
| Kaolinite         | Al2Si3O10(OH)4         | 3.6662  | /       | /    | 2.8151        | 2.9823          | 4.0037         | /              | 2.5731  | /      |
| K-feldspar        | KAlSi3O8               | 0.7592  | /       | /    | −0.4413       | −0.4982         | −0.0905        | /              | −0.1638 | /      |
| K-mica            | KAl3SiO10(OH)2         | 8.4601  | /       | /    | 6.8962        | 6.9598          | 8.3446         | /              | 6.5158  | /      |
| Quartz            | SiO2                   | 0.3947  | 0.4373  | 0.3922 | 0.1753        | 0.185           | 0.1992         | 0.2677         | 0.3685  | 0.3961 |
| Strontianite      | SrCO3                  | −0.828  | /       | /    | −0.4646       | −0.6661         | −0.728         | /              | −0.5423 | /      |
| Talc              | Mg5Si8O16(OH)8         | −0.3834 | 5.1953  | 5.3031 | 0.1793        | −1.131          | −1.513         | 3.9771         | 2.1202  | 5.5076 |
| Witherite         | BaCO3                  | −2.9842 | /       | /    | −3.4208       | −3.4933         | −3.7508        | /              | −3.092  | /      |
Figure 3: Log(Q/K) versus T (multicomponent geotemperature) plot for the four thermal springs calculated by the PHREEQC program (a) and WATCH program (b). The measured outcropping temperature is shown in Table 1.
The subsurface temperature of thermal groundwater, controlled by silica content (the solubility of quartz) and enthalpy, is widely used to estimate the maximum temperature of hot water in subsurface reservoir environments. The silicon-enthalpy graphic method makes it possible to calculate the ratio of thermal and cold water and the reservoir temperature in the subsurface before mixing with cold water [6]. This method is based on the assumption that quartz and other crystalline phases of silica stop precipitating as a solution cools below a fixed reservoir temperature during its ascent from the thermal reservoir underground to a cooler environment near the surface since most hot spring waters are greatly supersaturated with silica [5]. It is also necessary to correct the amount of steam separated from the hot spring thermal groundwater as it rises from the subsurface under high pressure to the surface environment with atmospheric pressure. With the maximum steam loss, 32% percent of the initial water would be converted into steam upon adiabatic cooling at constant enthalpy when the reservoir temperature of thermal groundwater is greater than 100°C [5, 36]. Butterfly Spring was selected and analyzed as an example of nonthermal groundwater for the local region. Butterfly Spring has chemistry close to local atmospheric precipitation, with a temperature of 15.4°C and the corresponding SiO_2 content of 5.54 mg/L that is very close to Gupta and Roy’s research area selected cold water data (10°C and 5 mg/L) [37].

Figure 5 is explained as follows: points A to B—the temperature and silica contents of the selected cold and hot spring thermal groundwater; point C—the enthalpy and silica content of the deep reservoir thermal groundwater without the maximum steam loss; point E—the temperature of 100°C and where steam loss before mixing begins; point F—the enthalpy of the thermal groundwater component before the onset of boiling; and point G—the original silica content of the thermal groundwater before steam loss occurred. The weight fraction of the original thermal groundwater steam loss (X) before mixing can be estimated by the following formula: \(X = 1 - \text{silica content at point G/silica content at point F}\) [6]. The results of the four hot springs are listed in Table 5.

The Lianchangping Hot Spring, with the highest discharge temperature (51.8°C) of the four hot springs, has the lowest weight fraction of the original steam loss of 12.1%. The Dalang Spring thermal groundwater reservoir temperature in the subsurface is 176.9°C without considering steam loss and 132°C considering the maximum steam loss, while the value varies between 132°C and 176.9°C if there is less steam loss (Table 5). Meanwhile, the weight fraction of the original thermal groundwater losing maximum steam accounts for 27.5%.

4.5. Inverse Modeling of the Hot Springs in the Study Area. The reaction path modeling was carried out to simulate the evolution of thermal spring waters from precipitation to discharge in well-developed, hydraulically connected fractures along the Bijiang River in the study area. In this study, the property of local glacier water is precipitation due to the similar hydrochemical characteristics and the local recharge occurs at high altitude. The differences in composition among four hot springs are assumed to be due to the reactions between the original recharge water and terminal groundwater of discharging thermal spring waters. Thus, it is necessary to understand quantitatively the mineral phases involved in chemical reactions during the surface and subsurface circulation process. The phase
of the selected reactants is critical to establish an inverse model of chemical reaction, based on the geological conditions, hydrochemical characteristics of waters, and assumed migration for spatial evolution.

18 chemical indicators, Ca, Mg, Na, K, Al, Sr, SiO$_2$, Cl, HCO$_3$, SO$_4$, F, Ba, NO$_3$, Fe, Mn, Br, Zn, and Li, and two physical parameters, pH and temperature, are determined as constraint variables of reaction simulations in mass balance.

Generally, the simulation of mass balance is expressed as the balance of reacted chemical elements. 11 kinds of minerals participated in precipitation and dissolution reaction equilibrium. Therefore, it is defined that the dissolution or precipitation of mineral $j$ is $X_j$ mol, mineral 1 is $X_1$ mol, mineral 2 is $X_2$ mol, ..., mineral 11 is $X_{11}$ mol, per liter water when thermal groundwater flows from spring A to spring B (SpringA-SpringB) along the flow path. Finally, the chemical...
compositions of spring A water changes to spring B water, and the increment of element $i$ in spring B water is $\Delta \text{MOL}_{T,i}$ compared with spring A water. Consequently, the expression of formula is as follows [38]:

$$\sum_{j=1}^{11} a_{i,j} X_j = \Delta \text{MOL}_{T,i}^{\text{SpringB}} - \Delta \text{MOL}_{T,i}^{\text{SpringA}} = \Delta \text{MOL}_{T,i},$$

$$i = 1, 2, 3, \ldots, 18, j = 1, 2, 3, \ldots, 11,$$

where $a_{i,j}$ stands for the stoichiometric number of element $i$ in mineral $j$ which numerically means that 1 mol mineral $j$ is completely dissolved, producing molar amount; $\Delta \text{MOL}_{T,i}^{\text{SpringA}}$ and $\Delta \text{MOL}_{T,i}^{\text{SpringB}}$ are the total molar concentration of element $i$ in spring A and spring B, respectively; and $\Delta \text{MOL}_{T,i}$ represents the change of the amount molar concentration of element $i$ in thermal water solution caused by the mineral dissolution, precipitation, and gas migration. Positive values indicate dissolution, and negative values indicate precipitation along the flow path.

The simulation of result, from recharge by precipitation to thermal spring water, is successfully performed by inverse modeling with the aid of the PHREEQC program [35, 39]. The evolution of travertine deposition from hydrogeochemistry of the hot spring waters is achieved, and the deposition progress is analyzed quantitatively [20]. The analytical data for the inverse modeling calculation of the chemical evolution of the hot water composition from the Dalang Spring, Dada Spring, Lianchangping Spring, and Hekou Spring and four flow paths are established. After the evolution of subsurface circulation, abundant mineral deposition from the Dalang Spring, Dada Spring, and Lianchangping Spring occurs when thermal groundwater is exposed to the surface forming a large area of fossil and new travertine deposits. However, the Hekou Spring is a nontravertine-depositing spring with a higher temperature of 54°C. The Hekou Spring is located on the west bank of the Bijiang River, but the other springs are situated on the east bank of the river distributed along a major fracture of the Bijiang Fault. As a result, several minerals and gases reacted in appropriate amounts for the hydrochemical evolution between recharge water and thermal groundwater. As mentioned above, 18 chemical parameters and 10 kinds of minerals (halite, gypsum, kaolinite, Ca-montmorillonite, calcite, dolomite, chalcedony, biotite, plagioclase, and fluorite) and $\text{CO}_2(g)$ gas are selected as the reactive phases in the simulation calculation and their mole transfers are given in Figure 6 and Table 6.

Six reasonable results are obtained from the flow paths of the four thermal springs which are shown in Figure 6,
and thermal water originates from precipitation. The results in case 1 of the Dalang Spring, case 5 of the Dada Spring, and case 1 of the Lianchangping Spring are invalid and ruled out from further consideration due to mass balance consideration. For the results presented in this study, the uncertainty limit of calcium is set in the range from 0.025 to 0.05 mmol/L. Overall, halite (NaCl), gypsum (CaSO$_4$·2H$_2$O), calcite (CaCO$_3$), dolomite (CaMg(CO$_3$)$_2$), chalcedony (SiO$_2$), biotite (K(Mg$_3$Al$_3$Si$_3$O$_{10}$(OH)$_2$)), calcite, dolomite, and CO$_2$(g) are strongly controlled by reservoir conditions, mixing behavior, and CO$_2$ storage. Simultaneously, this can explain the phenomenon and the reason that minerals in some thermal groundwater precipitate during the ascent from a hot region underground in a high pressure to a cooler environment near the surface at atmospheric pressure. In contrast, the geothermal area of central Greece degassing of CO$_2$ causes the participation of deep CO$_2$. In Greece, the carbon source comes from mixing magmatic and metamorphic decarbonation of limestone [40]. The compositions Na and Cl are dissolved from the halite, and SO$_4$ partly comes from the gypsum. Compared with the cationic contents in different geographic locations in the Aegean Volcanic arc (Greece), precipitation of sulfate minerals and reduction to sulfide cause changes in cationic composition which are attributable to consequent water-rock interaction mainly consisting in dissolution and precipitation of minerals [41]. Several kinds of minerals dissolve from the host rock and result in a large difference in hydrochemical characteristics among thermal groundwater. Gypsum (CaSO$_4$·2H$_2$O), Ca-montmorillonite (Ca$_{0.17}$Al$_{2.33}$Si$_{3.67}$O$_{10}$(OH)$_2$), biotite (K(Mg$_3$Al$_3$Si$_3$O$_{10}$(OH)$_2$)), calcite, dolomite (CaMg(CO$_3$)$_2$), chalcedony (SiO$_2$), and biotite (K(Mg$_3$Al$_3$Si$_3$O$_{10}$(OH)$_2$)) dissolve along the thermal groundwater flow path, and the thermal groundwater of the Lianchangping Spring circulates with

|          | Precipitation—Dalang | Precipitation—Dada |
|----------|----------------------|---------------------|
| Halite   | 12.70                | 11.19               |
| Gypsum   | 1.66                 | 0.90                |
| Kaolinite| 68.07                | 69.70               |
| Ca-montmorillonite | -72.45               | 0.00                |
| CO$_2$(g) | 29.51                | 21.95               |
| Calcite  | 11.54                | 41.47               |
| Dolomite | -5.64                | -4.84               |
| Chaledony| 65.20                | -31.88              |
| Biotite  | 2.72                 | 1.98                |
| Plagioclase | 21.71                | 29.46               |
| Fluorite | 0.07                 | 0.04                |

|          | Precipitation—Lianchangping | Precipitation—Hekou |
|----------|-------------------------------|---------------------|
| Halite   | 8.83                          | 11.01               |
| Gypsum   | 15.38                         | 11.01               |
| Kaolinite| 486.00                        | 44.99               |
| Ca-montmorillonite | -417.00             | -10.88              |
| CO$_2$(g) | -68.40                         | 7.25                |
| Calcite  | 68.20                         | -5.67               |
| Dolomite | 1.14                          | -6.52               |
| Chaledony| 558.00                        | 5.67                |
| Biotite  | 1.20                          | 8.41                |
| Plagioclase | 14.91                          | -7.14               |
| Fluorite | 0.04                          | 0.06                |
more favorable conditions to deposit minerals at the surface. Halite plays a key role in the hydrogeochemical evolution along the flow path while the content of Na is increased to 475 mg/L and the content of Cl is increased to 380 mg/L in the Hekou Spring. The contents of Ca and HCO₃ are increased to 721.4 mg/L and 1,171.6 mg/L in the Lianchangping Spring which suggest that there are 719.4 mg/L calcium and 1,165.2 mg/L bicarbonate dissolving from minerals of the host rock in long circulation paths.

5. Summary

By hydrochemistry analysis, we can find some differences between travertine and nontravertine springs. The Hekou Hot Spring displays a wide compositional variability compared to the other three hot springs as a result of circulation evolution and mixing processes. The nontravertine spring is enriched in silica, and the cold water mixing ratio is 68%-77% with a maximum steam loss of 26.6% which is about 10% higher than travertine springs. It has higher concentration of Cl, indicating a longer distance of circulation along the migration pathway. Strong negative correlation \((r = -0.99)\) between TDS and SiO₂ demonstrates the reservoir environment has an influence on the constituent of SiO₂. The Hekou Spring reservoir environment, indicated by geotemperatures from multicomponent geothermometry, is the highest at 160°C with the highest amount of SiO₂ at 42.9 mg/L.

The study results suggest that the water-rock reaction and reservoir environment are responsible for the main hydrochemical variability. The reservoir temperature range of the Dalang Spring is 80°C-100°C calculated by PHREEQC. The temperatures are more than 50°C and 83°C analyzed by minerals of chalcedony and quartz by WATCH. From the analyzed minerals, the equilibration of minerals assemblage constitutes a temperature indicator and helps us gauge the storage temperature of hydrothermal fluid. The stable mineral assemblage phases of the four hot springs are determined, and the temperature ranges are all greater than the discharge temperature of the thermal groundwater. The equilibration processes of the thermal waters are described by the Na-K-Mg geothermometer, and thermal groundwater samples are in the immature zone. The estimated minimum reservoir temperature achieved by considering the maximum steam loss provides reservoir temperatures around 105-132°C, and the estimated maximum temperature, ignoring the maximum steam loss, gives the reservoir temperatures around 112.3-177°C; moreover, the actual subsurface reservoir temperature, which may contain some steam loss, is within these temperature intervals.

The PHREEQC inverse modeling program is applied to quantify the mineral reaction processes. The simulated paths from precipitation are established from the analysis of mineral saturation, from the original precipitation recharge to thermal spring discharge, while the results indicate the hydrochemical characteristics in their evolution during circulation. The variation of elements dissolved or precipitated along the flow path results in different water types at the spring discharge. A fractional uncertainty limit of 0.025 (2.5%) is assumed for all of the analytical data. Modeling the results shows that gypsum, kaolinite, Ca-montmorillonite, calcite, dolomite, plagioclase, SiO₂, and CO₂(g) play an important part in keeping the geothermal waters in equilibrium during the subsurface circulation process. The major hydrochemical constituents appear to be the results of water-rock reactions of halite, gypsum, biotite, plagioclase, and fluorite which is consistent in the valid models simulated.

Data Availability

The hydrochemical (Dalang, Lianchangping, Lianchangping1, Lianchangping2, and Hekou) data used to support the findings of this study are included within the article. The data supporting the findings of this study are available in Table 1 and the original within the article. The hydrochemical (Dalang1, Dada, Lianchangping3, and Hekou1) data in Table 1 that support the findings of this study are derived from public domain resources. The data are cited as * and available in the “Hot springs ’Records in Yunnan Province’ Records” in 1999. The hydrochemical data (Glacier water) used to support the findings of this study in Table 1 have been published in the Scientia geographic sinica, vol. 31, no. 6, pp. 735-740, titled “Hydrochemical Characteristics of Three Rivers around Yulong Mountain in Rainy Season.” In our study, the reference number is assigned as [17].

Additional Points

Highlights. Travertine spring has SO₄-HCO₃-Ca-Na water type, and nontravertine spring is Cl-HCO₃-SO₄-Na type. A multimineral equilibrium method gives a reservoir temperature interval of 50-160°C. High cold water mixing ratio and steam loss change hydrogeochemical characteristics and affect travertine deposition. Simulation of flow paths of four springs suggests that the thermal water circulation evolved from precipitation.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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