Research papers

Hydrogeochemistry and geothermometry of deep thermal water in the carbonate formation in the main urban area of Chongqing, China

Pingheng Yang a,b,*, Qun Cheng c, Shiyou Xie a,b, Jianli Wang a,b, Longran Chang d,*, Qin Yu a,b, Zhaojun Zhan a,b, Feng Chen a,b

a School of Geographical Sciences, Southwest University, Chongqing Key Laboratory of Karst Environment, Key Laboratory of Eco-environments in Three Gorges Reservoir, Ministry of Education of the People’s Republic of China, Chongqing 400715, China
b Field Scientific Observation and Research Base of Karst Eco-environments at Nanchuan in Chongqing, Ministry of Land and Resources of China, Chongqing 408435, China
c College of Resources and Environment, Southwest University, Chongqing 400715, China

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A B S T R A C T

Many geothermal reservoirs in Chongqing in southwestern China are located in carbonate rock aquifers and exploited through drilling. Water samples from 36 geothermal wells have been collected in the main urban area of Chongqing. Chemical types of the thermal water samples are Ca-Mg-SO4 and Ca-SO4. High contents of Ca2+ and SO4 2− in the thermal water samples are derived from the dissolution of evaporates. Furthermore, the HCO3− concentration is constrained by the common ion effect. Drilling depth has no effect on the physical and chemical characteristics according to the results of a t-test. The geothermal reservoir’s temperature can be estimated to be 64.8–93.4 °C (average 82 °C) using quartz and improved SiO2 geothermometers. Values of δD and δ18O for the thermal water samples indicate that the thermal water resources originate from local precipitation with a recharge elevation between 838 and 1130 m and an annual air temperature between 10.4 and 13.9 °C. A conceptual model of regional scale groundwater flow for the thermal water is proposed. The thermal water mainly originates from the meteoric water recharged in the elevated areas of northeastern Tongluoshan and Huayingshan by means of percolation through exposed carbonate before becoming groundwater. The groundwater is heated at depth and moves southwest along the fault and the anticlinal core in a gravity-driven regime. The thermal water is exposed in the form of artesian hot springs in river cutting and low-elevation areas or in wells.

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1. Introduction

Geothermal energy is a type of clean energy that consists of heat, minerals, and water. It is characterized by its wide distribution, low levels of pollutants, direct utility, renewability, and significant environmental and economic effects. The global development of geothermal energy has become especially rapid since the 1970s (Lund et al., 2011). In response to the serious issues of population expansion, energy shortages, and environmental pollution, the exploration and exploitation of geothermal energy have attracted an increasing amount of attentions.

There are numerous geothermal reservoirs in China with vast potential for exploitation and utilization. The potential geothermal resources in the major sedimentary basins in China are approximately 2.5 × 1022 J, and the amount of exploitable geothermal energy is approximately 7.5 × 1021 J (Kong et al., 2014; Wang et al., 2015). The annual exploitable hydrothermal resources are estimated to be 1.8 × 1019 J, which is equivalent to a reduction of 1.4 × 108 t CO2 emission (Kong et al., 2014; Wang et al., 2015); of this quantity, the hot spring releases a total of 6.6 × 1017 J annually, which is equivalent to 2.26 × 107 t of standard coal or a reduction of 5.93 × 106 t CO2 emissions (Wang et al., 2015). Until 2014, China had found approximately 4000 hot water points (including hot springs, drilling, and mine water resources) with water temperatures above 25 °C (Zhao and Wan, 2014).

Chongqing municipality was named “the hot springs capital of China” in April 2011, due to its plentiful thermal water resources (Cheng et al., 2015). The area containing thermal water is approximately 1 × 104 km² (Cheng et al., 2015). The thermal water is
thought to form by means of non-volcanic heating and can emit 
\[3.32 \times 10^{11} \text{ kcal/yr} \quad (1.9 \times 10^{12} \text{ KJ/yr}),\]
which is equivalent to 
\[4.75 \times 10^{6} \text{ t/yr} \quad \text{of standard coal (Wang et al., 2015).}\]
The exploitation of the thermal water resources in Chongqing has focused on 
carbonate strata in the main urban area. The Bei hot spring has been used since the Song dynasty, and the Nan hot spring was 
exploited in the Ming dynasty. The Dong hot spring, later called the 
Xi hot spring, has become increasingly famous. Now, there are 
107 areas with thermal water resources in Chongqing, including 
65 geothermal wells, 26 hot springs, and 16 geothermal mining 
waters (Li and Liu, 2011). In 2012, the Chongqing Municipal 
Government planned to develop 10 groups of springs in five locations 
in the main urban area and 100 hot springs and thermal wells 
within a one-hour drive from the city center. However, from 
the mid-1980s to the early 1990s, the discharge and temperature of 
the water in the hot springs decreased rapidly due to overexploitation.
Some of the springs even dried up. Despite this interest, little 
have been published on the thermal water resources in Chongqing,
China, except the work of Li and Liu (2011), Xiao et al. (2015), and 
Cheng et al. (2015) in Chinese. However, these studies focus only 
on individual cases (Xiao et al., 2015) and on the general chemical 
characteristics and quantity of thermal water resources on a regio-
nal scale (Li and Liu, 2011; Cheng et al., 2015; Xiao et al., 2015).

The widely applicable fundamental tools for studying thermal 
water include regional scale hydraulics, water chemistry, \(^{2}H\) and 
\(^{18}O\) isotopic composition, and geothermometry. Studies on regio-
nal scale groundwater hydraulics can be traced back to Tóth 
(1962, 1963), and the subject has been further developed by a ser-
ies of researchers (e.g., Zijl, 1999; Jiang et al., 2011). The relation-
ship between groundwater temperature distribution and a single 
flow system in a unit basin was first studied by Domenico and 
body can be considered to be hydraulically continuous on a given 
time scale. The concept of hydraulic continuity can help us to inter-
pret carbonate reservoirs as a whole without separate warm and 
cold fluids and confined and unconfined parts. Evaluating the 
regional scale groundwater hydraulics and hydraulic continuity 
could be useful in geothermal exploration (Mádl-Szönyi and 
Tóth, 2015; Mádl-Szönyi and Simon, 2016). Typically, different 
flow systems differ greatly in hydrochemistry and isotopes (Tóth, 
2009). Therefore, the interaction and mixing of thermal water 
and surface water can be determined using the concentrations of 
major ions and the values of \(^{3}H\) and \(^{18}O\) to trace the origin of the 
thermal water (e.g., Lee et al., 2011; Wang et al., 2013; Pérez-Zárate et al., 2015; Chatterjee et al., 2016). The geother-
metros currently used to efficiently estimate reservoir tempera-
tures include cation geothermometers, e.g., K-Mg (Giggenbach, 
1988), Na-K (Can, 2002), Na-K-Ca (Fournier and Truesdell, 1973), 
and Na-Li thermometers (Fouillac and Michard, 1981); silica 
(quartz and chalcedony) geothermometers (Fournier, 1977); iso-
tope geothermometers (Millot and Négrel, 2007); and gas geothe-
ermometers (D'Amore et al., 1993).

In this study, we focus on characterizing the geochemistry of 
thermal water in 36 wells in the carbonate rock aquifer in the main 
urban area of Chongqing, identifying the sources of the major ions 
to estimate the reservoir temperature based on different geother-
mometric methods, and setting up a conceptual regional model 
for the circulation of thermal water. In addition, deep carbonate 
rock aquifers, most of which are to some degree karstified, are 
probably the most important thermal water resources outside of 
volcanic areas (Goldsheider et al., 2010). The deep karst aquifers 
in China containing hot water are ideal targets for future exploita-
tion and utilization due to their favorable characteristics, which 
include a high single-well yield, low salinity, easy re-injection, 
and fewer environmental effects when exploited (Kong et al., 
2014). Therefore, studying the thermal water resources in carbon-
ate strata in the main urban area of Chongqing can also provide 
useful references for the national strategy of geothermal energy 
exploitation in carbonate formations.

2. Study area description

The Chongqing municipality is situated at the transitional area 
between the Tibetan Plateau and the middle and lower plains of 
the Yangtze River basin (Fig. 1a). The main urban area of Chong-
ing is located in the western part of the Chongqing municipality; 
they consist of nine districts, including Yuzhong, Jiangbei, Yubei, 
Banan, and Beibei, etc. The total area is 5473 km\(^2\), and the populat-
on is 8.348 million in 2015. Our study area is in the southwestern 
valley between parallel mountains in the eastern Sichuan basin,
i.e., in the eastern Sichuan fold belts with an alternative anticline 
and syncline distribution (Fig. 1). Within this area, the anticlines 
form mountains and the synclines form valleys. In general, the pat-
ttern is characterized as “one mountain with two valleys and three 
ridges” or “one mountain with one valley and two ridges.” Geo-
morphologically, the altitude gradually decreases from the north-
west to the southwest in the study area. Ridges in the northwest 
are 700–1300 m a.s.l., whereas the ridges in the southwest vary 
between 500 and 600 m a.s.l. The Yangtze River, functioning as 
the local base level of erosion, runs through the study area from 
southwest to northeast. The Jialing River (one tributary of the 
Yangtze River) discharges into the Yangtze River at the center of 
the study area.

From west to east, there are five anticlines in the main urban area: 
the Wentangxia anticline, the Guanyinxia anticline, the 
Tongluoxia anticline, the Nanwenquan anticline, and the Taozi-
dang anticline (Fig. 1b). The Wentangxia anticline is long and linear 
with an “S”-shaped axis. The axis of the Guanyinxia anticline 
spreads from north-northeast to southwest with strata that are 
inclined gently in the east and steeply in the west. The southern 
end of the Tongluoxia anticline is connected to the Nanwenquan 
anticline by a slanted saddle that exhibits a typical box-shaped 
structure with an axis oriented 10–20° northeast; and this forma-
tion is steep in the east and gentle in the west. The axis of the Nan-
wenquan anticline has an arc-shaped distribution and is oriented 
north-northeast to south-southwest; it is gentle in the east wing 
and steep in the west wing. The axis of the Taozidang anticline is 
arc-shaped and slightly raised in the west. Geothermal resources 
are plentiful along these anticlines, and thermal water resources 
are distributed along both edges of them (Fig. 1b).

The geothermal system in the study area consists of geothermal 
reservoir, geothermal cap (the cover), and bottom layer. The 
geothermal reservoir is the aquifer for energy storage and heat 
transport. In this area, the geothermal reservoir is comprised of 
sections II (T1\(^{j3}\)), III (T1\(^{j3}\)), and IV (T1\(^{j3}\)) of the Lower Triassic Jian-
glingjiang Formation, the Middle Triassic Leikoupo Formation 
(T1\(^{j}\)), and section I (T1\(^{j}\)) of the Lower Triassic Jianglingjiang For-
formation; its total thickness is 540 m. The petrologic composition of T1\(^{j}\) 
is limestone, dolomite, and gypsum-salt breccia, whereas the 
petrologic composition of T1\(^{j}\) is dolomitic limestone and aqueous 
mica clay stone with an emerald color at the bottom. The hydraulic 
conductivity of the karst aquifer was calculated as 2.2 \times 10^{-3} \text{ m/s} 
based on a pumping test conducted in 2014. Both groups of dis-
solvable carbonates show well-developed karst conduits and cor-
rision fissures, which imply a good geothermal reservoir.

The geothermal cap (cover) consists of Upper Triassic Xujiahe 
Formation (T3\(^{xj}\)) clastic rock, a coal layer (the first cover, with a 
thickness of 375–425 m), and Jurassic (J) red sand and mudstone 
strata (the second cover, with a thickness of >1000 m). T3\(^{xj}\)
Fig. 1. (a) Location and main structural pattern of the main urban area of Chongqing. The outcrops in the Tongluoshan and Huayingshan areas are the suggested recharge zone for the thermal water of the study area. (b) General geology and DEM of the study area with sampling locations (after Cheng et al., 2015). The sample numbers are shown in Table 1. Numbers 12–15, 25–26, 27–28, and 31–26 are very close together. (c) Geologic section of A-A’ showing an alternative anticline and syncline distribution. The anticlines and synclines mainly consist of carbonate and clastic rock, respectively. WA: Wentangxia anticline, GA: Guanyinxia anticline, TA: Tongluoxia anticline, NA: Nanwenquan anticline, TZA: Taozidang anticline.
the Jurassic strata are located above T1j + T2j and are characterized by poor thermal and water conductivity that, to some extent, prevents thermal loss in the geothermal reservoir and forms a layer with low permeability.

The bottom of the geothermal reservoir consists of lower Triassic Feixianguan Formation (Tf) carbonate and clastic sediment. The petrology is mud limestone and shale with a thickness over 500 m. The shale layer exhibits poor porosity, low permeability, and low thermal conductivity.

The 36 geothermal wells in this study are distributed within the 2 km surrounding the axis of the Wentangxia, Guanyinxia, Tongluoxia, Nanwenquan, and Taozidang anticyclines (Fig. 1b).

The study area features a subtropical wet monsoon climate with an average temperature of 17 °C. The annual precipitation is heavy and peaks during late spring and summer; its annual average ranges from 1000 to 1400 mm (Bai et al., 2014).

3. Methods

3.1. Sample collection and experimental analysis

Water samples from the 36 thermal wells (Fig. 1b) were collected by pumping during the wet season in 2009. Each sample's temperature, pH, and total dissolved solids (TDS) were measured in the field with uncertainties of 0.1 °C, 0.1 unit, and 1 mg/L, respectively. The concentrations of Ca2+, Mg2+, and SO42− were measured using the EDTA titration method with relative errors of ±1%, ±1%, and ±0.6%, respectively. The concentrations of K, Na, and Li were determined using flame atomic absorption spectrophotometry with relative standard deviation of 0.5%. The HCO3− concentration was analyzed using argentometric titration with a relative error of ±1%. The SiO2 concentration was tested using Si-Mo yellow spectrophotometry with a relative standard deviation of 0.5%. The Cl− concentration was determined by titration with a relative error of ±1%. All the elemental concentrations were measured at the Geotechnical Engineering Testing Center of Chongqing in accordance with the Determination Method for Underground Water published by the Chinese government (The Geological and Mineral of the People's Republic of China, 1993).

No. 2 was collected during the dry season on December 17, 2009, and the other 35 samples were collected during the wet season in 2009. The values of δ18O and δD of nos. 2, 4, 15, 16, 26, 32 and 33 were obtained using a DELTA V Plus isotope ratio mass spectrometer connected with a GasBench II (Thermo Fisher Scientific Inc., Bremen, Germany). Both international and laboratory isotopic standards were utilized with external uncertainties of less than 0.2‰. The isotopic ratios were reported in delta (δ) notation relative to the V-SMOW standard and expressed in per mil (‰).

These measurements were made at the Laboratory of Geochemistry and Isotopes, Southwest University, Chongqing, China.

3.2. Data processing

3.2.1. Saturation index (SI)

The SI was calculated using Phreeqc version 3 (Parkhurst and Appelo, 2013). When SI < 0, the solution is considered undersaturated. When SI = 0, the solution is saturated, and equilibrium is achieved between mineral dissolution and precipitation. When SI > 0, the solution is oversaturated, and extra minerals precipitate.

3.2.2. t-test for independent samples and correlation analysis

The t-test for independent samples is designed to compare two independent samples from normal populations to test whether the mean and variance of the samples' sources are the same (e.g., Schipper and McGill, 2008). When Sig > 0.05, the difference between the samples is insignificant; when Sig < 0.05, the difference between the samples cannot be ignored.

Correlation coefficient analysis is used to measure the strength of the association between two continuous variables. A Pearson rank correlation analysis (two-tailed) was used to examine the possible correlations among various physical and chemical parameters.

The t-test and the correlation coefficient analysis were performed using IBM SPSS statistics 19.0.

3.2.3. Geothermometry

The geothermometric calculations of the reservoir temperatures used in this study are as follows:

Quartz (Fournier, 1977): TSiO2 = [1309/(5.19 − lgS)] − 273.15
Chalcedony (Fournier, 1977): TSiO2 = [1032/(4.69 − lgS)] − 273.15
Improved SiO2 (Verma and Santoyo, 1997): TSiO2 = −44.119 + 0.24469S − 1.7414 × 10−6S2 + 79.305lgS
K-Mg (Giggenbach, 1988): TK-Mg = 4410/[114 − lg(K2/Mg)] − 273.15
Na-Li (Fouillac and Michard, 1981): TNa-Li = 1049/[lg(Na/Li) + 0.44] − 273.15
Na-K (Giggenbach, 1988): TNa-K = 1390/[1.75 − lg(Na/K)] − 273.15 and
Na-K-Ca (Fournier and Truesdell, 1973): TNa-K-Ca = 1647/[lg(Na/K) + (4/3)[lg(Ca/Na) + 2.06] + 2.47] − 273.15,

where S is the concentration of SiO2 in the water (mg/L), and K, Mg, Na, Li, and Ca represent the concentrations (mg/L) of the corresponding elements.

3.2.4. Circulation depth

\[ Z = \left( T_2 - T_0 \right) / G + Z_0. \]

where Z is the circulation depth (m); T2 is the temperature of the geothermal reservoir calculated by a reasonable geothermometer (°C); T0 is the local annual average temperature (°C); G is thermal gradient (°C/m); and Z0 is the thickness of the constant temperature zone (m). The average temperature in this area is 17 °C, as mentioned above, and therefore, T0 = 17 °C, Z0 = 0, and G = 0.03 °C/m (Cheng et al., 2015) here.

3.2.5. Recharge altitude and its annual average air temperature based on δD

Because the study area has a regional scale, the recharge altitude and its annual average air temperature can be calculated using the general equation for China (Zhou et al., 2010):

\[ \delta D = -0.03ALT - 27. \]

\[ \delta D = 3T - 92. \]

where ALT is the altitude (m), and T is the annual air temperature (°C) in the recharge area.

4. Results

4.1. Hydrogeochemistry of the thermal water samples

The physical and chemical indexes of the 36 thermal water samples in the study area are presented in Table 1. Except for no. 21 (−7.32%), the relative uncertainties of all the ion equilibria are less than 5% (Table 1). The cation molarity (Tz = HCO3− + 2SO42− + Cl−) is 24.3–47.6 meq/L, and the anion molarity...
(‘TZ’ = Na+ + K+ + 2Ca2+ + 2Mg2+) is 24.3–45.6 meq/L, with the exception of nos. 11 and 21. The cation and anion molarities are exceptionally low compared to the rest of the thermal water samples, with values of 6.4 meq/L and 6.3 meq/L, respectively, for no. 11, and values of 5 meq/L and 5.8 meq/L, respectively, for no. 21. Except for nos. 11 and 21, the major cations are Ca2+ and Mg2+, which occur at concentrations of 329.4–697.6 mg/L and 59.5–166.6 mg/L, respectively, and with their proportions of 62.3–84.5% and 7.4–26.9%, respectively. The main anion is SO42-, which occurs at a concentration of 1005–2048 mg/L and in a proportion of 81.4–92.2%. The concentration of HCO3 is as low as 157–500 mg/L, and its proportion is 7.4–18.2%. Except for nos. 11 and 21, the TDSs of the thermal water samples are between 1620 and 3035 mg/L. The thermal water samples are generally brackish and contain significantly higher concentrations of SO42- and Ca2+ than the shallow karst water (fresh water) (Xiong et al., 2013). Piper plots of the major cations and anions (Fig. 2) were used to map the hydrogeochemical facies of the thermal water samples. All the samples are of the Ca-Mg-SO4 or Ca-SO4 type, except nos. 11 and 21 which contain Ca-Mg-HCO3 and Ca-HCO3-SO4. The TDS and ion molarity in nos. 11 and 21 are much lower than the values from other wells (Table 1), which is explained by the great impact of the mixture of shallow karst water characterized by Ca-HCO3 or Ca-Mg-HCO3.

As shown in Table 1, except for no. 11, the thermal water samples have medium-low temperatures in the range from 32.5 to 57.0°C. The pH range from 7.3 to 8.4 indicates weak alkalinity.

The depths of the drill wells range from 55.4 to 2336 m (Table 1). To check whether the physical and chemical properties of these 36 thermal water resources are influenced by depth, we arbitrarily classified each well as deep (depth > 1000 m) or shallow (depth < 1000 m). The independent sample t-test was performed on the physical and chemical data collected from the deep wells and the shallow wells. As shown by the results in Table 2, the confidence is always >0.05, which implies that there
are no significant differences in the physical and chemical properties of deep and shallow wells. Therefore, the drilling depth has no effect on the properties of the thermal water samples, which demonstrates that all the thermal water comes from a hydrogeological system characterized by the regional hydraulic continuity that is more effective in the carbonate basin due to the higher hydraulic diffusivity of the carbonates (Mádl-Szönyi and Tóth, 2015).

Table 3 shows the results of the correlation analysis of the physical and chemical parameters. The small correlation coefficients between the depth and each index imply that depth has an insignificant effect on the physical and chemical properties of the thermal water resources, which is consistent with the results inferred from the independent sample t-test. The TDS is highly correlated with the concentrations of $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$; their correlation coefficients are 0.99, 0.98, and 0.86, respectively. The correlation coefficients of the $\text{SO}_4^{2-}$ concentration with the concentrations of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ are 0.98 and 0.74, respectively. Negative correlations were observed for the concentration of $\text{HCO}_3^-$ with an average of $-0.65$, and $\text{Na}^+$ indicating strong correlation.

4.2. Geothermometry

The temperature ensures the geothermal utilization of water in the reservoirs. Table 4 shows the temperature of the thermal water samples calculated using different geothermometers. The temperatures determined using quartz (Fournier, 1977) are 64.6–93 °C. The chalcedony geothermometer (Fournier, 1977) provides temperatures of 32.6–62.4 °C. The improved $\text{SiO}_2$ geothermometer (Verma and Santoyo, 1997) yields temperatures of 65.1–93.7 °C. The temperatures derived from cation geothermometers, including $\text{K-Mg}$ (Giggenbach, 1988), $\text{Na-Li}$ (Fouillac and Michard, 1981), $\text{Na-K}$ (Giggenbach, 1988), and $\text{Na-K-Fe}$ (Fournier and Truesdell, 1973) geothermometers, are 25–89.5 °C, 64–271.8 °C, 291.9–1301.7 °C, and 111.7–394.3 °C, respectively.

4.3. Saturation index

Table 5 presents the results of the thermodynamic equilibrium SI. The SIs of anhydrite, gypsum, halite, pyrite, and siderite are less than 0; they imply unsaturation. The oversaturation of secondary minerals, such as goethite, hematite, and talc, can be observed. The SI of chalcedony is in the range from −0.1 to 0.4, which indicates that the solution varies between oversaturation and undersaturation, whereas the SIs for calcite, dolomite, and quartz are >0; they imply oversaturation. Quartz is oversaturated but close to saturation (Table 5). In the correlation between the $\text{SiO}_2$ and temperature graph (Fig. 3), the data points of thermal water fall between the solubility curves of quartz and amorphous $\text{SiO}_2$, which demonstrates that quartz is oversaturated at surface and shallow temperatures, and saturated at still higher temperatures at depth (Majumdar et al., 2009). The data points of the thermal water are aligned neither horizontally to reflect conductive cooling nor along the inclination to reflect cooling dilution (Fig. 3; Majumdar et al., 2009; Chatterjee et al., 2016). These results probably imply that the conductive cooling and diluted cooling of the thermal water are coupled in the upwelling thermal water.

4.4. $\delta^2$H and $\delta^{18}$O isotopic composition

Table 6 shows the values of $\delta^2$H and $\delta^{18}$O in seven typical thermal water samples: $\delta^2$H is in the range from −50.3 to −60.9‰ with an average of $-56.3\%e$, and $\delta^{18}$O is in the range from −7.6 to −9.2‰ with an average of $-8.4\%e$. These fairly stable values of isotopic composition are indicative of a similar hydrogeological genesis for the thermal water, which further supports the results of the t-test.

5. Interpretation and discussion

5.1. Origin of the major ions in thermal water

Thermal water can be considered a kind of evolved water whose initial composition has been changed by physical-chemical

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Table 2

Independent sample t-test of the physical and chemical parameters of shallow (depth < 1000 m) and deep (depth ≥ 1000 m) wells. The water temperature (T) is in °C; and the TDS and major ion concentrations are in mg/L. The temperature ensures the geothermal utilization of water in the reservoirs. Table 4 shows the temperature of the thermal water samples calculated using different geothermometers. The temperatures determined using quartz (Fournier, 1977) are 64.6–93 °C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Deep well</th>
<th>Shallow well</th>
<th>t</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>42.9</td>
<td>47.8</td>
<td>−1.33</td>
<td>0.19</td>
</tr>
<tr>
<td>pH</td>
<td>7.73</td>
<td>7.57</td>
<td>1.71</td>
<td>0.1</td>
</tr>
<tr>
<td>K</td>
<td>13.3</td>
<td>17.2</td>
<td>−1.98</td>
<td>0.06</td>
</tr>
<tr>
<td>Na</td>
<td>31</td>
<td>32.9</td>
<td>−0.2</td>
<td>0.85</td>
</tr>
<tr>
<td>Ca</td>
<td>561.7</td>
<td>507.7</td>
<td>1.08</td>
<td>0.29</td>
</tr>
<tr>
<td>Mg</td>
<td>106.8</td>
<td>91.5</td>
<td>1.46</td>
<td>0.15</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>189.1</td>
<td>188</td>
<td>0.09</td>
<td>0.93</td>
</tr>
<tr>
<td>Cl</td>
<td>19.4</td>
<td>19.3</td>
<td>0.02</td>
<td>0.98</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1667</td>
<td>1484</td>
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<td>0.26</td>
</tr>
<tr>
<td>TDS</td>
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<td>2309</td>
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</tr>
<tr>
<td>SiO₂</td>
<td>33.5</td>
<td>30.4</td>
<td>1.51</td>
<td>0.14</td>
</tr>
<tr>
<td>Li</td>
<td>0.19</td>
<td>0.23</td>
<td>−1.25</td>
<td>0.23</td>
</tr>
</tbody>
</table>

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** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

Table 3

Correlation analysis of the physical and chemical indexes of the thermal water samples. T is the water temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Deep well</th>
<th>Shallow well</th>
<th>t</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>1</td>
<td>−0.35</td>
<td>0.46</td>
<td>**</td>
</tr>
<tr>
<td>pH</td>
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<td>−0.15</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>K</td>
<td>1</td>
<td>0.35</td>
<td>0.04</td>
<td>0.28</td>
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<tr>
<td>Na</td>
<td>1</td>
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<td>0.37</td>
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<td>0.09</td>
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<tr>
<td>Mg</td>
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<td>0.04</td>
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<tr>
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<td>0.26</td>
<td>−0.65</td>
<td>0.08</td>
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<tr>
<td>Cl</td>
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<td>0.16</td>
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<tr>
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</tr>
<tr>
<td>TDS</td>
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<td>0.01</td>
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<tr>
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<td>Li</td>
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</tr>
</tbody>
</table>

---

**: Correlation is significant at the 0.05 level (2-tailed).
**: Correlation is significant at the 0.01 level (2-tailed).
Table 4
Temperatures of the thermal water samples determined using different geothermometers. The reservoir temperature is the average calculated using quartz and improved SiO₂ geothermometers. The circulation depth is in m; all other values are in °C; –: no datum.

<table>
<thead>
<tr>
<th>Sample ID no.</th>
<th>SiO₂ geothermometers</th>
<th>Cation geothermometers</th>
<th>Reservoir temperature</th>
<th>Circulation depth</th>
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<td>65.1</td>
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<td>81.8</td>
<td>50.56</td>
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<td>36.7</td>
<td>69.2</td>
<td>32.2</td>
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<td>75.8</td>
<td>44.26</td>
<td>76.6</td>
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<td>42.34</td>
<td>74.7</td>
<td>45.4</td>
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<tr>
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<td>53.55</td>
<td>85.4</td>
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</tr>
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<td>61.92</td>
<td>93.2</td>
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<td>81.6</td>
<td>47.5</td>
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<td>80.9</td>
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<td>31</td>
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<td>35</td>
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<td>36</td>
<td>93</td>
<td>62.43</td>
<td>93.7</td>
<td>50.3</td>
</tr>
</tbody>
</table>
11 and 21 are closer to the 1:4 line, which are attributed to the mixture of shallow karst groundwater. The correlation coefficient of 0.74 between Mg$^{2+}$ and SO$_4^{2-}$ demonstrates that the Mg$^{2+}$ originates from the dissolution of magnesium sulfate.

In general, the concentrations of Ca$^{2+}$ and SO$_4^{2-}$ in the thermal water of the Chongqing main urban area are high due to the dissolution of gypsum or/and anhydrite, which can restrain the dissolution of carbonate and reduce the concentration of HCO$_3^-$.

5.2. Reservoir temperature and circulation depth

Care must be taken to select the appropriate geothermometer to estimate the reservoir temperature and avoid incorrect results or explanations. Distinct differences were observed among the reservoir temperatures (Table 4), which emphasizes the necessity of selecting a suitable geothermometer for the study area.

The Na-K-Mg Gigenbach diagram (Gigenbach, 1988) can be used to identify the water-rock equilibrium and the degree of mixing. As shown in Fig. 5, the data for all the thermal water samples are distributed in the right corner representing “immature water”, which indicates possible mixing with cold water as the thermal water rises. Fig. 3 also demonstrates the potential effect of shallow cold water, which is to cause over- or under-estimated temperatures when cation thermometers, such as Na-K, Na-K-Ca, Na-Li, and K-Mg thermometers, are used (Table 4). Therefore, cation geothermometers are inappropriate for evaluating reservoir temperatures (Verma and Santoyo, 1997).

Some of the calculated temperatures given by the chalcedony thermometer (Fournier, 1977) listed in Table 4 are lower than the measured temperatures listed in Table 1. The average calculated temperature based on the chalcedony thermometer is 50.6 °C, which is slightly higher than the measured temperature (46.5 °C). Therefore, the chalcedony thermometer is not suitable.

The original SiO$_2$ content is preserved without significant loss during the ascent of the thermal water. No secondary equilibrium occurs, and the SiO$_2$ content is close to the solubility curve of quartz (Fig. 3). The stable SiO$_2$ content may be the result of conductive cooling in the upper low-temperature strata and
Table 6
δD and δ18O in typical thermal water samples. δD and δ18O are in ‰; the recharge altitude is in m; and the annual average air temperature is in °C.

<table>
<thead>
<tr>
<th>Sample ID no.</th>
<th>δD</th>
<th>δ18O</th>
<th>Recharge altitude</th>
<th>Annual average air temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-52</td>
<td>-7.6</td>
<td>838</td>
<td>13.3</td>
</tr>
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<td>4</td>
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<td>1130</td>
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<td>13.9</td>
</tr>
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<td>1103</td>
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</tr>
<tr>
<td>33</td>
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<td>1020</td>
<td>10.4</td>
</tr>
<tr>
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<td>-56</td>
<td>-8.4</td>
<td>977</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Fig. 4. Correlation between Mg2+ and HCO3− in the thermal water samples (modified from Wang et al., 2006). That most samples are far from the line representing a 1:4 ratio indicates that the dissolution of dolomite does not mainly contribute to the high concentration of Mg2+.

Fig. 5. Na-K-Mg Giggenbach plot (Giggenbach, 1988) of the thermal water samples. The water samples are located in the "immature water" region, which indicates that the thermal water mixes with the surface cold water.

The circulation depth is one of the significant factors influencing the reservoir’s temperature, as well as one of the important parameters in geothermal studies that analyze the origin and formation mechanism of thermal water and assess potential geothermal reservoirs. The circulation depth calculated using Eq. (1) is 1579–2520 m with an average of 2150 m (Table 4), which is consistent with the reservoir depth revealed by the well. For example, in the well called Tong-5, which was drilled four km southeast of well no. 14 in 1993, the layer with low permeability at the bottom of the geothermal reservoir (T1j) was 2002 m deep, which is approximately consistent with the estimated average circulation depth of 2150 m.

5.3 Recharge of the thermal water resources based on an isotopic analysis

The source of the water is an important factor when considering the heat source of thermal water. Hydrogen and oxygen isotopes can, to some extent, trace the circulation of water through the atmosphere and are, therefore, widely applied in studies of the origin of thermal water (e.g., Pastorelli et al., 1999; Chandrajith et al., 2013; Chatterjee et al., 2016). The values of δD and δ18O obtained from seven wells, nos. 2, 4, 15, 16, 26, 32, and 33 (Table 6), are graphed and compared with the global meteoric water line (GMWL; Craig, 1961) and the Chongqing meteoric water line (CMWL; Li et al., 2010). As shown in Fig. 6, all the data points are close to the GMWL and the CMWL without shifting. This implies that local precipitation is the major factor in recharging the geothermal water, which is consistent with other studies demonstrating meteoric origins for thermal water around the world (e.g., Grasby et al., 2000; Ahmad et al., 2001; Lee et al., 2011; Moreira and Fernández, 2015), especially in carbonate reservoirs (e.g., Goldscheider et al., 2010; Sun et al., 2016).

The values of δD for the thermal water resources show that the recharge altitude can be calculated to be 838–1130 m using Eq. (2), with an average of 977 m (Table 6). The annual temperature of the recharge area ranges from 10.4 to 13.9 °C, according to Eq. (3), and the average is 11.3 °C (Table 6).

Dating by means of the radioactive carbon isotope 14C is one of the most useful methods for dating groundwater that is between 1000 and 45,000 yrs old (Zhu and Murphy, 2000). This method has recently been well developed (Samborska et al., 2013). The 14C data in this paper are from a geological investigation report (Chongqing Monitoring Station of Geological Environments, 2009). According to the 14C analyses of nos. 2, 3, 5, and 8 at the Guanyinxia anticline, the 14C ages increase from the north to the south from 14830 ± 220 to 17550 ± 250 yrs, which indicates that...
the thermal water at the Guanyinxia anticline moves from the north to the south.

5.4. Conceptual model of thermal water circulation

In the surrounding area, Tongluoshan and Huayingshan, which are approximately 175 km northeast (Fig. 1a), satisfy the elevation (838–1130 m) and annual air temperature (11.3°C–17.6°C) criteria for the thermal water recharge area. The elevation of the highest peak in these areas is 1704.1 m; the annual average temperature is 11.5°C, and the average precipitation is 1282.2 mm (Luo et al., 2013).

On the basis of the above interpretation and discussion, a conceptual regional flow model shown in Fig. 7 is proposed; this model is not intended to represent the detailed heterogeneity and anisotropy of the system, rather its main features. The presence of a structurally weak zone, such as a permeable fault, is more favorable for the percolation of meteoric water to shallow depths (Chandrajith et al., 2013). These regions exhibit two faults, the Tongluoshan fault and Huayingshan fault whose structure extends from northeast to southwest (Zhang et al., 2015; Shi et al., 2016) shown in Fig. 1a. Carbonate is widely distributed in the Tongluoshan and Huayingshan areas, especially on the exposed anticline; caves, sinkholes, shafts, and fractures are well developed and acts as unconfined carbonate outcrops and provide ideal channels for the vertical infiltration and recharge of meteoric water.

On the regional scale, groundwater movement from recharge to discharge areas is generally gravity (topography) driven (Tóth, 1963; Jiang et al., 2012; Mädl-Szönyi and Tóth, 2015; Mädl-Szönyi and Simon, 2016). Meteoric water falling in the Tongluoshan and Huayingshan areas percolates to the geothermal reservoir and is heated continuously by the bedrock until it becomes thermal water. An ideal reservoir has a high hydraulic conductivity and large specific storage for long term productivity and is characterized by hydrostatic pressure-like conditions (Mädl-Szönyi and Simon, 2016). Deep carbonate rocks are often more permeable than other reservoirs (Goldscheider et al., 2010). Based on information on the drilled wells in Chongqing, the geothermal reservoirs of the study area exhibit porosities of 3–4% (Cheng et al., 2015), which could provide good conditions to produce a high productivity rate of thermal water. The high topographic gradient between the higher altitude recharge areas of Tongluoshan, Huayingshan, and the low-lying discharge zone in the main urban area of Chongqing drives the thermal water along the fault and the anticline core of the east Sichuan fold belts to the southwest (Figs. 1 and 7). The pattern of thermal groundwater flow in our study area characterized by confined carbonate is similar to the confined part of Budapest in Hungary, where intense heat accumulation could be established under the confined part of a carbonate basin (Mädl-Szönyi and Tóth, 2015).

The residence time of the regional groundwater flow is relatively long; therefore, the water-rock interaction is sufficient to continuously dissolve evaporates during its transport (Fig. 7), which results in elevated TDS (Table 1). The dissolution of gypsum could increase the porosity and the permeability in the carbonate aquifer, which can provide an initial secondary porosity to allow the deep penetration of groundwater that is not saturated with calcite, and accelerate karstification and increase the productivity (Gunn et al., 2006). During the transport of the thermal water, the cover pressure is reduced along river cutting and in lower-elevation areas, which leads to natural exposures of thermal water.
in the form of artesian hot springs that form a geothermal artesian karstic system, as in the case reported by Frumkin and Gvirtzman (2006) or drainage in the form of drained wells.

6. Conclusion

The thermal water in the main urban area of Chongqing comes from the karst aquifer formed by Lower and Middle Triassic carbonate rock. Using its physical and chemical properties and the values of δ18O, δD, and δ13C, its origin, reservoir temperature, circulation depth, recharge, and drainage have been investigated. The chemical types of most of the thermal water samples are Ca-Mg-SO4 and Ca-SO4. The independent sample t-test demonstrates that the well depth has no effect on the physical and chemical properties. Concentrated SO4 and Ca2+ are formed through the dissolution of gypsum and anhydrite in the karst strata; the dissolution of carbonate is restrained by the common ion effect, which results in dilute HCO3. Furthermore, Na+ and Cl− originate from the dissolution of salt in the strata.

The Na-K-Mg diagram shows that the thermal water is immature, which indicates that cation thermometers (Fournier and Truesdell, 1973; Fouillac and Michard, 1981; Giggenbach, 1988) cannot be used. Quartz (Fournier, 1977) and improved SiO2 thermometers (Verma and Santoyo, 1997) are selected; they yield reservoir temperatures in the range from 64.8 to 93.4 °C and circulation depths from 1579 to 2520 m with an average of 2150 m. The δ18O and δD values for the thermal water samples are mainly distributed near the local meteoric water line. Combined with the region’s geology and tectonic characteristics, a large volume of meteoric water infiltrates through the unconfined carbonate rock. Using its physical and chemical properties and the thermal water in the main urban area of Chongqing (in Chinese).

The authors also appreciate the constructive comments and suggestions generously provided the digital elevation model (DEM) data of the study area by Dr. Cong (no. 2), respectively. The authors also appreciate the constructive comments and suggestions by anonymous reviewers. Additional thanks are given to Xinyi Xiang for her valuable comments. This work was supported by the National Key Technology R&D Program of China (Grant Nos. XDJK2016E041, and XDJK2016D046). The 2014 Scientific by the National Key Technology R&D Program of China (Grant Nos. XDJK2014A016, XDJK2016E022, XDJK2016E023, XDJK2016E042, and XDJK2016D046).

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