1	A Preliminary Analysis of the Formation of Travertine and Travertine Cones in the Jifei
2	Hot Spring, Yunnan, China
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17	Abstract: The Jifei hot spring emerges in the form of spring groups in the Tibet-Yunnan
18	geothermal zone, southwest of Yunnan Province, China. The temperatures of spring waters
19	range from 35°C to 81°C and are mainly of HCO ₃ -Na·Ca type. The total discharge of the hot
20	spring is about 10 L/s. The spring is characterized by its huge travertine terrace with an area of
21	about 4000 m^2 and as many as 18 travertine cones of different sizes. The tallest travertine cone
22	is as high as 7.1 m. The travertine formation and evolution can be divided into three periods:
23	travertine terrace deposition period, travertine cones formation period and death period. The
24	hydrochemical characteristics of the Jifei hot spring was analyzed and compared with a local
25	non-travertine hot spring and six other famous travertine springs. The results indicate that the
26	necessary hydrochemical conditions of travertine and travertine cones deposition in the Jifei
27	area are (a) high concentration of HCO_3^- and CO_2 ; (b) about 52.9% deep source CO_2 with
28	significantly high P_{CO_2} value; (c) very high milliequivalent percentage of HCO_3^- (97.4%) with
29	not very high milliequivalent percentage of Ca^{2+} (24.4%); and (d) a large saturation index of

1 calcite and aragonite of the hot water.

2 Key words: Travertine, Hot spring, Thermal groundwater, Hydrochemistry, China

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4 Introduction

The Jifei hot spring (99°28'13.4"E, 24°44'20.7"N) (also called Zhushanxizaotang, 5 Jifeizaotang, Shiliu or Shipen hot spring) is located on a river valley at a distance of 17 km 6 from the center of Changning County (99°16′-100°02′E, 15°12′-24°14′N and about 3774 km²) 7 in southwest of Yunnan (Fig. 1), one of the richest geothermal resources regions of China 8 (Chen et al. 1994; Kearey and Wei 1993; Taylor and Zheng 1996). The hot spring is 9 characterized by approximately 4000 m² travertine landscape with as many as 18 travertine 10 cones. This spectacular travertine landscape, especially its travertine cones is very rare in 11 12 China. Several studies have been carried out on the Jifei hot spring since the 1970s (Local 13 chronicles codification committee of Yunnan Province 1999; Chinese People's Liberation Army 1980; Liang 2000). However, these previous studies mainly focused on briefly 14 15 describing hydrochemical compositions and travertine shapes. The relationship between hydrochemistry of the hot water and the travertine formation has not been investigated in 16 17 detail. The travertine formation is an important hydrothermal manifestation, and may provide very useful information for the reconstitution of paleoclimate, paleoenvironment and 18 paleohydrology (Minissale et al. 2002; Liu et al. 2003; Dilsiz et al. 2004; Veysey et al. 2008; 19 Sun and Liu 2010). It also provides helpful information for active tectonics location diagnosis 20 21 (Brogi and Capezzuoli 2009), palaeoseismological actives identification (Gürsoy et al. 2007) 22 and more. However, the relationship between the hydrochemistry and carbonate precipitation must be determined before travertine can be confidently used as a paleoclimatic tool or so. 23 (Liu et al. 2010). Therefore it is important to find hydrochemical controlling factors to identify 24 25 origins of the travertine and travertine cones in the Jifei hot spring area.

The purpose of the present study is to give a qualitative description of the travertine and travertine cones formation process in the Jifei area based on field observation. The present study also tries to reveal the hydrochemical conditions of the travertine and travertine cone formation in the Jifei area by comparing the hydrochemical compositions of the Jifei hot spring, the Wenquanxiang hot spring $(99^{\circ}41'45.2''E, 24^{\circ}41'56.6''N)$ (also named

1 Changning, Xiaoshiqiao or Xiaoshijie hot spring and is 7.7 km far from the Jifei hot spring but 2 has no travertine sediments) (Fig. 1), and six other travertine springs. The six travertine 3 springs are the Huanglong spring and the Kangding thermal spring in Sichuan, China; the 4 Baishuitai spring and the Zhongdianxiagei hot spring in Yunnan, China; the Pamukkale 5 thermal spring in Turkey and the Mammoth thermal spring in Yellowstone National Park in 6 the US.

7 Site description

8 Geological and hydrogeological setting

9 The study area is situated in the Tibet-Yunnan geothermal zone, which is a very 10 important geothermal zone in China (Chen et al. 1994; Kearey and Wei 1993). 11 Administratively, the study area is attached to the Changning County of Yunnan Province, 12 China. The Changning County has a subtropical plateau monsoon climate with annual average 13 temperature of about 17.5°C. The average precipitation is around 1200 mm and about 80% 14 precipitation falls from May to October (Geo-Environmental Monitoring Central Station of 15 Yunnan Province, 2004).

Stratigraphically, the rocks in this area mainly consist of sedimentary rock, magmatic 16 17 rock and metamorphic rock from Cambrian to Neogene except Cretaceous. The aquifer in which the Jifei thermal groundwater occurs is the red sandstone of Neogene lacustrine 18 deposition. Rocks underlying the Neogene lacustrine sediments include Paleozoic 19 (Carboniferous, Devonian, Silurian, Ordovician and Cambrian) shallow marine rocks and 20 21 interbedded marine and continental rocks. These settlement rocks are composed of clastic 22 rocks including mudstone rocks, clastic rocks mixed with carbonate rocks and epimetamorphic clastic rocks including carbonate rocks, with a total thickness of 2473-5998 m. As for the 23 Wenquanxiang hot spring, it occurs in the Permian carbonate rock and the underlying rocks 24 are Paleozoic carbonatite, clastic rocks with carbonate lens and epimetamorphic rock and 25 biotite adamelite of the early Yanshan Epoch (Jurassic), with a total thickness of about 2473 m 26 (Geological Bureau of Yunnan Province 1980; Chinese People's Liberation Army 1980). 27

Three major tectonic systems, the middle segment of Qinghai-Tibet-Yunnan Burma
Indonesia eta-type structure (which is shaped as the Greek letter "η"), the Sanjiang (Nujiang,
Lancangjiang and Jinsajiang rivers) radial tectonic system and the Changning-Yingpan-Yalian

1 arcuate tectonic system, constitute a basic tectonic framework in this area (Fig.1) (Chinese People's Liberation Army 1980; Geological Bureau of Yunnan Province 1980). Apianzhai 2 fault (F_1), Dashitoujie fault (also called Changning fault, F_3), Lancangjiang fault (F_4) and 3 Kejiehe fault (F_5) are the mainly controlling faults which divide the study area into several 4 5 geological units. The F₁ and F₅ faults divide the Paleozoic sedimentary rocks and Cambrian metamorphic rocks while the F₃ fault separates the Pre-Ordovician metamorphic rocks from 6 7 the Cambrian metamorphic rock. Jurassic and Paleogene rocks expose along the F₁ fault. The upper Triassic rocks change significantly from one side of F₃ fault to the other. The granite of 8 9 the early Yanshan Epoch mainly outcrops along the north segment of fault F_5 in the study area. Some segments of F₁, F₃ and F₅ faults are covered by Neogene sediments. These evidences 10 illustrate that F1, F3 and F5 faults were formed before Neogene, i.e. F1 and F5 were formed 11 in/before Jurassic period and F₃ in Triassic period. In addition, all of these major faults are 12 characterized by multi-stage, multi-phase and multi-period processes. For instance, F₅ fault 13 14 exhibits compressive/compresso-shear structural features but transtensional activity characteristics have also been observed. 15

Hot springs occur along with these controlling faults or their secondary faults in the study 16 17 area. The Jifei hot spring emerges at the potential connection part of Apianzhai fault (F_1) and the extension line of the Houshanbei fault (F_2). More than 20 hot springs occur in the 18 Changning County. All of these hot springs are of low to medium temperature (≤90°C) and the 19 temperature of Jifei hot spring is the highest with up to to 81°C (Local chronicles codification 20 21 committee of Yunnan Province 1999). Zhou et al. (1995) performed a data statistical analysis 22 of several thermal springs in west Yunnan region. It revealed a far weaker hydrothermal activity in the study area's geological unit than in that of Tengchong in which recent volcanic 23 activity occurred, i.e. the magma pocket in the geological unit of the study area is small or 24 25 absent. Therefore, we can infer that the Jifei hot spring is restricted to faults. These faults provide a high-permeability flow path that allows deep circulation of meteoric water. 26

27 Description of the Jifei hot spring

The Jifei hot spring occurs in the form of spring groups in the Jifei canyon. The elevations of 12 vents (Fig.2) range from 1138 to 1206 m with a temperature ranging between 30 35°C and 81°C, pH from 6.77 to 7.27, and the total discharge speed of the hot springs is about

1 10 L/s. A travertine terrace (Fig. 2) outcrops on the right side of a small river in the Jifei geothermal area. It is 150 m long, 50 m wide and 20 m high. The total area is about 4000 m^2 . 2 3 This travertine terrace trends from nearly north to south and gradually decreases in height from northwest to southeast. Fifteen travertine cones grow on the terrace and 3 separate 4 5 travertine cones (G₁, G₂ and G₃ in Fig. 2) deposit near the terrace. The color of the travertine terrace and travertine cones varies from grayish to black and many plants (glasses and bushes) 6 7 are growing on them except on a few spots where new travertine is depositing (Fig. 4). This 8 implies that the travertine terrace and travertine cones have stopped growing on the whole in 9 the Jifei area.

Before analyzing the formation of travertine and travertine cones, it is necessary to first 10 categorize the travertine cones in the Jifei area. Based on the different locations, shapes and 11 12 formations, 18 travertine cones can be classified into the following 4 categories. (1) The small 13 travertine cones which grow on the travertine terrace with height of 1-3 m. All of these 14 travertine cones have stopped growing and no geothermal activities occur nearby them. (2) The female tower travertine cone (G_1 in Fig. 3) which consists of two travertine cones 15 deposited side by side. The main cone and the attached cone are respectively 4.8 m and 2.2 m 16 17 high. A hot spring with water temperature of 76.5°C emerges under the female tower travertine cone but no new travertine formed. (3) The male tower travertine cone (G_2 in Fig. 3) at half 18 height of which there is a 10 cm thick gravel interlayer. The male tower travertine cone is the 19 highest in the Jifei area (7.1 m). The gravel interlayer was probably caused by a surperflood 20 21 which happened during the growth process of the travertine cone and transported gravels to 22 the middle part of the travertine cone. (4) A single growing travertine cone (G_3 in Fig. 3) on top of which a hot spring $(S_5, in Fig. 3)$ emerges but with no new travertine deposition. The 23 height of this travertine cone is 5.4 m. 24

25 Methods

A field observation and hot water sampling were conducted during a field survey that took place on August 9th, 2007. The unstable parameters such as water temperature (T), pH value, and electrical conductivity (EC) were measured in situ (Tables 1 and 2). Water flowing from one vent (S_4 , Fig. 2) of the Jifei hot spring was collected in polyethylene bottles for hydrochemical and isotopic analysis. Another nearby hot spring but with no travertine

1 formation (the Wenquanxiang hot spring) was also sampled for hydrochemical and isotopic 2 analysis. The hydrochemical analysis (Tables 1 and 2) was performed in the Laboratory of 3 Beijing Institute of Geological Engineering based on the China national standard methods for examination of drinking natural mineral water (GB/T 8538-1995). The carbon isotope (Table 4 5 2) of dissolved inorganic carobon (DIC) was determined in the Key Laboratory of Isotope Geology, Ministry of Land and Resources of the People's Republic of China. For carbon 6 7 isotope composition measurement, phosphoric acid method was used and the result was reported in per mil deviation relative to Vienna-PeeDee Belemnite (V-PDB) standard with an 8 accuracy of $\pm 0.2\%$ for $\delta^{13}C_{DIC}$. 9

10 **Results and discussion**

11 Genetic analysis of travertine and travertine cones formation

12 The formation and evolution of travertine in the Jifei area can be divided into three main 13 periods (Gibert et al. 2009; Liu 2005). (1) Deposition period of the travertine terrace, when 14 numerous hot springs occurred with large flux. (2) Formation period of travertine cones (including all the small travertine cones and three separate large travertine cones), when the 15 number of springs and total discharge flux were less than those in the first period. (3) Death 16 17 period, which began when the travertine cones deposition stopped until now. The hydrothermal activity further decreased and the discharge of geothermal springs reduced 18 considerably. During the last period, new travertine only deposits around some spring vents 19 and travertine cliffs where hot waters flow through (Fig. 4). 20

21 The mineral composition of the travertine includes aragonite and other minerals but more 22 than 90% of travertine consists of calcite carbonate (Jones and Renaut 2008; Pentecost 1995a). Thus the process of the travertine formation depends on the mechanism of calcite carbonate 23 deposition. Here, the factors which influence the CaCO₃ precipitation were classified as 24 25 internal factors. They are the key factors for travertine sedimentation. Other factors such as weathering, erosion, etc. are classified as external factors. The external factors are only 26 responsible for the shape of travertine. The internal factors can be further divided into 3 parts: 27 28 (1) environment factors: climate, topography geology etc. (Pentecost 1995b, Brogi and Capezzuoli 2009), (2) physical and chemical properties of water: chemical composition, water 29 30 temperature, flow rate and so on (Drysdale et al. 2002; Dilsiz et al. 2004) and (3) biological

1 effect: biogenic encrustation, etc. Environmental and Biological factors affect travertine 2 formation mainly through sedimentation rate and shaping. For instance, the diurnal 3 temperatures influence the sedimentation rate of calcium carbonate by controlling the rate of CO₂ efflux to atmosphere (Drysdale et al. 2003; Liu et al. 2006). The physical and chemical 4 5 properties of water, i.e. hydrochemical conditions and hydrodynamic conditions, are the most important factors for travertine sedimentation. The hydrochemical conditions (for example, 6 concentrations of Ca^{2+} , HCO_3^{-} and CO_2) are factors controlling whether travertine 7 sedimentation can occur and hydrodynamic conditions (including flow rate and thickness of 8 9 flow water and so on) are factors controlling whether travertine sedimentation should occur 10 (Zhou et al. 2010).

In the Jifei geothermal area, travertine precipitated on various landforms. For example, 11 travertine terrace was formed on a slight gradual slope, some travertine cones grew in lowland 12 13 of the river valley and some new travertine deposits on the steep travertine cliff (Fig. 4). 14 Hydrodynamic conditions of the hot waters flowing through various landforms must be much more different. However, no matter what hydrodynamic conditions are, it is hydrochemical 15 conditions that play an important role in causing travertine deposition in the Jifei area. 16 17 Therefore, it is necessary to bring out the main hydrochemical factors for travertine and travertine cones formation in the Jifei area. 18

19 Comparison of the Jifei and the Wenquanxiang hot springs

The Wenquanxiang hot spring, a non-travertine depositing hot spring, occurs 7.7 km far from the Jifei hot spring (Fig. 1). The environmental factors, the climate conditions and hydrological conditions are similar in these two regions. From the geological setting, it is found that both of these two hot springs are restricted by faults and are formed by deep circulation of meteoric water. The outcrop rocks around these two hot springs are also similar. Those rocks are from Paleozoic: carbonate rock, clastic rock and epimetamorphic rock.

Hydrochemical analysis (Table 1) shows that both of the Jifei and the Wenquanxiang hot springs are of low-to-medium temperature ($\leq 90^{\circ}$ C) and of HCO₃-Na·Ca water type hot springs. The major cations are Na⁺+K⁺ and Ca²⁺, accounting for 65.8% and 24.4% equivalent of the cations in the Jifei hot spring versus 64.9% and 30.7% in the Wenquanxiang hot spring. The major anions of both of these two hot springs are HCO₃⁻, constituting 97.4% and 83.9% equivalent of the anions, respectively. The pH values are 6.97 and 7.36 respectively, and the TDS are 993 mg/L for Jifei and 832 mg/L for Wenquanxiang. While Ca^{2+} concentrations are very similar, HCO_3^- and CO_2 contents in the Jifei hot spring are significantly higher than those in the Wenquanxiang hot spring.

5

$$Ca^{2+} + 2HCO_3^{-} \ll H_2O + CO_2^{-} + CaCO_3^{-}$$
 (1)

Based on this equation, it can be stated that calcium carbonate precipitation is related to CO₂ 7 outgassing. In other words, if the concentration of dissolved carbon dioxide is less than the 8 9 dissolved carbon dioxide regulating equilibrium, then precipitation of calcium carbonate will occur. Thus the CO₂ is a very important factor for travertine formation. Previous studies 10 (Clark and Fritz 1997, Liu et al 2003) pointed out that $\delta^{13}C$ value is about -7‰ for 11 atmospheric CO₂, around -25‰ (ranges from -16‰ to -28‰) for CO₂ formed by soil 12 13 organisms or modern biological carbon and almost nil for CO₂ formed by Marine limestone. According to Deines et al. (1974), δ^{13} C values of carbonate and CO₂ gas are related to absolute 14 temperature as follows: 15

$$\delta^{13}C_{HCO_3} - \delta^{13}C_{CO_2} = -4.54 + 1.099 \cdot 10^6 / T^2$$
 (2)

As the temperature of hot spring water in the Jifei area is 79 °C (352.15 K) and $\delta^{13}C_{HCO_2}$ -17 $(\delta^{13}C_{DIC}) = -7.6\%$, the $\delta^{13}C_{CO_2}$ value is -11.92‰ when isotopic exchange reaches equilibrium. 18 However, this value doesn't belong to any values range or close to any value of $\delta^{13}C_{CO_7}$ 19 20 mentioned above. The probable reason is that the CO₂ in the Jifei area originates from at least 21 two sources. Considering the geological setting, the deep fault provides a convenient route for gas ascension from deep earth, i.e. the mantle is one source of CO_2 . In addition, the CO_2 22 coming from metamorphic carbonate rock shouldn't be neglected as temperatures probably 23 reach the calcite decomposition temperature threshold (400 °C) in the deep geothermal 24 reservoir. If there is only one geothermal reservoir, the various temperatures (35-81°C) of 25 different spring vents in the Jifei geothermal area indicate a phenomenon of mixing between 26 27 shallow cold groundwater and deep thermal groundwater. In other words, the hot water was mixed by the shallow cold groundwater dissolving a lot of CO₂ gas from soil organisms before 28

1 it issued as hot spring. In short, the solution CO_2 in the Jifei hot spring water comes from deep 2 source (mantle and metamorphic carbonate rock) and shallow source (soil organisms).

3 If we suppose that the ratio of CO_2 from shallow source is X%, the ratio from deep 4 source is (100-X) %. Based on the isotope mass balance, the following equation can be 5 obtained (Liu et al 2000):

6

$$X\& \ \mathcal{C}_{\text{shallow}}(100 - X) \& \ \mathcal{C}_{\text{deep}} \neq 00 \quad \delta \ \mathcal{C}_{\text{CO}_2} \quad (3)$$

A δ^{13} C of -5.5 \pm 0.5% for mantle carbon was used to clarify CO₂ source in the 7 Huanglong Ravines, Sichuan, China (Yoshimura et al. 2004). In this study, the mean value 8 of $\delta^{13}C_{\text{mantle}}$ and $\delta^{13}C_{\text{metamorphism}}$ was taken as the value of $\delta^{13}C_{\text{deep}}$ and then $\delta^{13}C_{\text{deep}} = -2.75\%$. 9 The $\delta^{13}C$ value of CO₂ from soil organism or modern biological carbon was used as 10 $\delta^{13}C_{shallow}$ value and then $\delta^{13}C_{shallow}\mbox{=-}25\mbox{\%}.$ The calculated results show that about 47.1% 11 CO₂ comes from shallow source and about 52.9% CO₂ comes from deep source in the Jifei 12 geothermal area. The same method was applied to estimate the CO₂ source ratios in the 13 14 Wenquanxiang hot spring and the estimated results are that about 30.7% and 69.3% of CO₂ comes from deep source and shallow source, respectively. It should be noted that maybe 15 more CO₂ comes from deep source in the Jifei geothermal area as influencing factors of 16 17 carbon isotopes widely exist. Use of inert gases (He, Ar etc.) isotopes to further determine the source of CO_2 is necessary and should be carried out in the future works. 18

19 Five kinds of minerals were chosen to analyze their saturation index (Fig. 5) by using PHREEQC-2 program, and the results indicate that the calcite (CaCO₃), aragonite (CaCO₃), 20 dolomite $(CaMg(CO_3)_2)$ of the Jifei hot water are in a saturation state and the saturation 21 indexes for all of them are higher than 0.5. As for the Wenquanxiang hot spring, the calcite 22 and aragonite reach saturation state, however, saturation indexes of these two minerals are 23 less than 0.2. Combined with the difference in hydrochemical compositions in these two hot 24 springs, it is found that the high contents of HCO₃⁻ and CO₂ are one of the major parameters 25 26 that control the travertine and travertine cones formation in the Jifei area. The source of CO₂, half of which comes from deep source, as well as the high saturation indexes of calcite and 27 aragonite mineral are also important factors of travertine and travertine cones precipitation in 28 the Jifei geothermal area. 29

1 Difference in hydrochemistry among the Jifei hot spring and six other travertine springs

2 Six famous travertine springs (Table 2) were selected to compare with the Jifei hot spring 3 in terms of hydrochemical composition. These six travertine springs are the Huanglong spring (Yoshimura et al. 2004, Lu et al. 2000) and the Kangding thermal spring (Liu et al. 2000) in 4 5 Sichuan, China; the Baishuitai spring (Liu et al. 2003) and the Zhongdianxiagei hot spring (Liu et al. 2000) in Yunnan, China; the Pamukkale thermal spring in Turkey (Dilsiz 2005) and 6 7 the Mammoth thermal spring in the Yellowstone national park in the US (McCleskey et al. 8 2004). Huge travertine landscape can be found around all of these springs, and their carbon 9 dioxide mainly comes from the deep earth. However, travertine cones formation occurred only in the Jifei area except one travertine cone formed near the Mammoth thermal spring (Zhou et 10 al, 2010). 11

Hydrochemical and isotopic data of these seven travertine springs are shown in Table 2. 12 Note that these springs temperatures are \leq 90 °C and the TDS values are \leq 3000 mg/L. In other 13 14 words, the travertine is a formation of low-to-moderate temperature geothermal system with low mineralization. The hydrochemical compositions of these spring waters are plotted in a 15 Piper diagram (Fig. 6). Data plots in the diagram demonstrate that these travertine springs 16 water are rich in HCO₃, lack of Cl⁻ and are of HCO₃ type water. The Ca²⁺ and/or Na⁺ cation 17 are dominant for all the spring waters studied and the concentrations of SO_4^{2-} are quite high 18 for the Pamukkale and the Mammoth hot waters which have higher values of TDS than the 19 others'. The difference in hydrochemistry of the travertine springs is probably due to the rock 20 21 type from which the waters issue (Appelo and Postma, 2005). The milligram equivalent percentages of Ca^{2+} and/or HCO_3^{-} are high in all of these springs (Fig. 7) and at least one of 22 them is especially high, not less than 56.3%. The high contents of Ca^{2+} and/or HCO_3^{-} 23 constitute the necessary material conditions for travertine formation. For the Jifei hot spring, 24 Na^+ is the first major cation accounting for 61.5% equivalent to the sum of cations and Ca^{2+} 25 only accounts for 24.4%. HCO_3^- is the major anion and the milliequivalent percentage is 26 97.4%. Thus, the very high milliequivalent percentage of HCO_3^- with not very high 27 milliequivalent percentage of Ca^{2+} is probably the necessary hydrochemical condition for the 28 formation of travertine cones. The chemistry of the Zhongdianxiagei hot spring water is very 29 30 similar to the Jifei hot spring water (Fig. 6) but no travertine cone was found around the

Zhongdianxiagei hot spring. Its milliequivalent percentage of HCO_3^- is 91.7% and Ca^{2+} is 1 30.7%. There is yet a significant difference in $\delta^{13}C_{DIC}$ values between the Jifei and the 2 Zhongdianxiagei springs (-7.6% versus 0.9%). In other words, the CO₂ sources are different 3 in these two areas. The calculated CO_2 in the Jifei geothermal area shows that 47.1% comes 4 5 from shallow source (soil organisms or modern biological carbon) and about 52.9% comes from deep source (mantle and metamorphism). Liu et al. (2000) pointed out that the CO₂ of 6 the Zhongdianxiagei hot spring is mainly from deep source (66% is limestone metamorphic 7 CO_2 and 34% is magmatic CO_2). Therefore, the source of CO_2 is also very important for the 8 travertine cones formation. 9

The CO₂ pressures ($10^{-1.8} \sim 10^{+0.52}$ atm) of these 7 springs are very high, and they are much 10 higher than that of atmosphere $(10^{-3.5} \text{ atm})$ and in the Pammukkale geothermal area, the 11 pressure of CO₂ in the spring water even reaches to thousands of times of the atmospheric 12 pressure. The high P_{CO₂} value shows that strong gas-water-rock interaction effect and boiling 13 phenomena etc. exist under land surface. This high pressure of CO₂ is also a very necessary 14 condition for the travertine formation. The saturation indexes diagram of five minerals for 15 these 7 spring water calculated with the PHREEQC-2 program (Fig. 8) shows that the 16 17 saturation index of calcite floats around zero, i.e., calcite is under or near the saturation state. 18 Aragonite and dolomite are also under or near the saturation state. Thus, the minerals of calcite, aragonite and dolomite in saturation condition are also very important controlling factors for 19 travertine sedimentation. Especially, in the Kangding, Jifei, Mammoth and Zhongdianxiagei, 20 the calcite and aragonite of the hot waters are in saturation state. Saturation index of calcite 21 and aragonite in the Jifei area is larger than in the Zhongdianixiagei area, indicating that 22 calcium carbonate is easier to deposit around the spring in the Jifei area than in the 23 Zhongdianxiagei area. That's why although hydrochemistry of the Zhongdianxiagei and the 24 Jifei springs is similar, travertine cones formed only in the Jifei area. 25

26 Summary and Conclusion

The Jifei hot spring occurs in the form of a spring group with temperature of 35-81°C, pH 6.77-7.27, 993 mg/L TDS and HCO₃-Na·Ca type water in Changning County, southwest Yunnan, China. The total flow is about 10 L/s. Local geological setting shows that the hot

1 spring is restricted to faults and is developed from deep circulation of meteoric water. A 150 m 2 long, 50 m wide and 20 m high travertine terrace has deposited in the Jifei geothermal area. 3 Eighteen travertine cones with heights ranging from 1 m to 7.1 m formed near or on the travertine terrace. Based on the different locations, shapes and formations, the 18 travertine 4 5 cones were classified into 4 categories: (1) Small travertine cones growing on the travertine terrace; (2) The female tower travertine cone constituted by two travertine cones growing side 6 7 by side; (3) The male tower travertine cone, with a 10 cm gravel interlayer at half height; (4) A single growing travertine cone (G_3) on the top of which a hot spring emerges. The whole 8 9 process and evolution of travertine formation can be divided into 3 periods: travertine terrace 10 deposition period, travertine cones' formation period and death period.

The hydrochemical conditions play an important role in causing travertine deposition in 11 the Jifei area. Through the hydrochemical composition comparison of the Jifei hot spring with 12 13 the nearby Wenquanxiang hot spring without travertine sedimentation, it is found that high concentrations of HCO₃⁻ and CO₂ are the key hydrochemical factors for the travertine and 14 travertine cones formation in the Jifei area. The CO₂ half of which comes from deep source is 15 also very important for the travertine and travertine cones formation in the Jifei area. 16 Comparison of six other travertine springs in China, Turkey and the US with the Jifei hot 17 spring shows that the travertine is a formation of low-to-moderate temperature geothermal 18 system with low mineralization. The high contents of Ca^{2+} and/or HCO_3^{-} (\geq 56.3%) and the 19 high pressure of CO_2 (much higher than in atmosphere) constitute the necessary material 20 21 conditions for travertine formation. The high milliequivalent percentage of HCO_3^- (97.4%) with not very high Ca^{2+} (24.4%) is probably the necessary hydrochemical condition for the 22 formation of travertine cones. In addition, the source of CO₂ and the large saturation index of 23 calcite and aragonite of the hot water are also important for travertine cones deposition. 24

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- Fig. 1 Schematic diagram of tectonic systems (after Geological Bureau of Yunnan Province
 1980 and Chinese People's Liberation Army 1980)
- 5 Here the *Eta-type structure* is a part of the Qinghai-Tibet-Yunnan Burma Indonesia eta type
- 6 structure which is shaped as Greek letter "Eta". The *Epsilon-type structure* is the structure
- 7 which is shaped as Greek letter "Epsilon"



Fig. 2 Sketch map of locations of springs and travertine cones of the Jifei hot spring



Fig. 3 Male tower (far) and Female tower (near) travertine cones



Fig. 4 New travertine (*white part*), nearby Zhengtang pool spring (S₇ in Fig. 1)



5 Fig. 5 Saturation index diagram of five minerals for the Jifei hot spring and the Wenquanxing

hot spring



Fig.6 Piper diagram of travertine springs





Fig. 8 Saturation Index variations with respect to five kinds of minerals for travertine springs

Table 1 Hydrochemical compositions (concentrations in mg/L) and isotopic compositions

Items	T (°C)	\mathbf{K}^+	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl	SO4 ²⁻	Free CO ₂	pН	TDS	$d^{13}C_{DIC}{}^a(\%)$
The Jifei hot spring	79.0	20.0	168.0	58.1	14.2	714.0	9.6	2.0	35.2	7.0	993.0	-7.6
The Wenquanxiang hot spring	54.8	8.89	131.0	56.1	4.9	458.0	17.6	45.2	8.8	7.4	832.0	-10.8

9 ^a DIC is dissolved inorganic carobon

1 Table 2 Hydrochemical and isotopical data of seven famous travertine springs										
Country China		China	Turkey	China	America	China	China			
Spring	Huanglong	Baishuitai	Pamukkale	Zhongdianxiagei	Mammoth	Jifei	Kangding			
Sampling	A-1	Spring	PM	Spring No.3	02WA143	spring S ₄	Guanding			
		No.1-1					spring			
Data Source	Liu et al.	Liu et al.	Dilsiz (2005)	Liu et al. (2000)	McCleskey et al.	This study	Liu et al. (2000)			
	(2000);	(2003)			(2004)					
	Yoshimura									
	et al.									
	(2004)									
T (°C)	6.2	10.7	35.4	58	73	79	88			
pН	6.4	6.61	5.81	6.48	6.5	6.97	7.2			
Ec (µs/cm)	-	990	2755	-	2310	1500	-			
TDS (mg/L)	1234.1 ^a	594.8	2018.1 ^a	583.6 ^a	1662.8 ^a	993	976.6			
K ⁺ (meq/L)	0.009	0.028	0.28	0.55	1.32	0.51	1.02			
Na ⁺ (meq/L)	0.106	0.35	2.31	10.51	5.65	7.31	9.14			
Ca^{2+} (meq/L)	10.9	9.55	20.26	5.14	17.1	2.9	9.9			
Mg ²⁺ (meq/L)	1.96	2.26	6.6	0.53	6.32	1.17	0.85			
Cl ⁻ (meq/L)	0.013	0.1	0.4	0.87	4.68	0.27	4.91			
SO4 ²⁻ (meq/L)	0.462	0.52	12.4	0.52	11	0.04	1.2			
HCO_3^- (meq/L)	12.57	11.45	18.32	15.26	13.87	11.7	16			
$\delta^{13}C_{DIC}$ (‰)	-1.51	-1.27	-	0.9	-	-7.6	-1.6			
$P_{CO_2}(atm)$	$10^{-0.65}$	$10^{-0.85}$	$10^{+0.41}$	$10^{-0.32}$	-	-	$10^{-0.8}$			
Accuracy ^a (%)	-0.3	0.4^{a}	1.46	0.2^{a}	3.9	-0.4	-2.8 ^a			
SI_c	-0.22	-0.03	-0.16 ^a	0.31	0.8^{a}	0.66	1.57			
Water-type	HCO ₃ -Ca ^a	HCO ₃ -Ca·Mg l	HCO ₃ ·SO ₄ -Ca·Mg ^a	HCO ₃ -Na·Ca	HCO ₃ ·SO ₄ -Ca·Mg ^a	HCO ₃ -Na·Ca	HCO3·Cl-Ca·Na			

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2 Accuracy charge balance error, SIc e saturation of calcite, DIC dissolved inorganic carobon, - no data

3 ^a Data were calculated calculated by AquaChem or Phreeqc-2 Program

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