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Hydrochemical evolution and reaction simulation of travertine deposition of the Lianchangping hot springs in Yunnan, China

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ABSTRACT

Located in western Yunnan of China, the Lianchangping hot springs are of $SO_4 \cdot HCO_3$–$Ca \cdot Na$ type with total dissolved solids (TDS) ranging from 3560 to 4240 mg/L. Large amounts of travertine are deposited near the hot springs with a variety of travertine morphology, including travertine terrace, slope and ridge. Travertine is precipitating along the slope near one of the spring's thresholds. Chemical compositions of the hot water samples collected along travertine slope show that P_{CO_2}, TDS and contents of HCO_3 and Ca decrease downstream along the travertine slope due to travertine deposition. The initial milliequivalent ratio of $\gamma Ca^{2+}/\gamma HCO_3^-$ is greater than 1.5 before travertine precipitation and there is an increasing trend in the ratio downstream along the travertine slope. High levels of sulphate are probably the result of gypsum dissolution in the sediments widespread in the Lianchangping area. The spring waters issuing from the land surface are slightly supersaturated with respect to calcite, dolomite, fluorite, kaolinite, halite, plagioclase, and carbon dioxide. Hydrochemical evolution of the Lianchangping spring water along the slope is calculated with the Phreeqc Interactive 2.12.5. Sets of minerals and gases reacted in appropriate amounts are recognized through reaction simulation, quantitatively accounting for the variations in chemical compositions, especially depositing minerals along the flow path on the travertine slope.

1. Introduction

Carbonate sinter precipitated from hot springs is called travertine in its narrow sense (Sanders and Friedman, 1967; Pentecost, 1995; Ford and Pedley, 1996; Fouke et al., 2000). Although travertines deposit from hot water only in small parts of hot springs (Zhou et al., 2010), various types of travertines have different crystal fabrics and their compositions are composed of several major kinds of minerals (Fouke et al., 2000; Kele et al., 2011). Hydrogeochemical indicators can be used to study the process of evolution of mineral dissolution and precipitation, such as major ions and gases (Capasso et al., 2001; Vengosh et al., 2002). Earlier studies of travertine generally focus on eye-catching morphological features, travertine fabrics and photomicrographs of travertine fragments (Pentecost, 1999; Fouke et al., 2000; Bonny and Jones, 2008; Di Benedetto et al., 2011; Kele et al., 2011; Özkul et al., 2013). Due to travertine precipitation, hydrochemical compositions of the hot water may change in the course of the hot water flow. Travertine precipitation occurs as the consequence of 3 types of process: physico-chemical, physical, and biological processes. The physico-chemical process is the most important one, including three phases: solid (carbonate), liquid (water), and gas (CO_2) that comprise the carbonate system. Major chemical composition and ionic ratios (Fig. 9) can act as a track-record of water–rock interaction during the groundwater cycle (Edmunds et al., 2003; Han et al., 2010; Pasvanoğlu, 2013). Water dissolves different calcium salts, for example, calcite, dolomite, and gypsum. If the mineral saturation index (SI) is greater than zero, the solution is oversaturated and the mineral tends to precipitate. If the mineral saturation index is below zero, the solution is undersaturated and the mineral will continue dissolving (Andreo et al., 1999). However, CO_2 concentrations move toward equilibrium due to the gradient between atmospheric CO_2 and dissolved CO_2 in thermal water through outgassing, and the thermal water becomes supersaturated with $CaCO_3$ (Malusa et al., 2003). $CaCO_3$ precipitates from the hot water

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and forms travertine deposition. Quantification of mineral dissolution and precipitation based on water chemistry and corresponding reaction simulations is needed to determine the water quality and travertine formation. The travertine deposit shows textural and geochemical characteristics which can be used in the interpretation of geochemical data. $CaCO_3$ abundance and mineralogical compositions of the carbonate are highest (Kele et al., 2008). The $CaCO_3$ content of the travertines ranges from 91.3% to 96.0% with 1.7%–4.1% $CaSO_4$, and traces of other organic matter and acid-insoluble minerals (Pentecost, 1995). Calcite is the most common mineral in travertines, and dolomite is also present in travertines. The white crystalline crust travertine precipitated on the slope of Jandarma travertine at Pamukkale is formed mainly by dendritic calcite. Some travertines contain detrital minerals, including gypsum, kaolinite, and quartz in very small amounts (Özkul et al., 2013). The abundance of precipitates in the Lianchangping hot springs in Yunnan of China varies along the flow path downstream with constantly changing physiochemical conditions. The Lianchangping thermal field can be used as an ideal experimental site depositing travertine from a hot spring, which cannot be achieved in a laboratory. The purpose of the present study is to show the effects of travertine deposition on hydrochemistry of hot water during travertine precipitation from hot springs. The origin of the thermal groundwater is examined by comparing $\delta^{18}O$ and $\delta^{2}H$ of hot water samples with meteoric precipitation (Zhou et al., 2008). High-resolution analysis of fluctuation in hydrothermal water chemistry is important in exploring the characteristics of travertine deposition. Calculated $CaCO_3$ mass transfer rates are also addressed in this paper.

2. Geological and hydrogeological settings

2.1. Physical geography

The Lianchangping hot springs are located 93 km northwest of the city of Dali. The Dali area has a low latitude plateau monsoon climate with an annual mean temperature of 16.3 °C and an average annual rainfall of 693 mm. The average precipitation in Dali varies from 0 mm in November to 192 mm in July and correspondingly, the levels of sunshine per month range from 92 h in July to 270 h in March in 2013. Yunlong county is characterized by a three-dimensional climate with clearly demarcated dry and wet seasons. The county can be roughly divided into 4 climate zones: hot-semi-humid zone, middle-warm-semi-humid zone, cold and humid zone, and alpine humid zone. The temperature decreases by 0.5°C–0.59 °C with an increasing altitude of 100 m, with 6.9 C° in temperature difference between the top and the valley. High altitudes occurs in the east and west regions. Low altitude occurs in the middle region, and declines gradually from north to south, regionally with a sharp altitudinal variation. Annual precipitation and annual temperature (based on the 1962–2013 period) can be easily used to reflect the fluctuation of climate (Fig. 4).

The Lianchangping hot springs (99°28′33.0″E, 26°01′52.6″N at an altitude of 2016 m) is located in the Lianchangping village beside a stream valley about 20 km northeast of Yunlong county. Yunlong county lies in the west part of the Dali area (the Dali Bai Autonomous Prefecture) in northwestern Yunnan province. The western part of the Yunnan province is one of the well-known high-temperature geothermal zones of China. The Lianchangping geothermal field, located near the border between China and Myanmar, occurs in the Tibet–Yunnan geothermal zone (Kearey and Wei, 1993).

The Lianchangping village is situated on top of the fossil travertine terraces. Fossil travertines are exposed in the front of the mountain and were precipitated from old travertine-depositing hot springs water. Old travertine occurrences can be classified into four units (terraces T1, T2, T3 and T4) (Fig. 2) based on field observations of morphology and topography. The gentle fan-shaped terrace (T1), which has the highest elevation of the four fossil travertine terraces, is nearly 60 m above the stream valley, on which most of the village houses are located. The terrace (T2) is shaped like a placanticline (about 350 m long, 65 m wide), 15 m below the terrace (T1). There are three dissolved caves between travertine terraces T1 and T2, and there is a stalagmite (1 m in diameter, 1.5 m high) in one of the caves. Parts of terrace T3 runs directly into the stream valley. Between terraces T3 and T4, travertine ridges are exposed in the study area. One of the travertine ridges varies from 3 to 5 m in height, about 100 m in length.

The huge massif of travertine deposited in the Lianchangping hot springs is characterized by depositing on the left river bank and is mainly influenced by the amount of hydrothermal water in addition to paleoclimate conditions. Various morphologies of travertine developed in the study area, which are regarded as a magnificent natural scene and very valuable geothermal resources (travertine terrace, travertine slope, travertine mound, travertine ridge, and cave and stalagmite). They are also used for providing the indication of evolution of paleoenvironment and paleoclimate conditions.

2.2. Geological setting

In western Yunnan, there are a number of hot springs, some of which (including the Lianchangping hot springs in the Yunlong county) deposit travertines. Yunlong county is located in the middle of the Hengduan Mountains with steep terrains and complicated geological conditions. Two first-order tectonic units of the Tanggula-Changdu–Lanping-Simao fold system and the Gangdisi–Nianqing-Tanggula fold system show an intense structural deformation in folds and fractures (mainly in an NW–NNW direction, partially in SN and NNE) (Fig. 1). Yunlong county lies in the bend of the southeast arcuate structure of the Tetisi-Himalayan tectonic area, in the split zone between the Gondwana and Eurasia (Wang et al., 2013). There are two main fault zones, the western Lancangjiang river fault zone and the eastern Lanpin–Yunlong fault zone.

The Lanping basin, which underwent the stage of back-arc basin/foreland basin from the middle Triassic to the early Cretaceous and is a Cenozoic strike-slip pull-apart basin, is located in the middle part of the Sanjiang orogenic belt between the Jinshajiang river fault and the Lancangjiang river fault. Yunnan province is cut by the NW–SE trending Red River fault zone, which marks the southwestern boundary of the Yangtze platform or South China block (Cheng, 1987; Tapponnier et al., 1990). The occurrence of the strata around the Lianchangping hot springs progresses from west to east. The stratigraphy, which is controlled by tectonics, is characterized by a gradual change from the younger strata to the older ones to the younger ones in the horizontal direction. The formations are old in the middle and new on both sides, centering on the Lianchangping spring. The bedrock is purplish red mudstone and siltstone of Jurassic and gray sandstone mixed with coral black Triassic shale around the Lianchangping hot spring, purple sandstone with glutenite, Cretaceous mudstone in the west, and white Cretaceous sandstone with purple and grey mudstone.

2.3. Hydrogeological characteristics

The Red rock area of Yunnan Province with valley and slope as well as topographic relief is mainly composed of Jurassic,