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Geochemical constraint on origin and evolution of solutes in geothermal springs in western Yunnan, China

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ABSTRACT

Geothermal resources are very rich in Yunnan, China. However, source of dissolved solutes in geothermal water and chemical evolution processes remain unclear. Geochemical and isotopic studies on geothermal springs and river waters were conducted in different petrological-tectonic units of western Yunnan, China. Geothermal waters contain Ca–HCO_3, Na–HCO_3, and Na (Ca)–SO_4 type, and demonstrate strong rock-related trace elemental distributions. Enhanced water–rock interaction increases the concentration of major and trace elements of geothermal waters. The chemical compositions of geothermal waters in the Rehai geothermal field are very complicated and different because of the magma chamber developed at the shallow depth in this area. In this geothermal field, neutral-alkaline geothermal waters with high Cl, B, Li, Rb Cs, As, Sb, and Tl contents and acid–sulfate waters with high Al, Mn, Fe, and Pb contents are both controlled by magma degassing and water–rock interaction. Geothermal waters from metamorphic, granite, and sedimentary regions (except in the Rehai area) exhibit varying B contents ranging from 3.31 mg/L to 4.49 mg/L, 0.23 mg/L to 1.24 mg/L, and <0.07 mg/L, respectively, and their corresponding $\delta^{11}B$ values range from −4.95‰ to −9.45‰, −2.57‰ to −8.85‰, and −4.02‰ to +0.06‰. The B contents of these geothermal waters are mainly controlled by leaching host rocks in the reservoir, and their $\delta^{11}B$ values usually decrease and achieve further equilibrium with its surrounding rocks, which can also be proven by the positive $\delta^{18}O$-shift. In addition to fluid–rock reactions, the geothermal waters from Rehai hot springs exhibit higher $\delta^{11}B$ values (−3.43‰ to +1.54‰) than those yielded from other areas because mixing with the magmatic fluids from the shallow magma. The highest $\delta^{11}B$ of steam–heated waters (pH 3.25) from the Zhenzhu spring in Rehai is caused by the fractionation induced by pH and the phase separation of coexisting steam and fluids. Given the strong water–rock interaction, some geothermal springs in western Yunnan show reservoir temperatures higher than 180 °C, which demonstrate potential for electricity generation and direct-use applications. The most potential geothermal field in western Yunnan is located in the Rehai area because of the heat transfer from the shallow magma chamber.

1. Introduction

The Cenozoic India–Asia collision is the most spectacular tectonic event on earth resulting in the uplift of the Tibetan plateau. The rapid uplift and exhumation in mountain belts have created steep geothermal gradients that can drive hydrothermal circulation (Koons et al., 1998; Derry et al., 2009). More than half of the active continental hydrothermal areas in China are located in Tibet and western Yunnan, wherein many geothermal springs are located in basins, grabens, and deeply incised valleys formed by collisional tectonics.

Hydrothermal activities in western Yunnan include hydrothermal explosions, geysers, boiling springs, hot springs, warm springs, fumaroles, steaming grounds, hydrothermal alterations, and geothermal deposits of calc–sinters or silica sinters. However, present studies on geothermal springs in this area are mainly focused on the Rehai geothermal field (e.g. Liao and Guo, 1986; Zhang et al., 1987, 2008; Bai et al., 1994; Shangguan et al., 2000, 2005; Du et al., 2005; Zhao et al., 2012), which has been developed into a tourist region. As surface manifestation of a hidden magma chamber at a shallow depth (Liao and Guo, 1986; Bai et al., 2001; Zhao et al., 2012), Rehai geothermal fluids exhibit high enthalpy, mantle–sourced helium, and abundant volatile gases

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from degassing magma (Shangguan et al., 2000; Xu et al., 2004; Zhao et al., 2012). Numerous geothermal areas in western Yunnan without obvious mantle contribution show strong hydrothermal manifestations. Although these areas can be developed and used in the future, most of them have never been investigated. No data have been published on the detailed element and isotope compositions of these geothermal waters. The geothermal waters in this study area have high B, As and other harmful or toxic elements contents. For example, The World Health Organization (WHO) guideline values for B and As are 0.5 mg/L and 0.01 mg/L respectively. However, according to our research, B and As concentrations in some geothermal waters exceed these values by dozens of times. Most of the geothermal areas in western Yunnan are close to the residential areas and surface geothermal waters discharge into local rivers directly. Thus, no matter from the perspective of the environmental management or solid deposit formation research in future geothermal resource utilization, it is important to investigate the major and trace element characteristics and their sources in geothermal waters of western Yunnan. The B content of geothermal waters have been used to obtain information on the origin of these waters, to evaluate mixing of hot and cold water in the upflow zones of geothermal systems, and to assess other characteristics of such systems (Arnórsson and Andrésdóttir, 1995). In this study, the content and isotopic composition of B in geothermal waters are combined with other chemical and isotopic data (H and O) to attempt to evaluate the influence of geological factors, such as aquifer lithology, water–rock interaction and shallow magma, on the origin and evolution of solutes in geothermal springs in western Yunnan.

We present new chemical and isotopic data (including major and trace elements, as well as boron, hydrogen, and oxygen isotopes) of 8 river and 16 geothermal water samples obtained from western Yunnan. This study aims to define the hydrochemistry of hot springs and related rivers in western Yunnan, analyze their geothermal fluid evolution, estimate their reservoir temperatures, and determine their isotopic characteristics and fractionation to infer the sources of geothermal waters. This study also discusses the influence of lithology and the hidden magma chamber on the element and isotope compositions, as well as boron isotope fractionation of geothermal fluids. Our findings can be used for future development of geothermal resources in western Yunnan.

2. Geotectonic background and geothermal spring distribution

Western Yunnan comprises high and low topographies in the north and southeast areas, respectively, with altitudes varying from 620 m to 3780 m. Most areas of western Yunnan are characterized by a sharp altitude difference and a series of parallel mountain ranges and rivers from south to northwest. From east to west, our study area can be divided into the Lancangjiang zone, Baoshan Block and Tengchong Block (Fig. 1) (Zhong, 1998; Wang et al., 2006).

The Lancangjiang zone is bounded to the southwest by the volcanic belts of northern Thailand, to the east by the Lanping–Simao Block with an affinity to the Yangtze Craton (Liu, 1993; Zhong, 1998), and to the west by the Baoshan Block. The southern Lancangjiang zone, which runs along the Lancang River down to the border with Laos, is affected by the Paleozoic–Mesozoic collisional tectonics related to closure of the Paleo–Tethys and by the ongoing Himalayan escape tectonics with large strike–slip movements (Hennig et al., 2009). The Lancangjiang tectonic zone comprises an arc magmatic zone, the Lincang granite batholiths, and the Damenglong and Lancang metamorphic rocks (Fig. 1).

The Baoshan and Tengchong blocks are fragments of the Sibumasu continent with stratigraphic and paleontological similarities to Gondwana (Fan and Zhang, 1994; Metcalfe, 1996; Zhong, 1998; Feng, 2002; Fontaine, 2002; Metcalfe, 2002). The Baoshan block comprises Carboniferous and Permian deposits, such as limestone, muddy limestone, sandstone, and shale. In the Tengchong block, the outcrop of the Gaoligong pluton complex is an elongated ductile deformation zone restricted by the Nujiang Fault in the east. The Gaoligong granites share geochemical and chronological similarities with the Gandese granites; hence, these granites represent the eastension of the Gandese belt (Yang et al., 2006). The Tengchong Cenozoic volcanic activity in western Yunnan is considered rift–related after the Indo–Eurasia collision (Chen et al., 2002). Thus, given the plate collision and eastward extrusion of the Tibet Plateau, the geothermal springs in western Yunnan comprise surrounding rocks with similar origins and tectonic evolutions. Some Cenozoic volcanoes in the Tengchong block have not entered the dormant phase until the late Pleistocene era (Zhang et al., 1987). According to the magnetotelluric survey of the Chinese Academy of Sciences (e.g. Bai et al., 1994, 2001; Jiang et al., 2012), the middle of the Tengchong block includes a water-retaining magma chamber with a depth of 7 km and a thickness of 20 km below Rehai. This magma chamber retains copious amounts of residual heat, which warms up the infiltrated meteoric waters and creates hydrothermal convective systems that discharge hydrothermal fluids with complex chemical compositions (Zhang et al., 1987).

The Lancangjiang zone and the Tengchong block are the main geothermal areas in western Yunnan, and several boiling and hot spring fields, including the famous Rehai geothermal field, are located in the metamorphic and crystalline rocks of these two tectonic units. Some low-temperature springs are also distributed in the sedimentary units of the Baoshan block and the Changning–Menglian Belt.

3. Sampling and analysis

Field observation and sampling were conducted in September 2013. Eight river and 16 geothermal spring samples from different areas in western Yunnan were obtained during the investigation (Fig. 1). The geomorphology, stratum, and structure of each sampling site were recorded before sampling, and all these records combined with other related reports were used to classify the stratum structural units of geothermal areas. The sampling locations, major characteristics, and hydrochemical types of all water samples are listed in Table 1. River water samples were obtained from the main rivers and upper reaches of some streams flowing through the geothermal field in various rocks of western Yunnan to determine variations in the chemical components of cold surface waters with meteoric origins. All water samples were filtered through 0.45 μm MF–Millipore membrane filters in the field and stored in high-density polyethylene bottles (50 mL). Prior to sampling, the bottles were cleaned with nitric acid (HNO_3) and rinsed with deionized water. During sampling, the electrical conductivity, pH, and temperature were measured in the field by using standard handheld calibrated field meters. HCO_3 was measured in the field by titration. $SO_4{}^{2-}$ and Cl were analyzed by ion chromatography (IC), whereas Ca, Mg, K, Na, Sr, and Si were determined by ICP–AES with uncertainties of ±5% or better. Trace and rare earth elements were determined by HR–ICP–MS at the Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Sciences. The standard reference materials NBS–1633, SY–4, and Rh were used as internal standards. The analytical reproducibility for trace elements was ±5%.

δD and δ^{18}O analysis was performed at the State Key Laboratory of Hydrology–Water Resources and Hydraulic Engineering, Hohai University. For isotopic analysis the dehydrated water was directly introduced into sample injection system of a Flash EA attached *via* a micro–pump to a Mat 253 mass spectrometry. This technique