Geochemical Constraints on the Origin and Evolution of Spring Waters in the Changdu-Lanping-Simao Basin, Southwestern China

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Abstract: Chemical and isotopic data were measured for 51 leached brine springs in the Changdu-Lanping-Simao Basin (CD-LP-SM), China. The predominance of Cl and Na, saturation indices of carbonate minerals, and Na/Cl and Ca/SO4 ratios of ~1 suggest that halite, sulphate, and carbonate are the solute sources. Integration of geochemical, δ18O, and δD values suggests that springs are mainly derived from meteoric water, ice-snow melt, and water-rock interactions. B concentrations range from 0.18 to 11.9 mg/L, with δ11B values of −4.37‰ to +32.39‰, indicating a terrestrial source. The δ11B-Cl/B relationships suggest B sources of crustal origin (marine carbonates with minor crust-derived volcanics); we did not identify a marine or deep mantle origin. The δ11B values of saline springs (+4.61‰ to +32.39‰) exceed those of hot (~4.37‰ to +4.53‰) and cold (~−3.47‰ to +14.84‰) springs; this has contributed to strong water-rock interactions and strong saturation of dissolved carbonates. Conversely, the global geothermal δ11B-Cl/B relationship suggests mixing of marine and non-marine sources. The δ11B-Cl/B relationships of the CD-LP-SM are similar to those of the Tibet geothermal belt and the Nangqen Basin, indicating the same B origin. These differ from thermal waters controlled by magmatic fluids and seawater, suggesting that B in CD-LP-SM springs has a crustal origin.

Key words: Changdu-Lanping-Simao Basin, δ18O, δD, δ11B, Boron, spring water origin

1 Introduction

The Changdu-Lanping-Simao basin (CD-LP-SM) is a typical rift basin in southwestern China (22°00′–32°00′ N, 96°10′–102°40′ E); it extends NW–SE from southeastern Qinghai Province (Nangqen Basin) in the north, to northern Laos and Vietnam in the south. The basin belongs to the middle and southern parts of the Sanjiang fold system, which are arranged successively from north to south in the same tectonic belt. It is located in the main tectonic zone between the Bitu-Changning and Jingshajiang-Ailaoshan suture belts in an area of intense tectonic deformation. The area hosts more than 1000 springs.

The CD-LP-SM is well-known for its evaporite deposits, which contain gypsum, magnesite, and potash. The Mengyejing Potash Deposit is the only solid potash deposit discovered in China to date. Thus, previous studies have focused on further prospecting using geochemical characteristics to investigate hydrothermal circulation in springs and deposits of the CD-LP-SM (Bo et al., 2014, 2015; Qin et al., 2017). However, the chemical sources and formation environments of springs and evaporite deposits in the CD-LP-SM have rarely been described.

The hydrochemistry of springs is of great importance for understanding solute sources. The δD and δ18O values can fingerprint water recharge sources, the route of water circulation, and the water-rock interaction (Clark et al., 1997; Clayton et al., 1966; Craig, 1961; Tan et al., 2012; Tan et al., 2014). Boron is a relatively light crustal element, which has two stable isotopes (10B and 11B). Owing to its incompatible and soluble character, mobile B in aqueous environments (e.g., springs) suggests that B and its isotopes can provide a distinctive geochemical tracer of chemical sources and formation environments (Kalivoda et al., 2011). The δ11B value of a spring reflects its different sources, depending on local host rocks (Kasemann et al., 2004; Palmer et al., 1990), seawater input (Nomura et al., 1982), B isotope fractionation (McMullen et al., 1961; Schwarcz et al., 1969) and groundwater mixing (Palmer et al., 1990; Yuan et al., 2014). Previous studies have reported on the B isotope characteristics of thermal springs or brines in the Tibet,

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Western Yunnan, Xinjiang, and Inner Qinghai provinces of western China. However, no B isotopic study has been conducted on springs in the CD-LP-SM. This study aims to understand the recharge source of CD-LP-SM springs, and to use hydrochemistry and B isotopes as a tracer to determine the solute source and formation environment of springs and evaporite deposits. Cl and B are highly soluble in thermal waters; Arnórsson et al. (1995) attributed variations in the Cl/B ratios of waters to conservative mixing between several distinct end-members (high Cl/B for seawaters, surface waters and leached brines; intermediate Cl/B for leaching of basalts; low Cl/B for magmatic volatiles). On this basis, a comparative study of B intermediate Cl/B for leaching of basalts; low Cl/B for conservative mixing between several distinct end-members. Qin et al. (1995) attributed variations in the Cl/B ratios of waters to the formation environment of springs and evaporite deposits.

2 Geological and Hydrological Setting

The Sanjiang region of the southeastern Tibet Plateau and the western Yunnan region of southwestern China constitute a collage of Gondwana-derived microcontinental blocks and arc terranes that were accreted together after the closure of the Paleoethys Oceans in the Permo-Triassic (Deng et al., 2014). The Changdu Basin (29°00′−32°00′ N, 96°00′−99°30′ E) is located in the central part of the Sanjiang fold system, northeast Tibet; it has experienced complex tectonic evolution, including a stable craton stage (Sinian Period-D), ocean spreading stage (C-P1), subduction stage (P2−P3), collision stage (T1−E), and Changdu continental rift basin stage (N-Q). The sedimentary formation of the Changdu Block, which is characterized by SM rocks (purple, maroon, or brick red sand and mud), bibby-rocks with interbedded evaporites (gypsum, argillaceous limestone, and halite) from the Jurassic to Eocene, and quartz sandstone, limestone, mudstone dominate, and volcanics distributed in the Carboniferous-Triassic sequence (Du et al., 1997; Lin, 2007).

The Lanping-Simao Basin belongs to the southern section of the Sanjiang fold system in western Yunnan; it is bounded to the west by the Lancangjiang deep fault, and extends along a NW−SE direction from northern Weixi in the north to northern Laos and northern Vietnam in the south. The Lanping-Simao Basin is wider in the south and narrower in the north; the narrowest part is Jingdong, located in the central area. The Lanping sub-basin (25°00′−29°00′ N, 99°00′−101°00′ E) is located to the north of Jingdong, and the Simao sub-basin (23°00′−25°00′ N, 100°30′−102°30′ E) is located to the south of Jingdong (Sun et al., 1990). The Lanping-Simao Basin is an intracontinental polycyclic superimposed basin that has experienced four tectonic evolutionary stages: (1) a continental rift basin (T3−J1); (2) a depression basin (J2−K1); (3) a foreland basin (K); and (4) a strike-slip basin (E). Volcanic rocks are widely distributed in the Devonian-Triassic strata; silicate rocks are primarily distributed in the Carboniferous-Triassic sequence; carbonate rocks are developed in the Devonian and Triassic strata (Fig. 1). Red beds with interbedded evaporates are well developed in Jurassic–Eocene (J-E2) strata, and upper Cretaceous–Paleocene strata are characterized by salt-bearing deposits (Qu et al., 1998).

Our study area included the Nangqen Basin, Tibet geothermal belt, and the western Yunnan geothermal belt (Tengchong-Baoshan-Lincang Block). The Nangqen Basin (32°00′−32°40′ N, 96°00′−97°00′ E) is a typical Tertiary pull-apart basin on the northeastern Qinghai-Tibetan Plateau; it belongs to one part of the Sanjiang fold system (Han et al., 2016). The Tibet geothermal belt (27°00′−35°00′ N, 78°00′−96°00′ E) is bounded to the west by the Ngari area of Tibet, and to the east by the Tengchong geothermal field, which is part of the Himalayan geothermal belt (Li et al., 2014). From east to west, the Western Yunnan geothermal belt (21°00′−26°00′ N, 96°00′−102°00′ E) can be divided into the Lancangjiang zone, Baoshan Block, and Tengchong Block (Wang et al., 2006; Zhong, 1998); the eastern end of the Lanping-Simao Block has an affinity to the Yangze Craton. The lithologies of formations in the Western Yunnan geothermal belt are mainly characterized by carbonatites dominated by SM rocks and volcanics (Qu et al., 1998); a water-retaining magma chamber with a thickness of 20 km and a depth 7 km sits below the middle of the Tengchong block (Bai et al., 1994; Bai et al., 2001; Jiang et al., 2012).

3 Methodology

3.1 Sampling

Field observation and sampling were conducted in November 2014 and January 2015. The sampling locations included 12 springs from the Changdu basin, 18 springs from the Lanping basin, and 21 springs from the Simao basin (Fig. 2).

3.2 Analytical methods

Spring samples were sent to the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences for chemical analysis. Concentrations of Ca2+, Mg2+, K+, Na+, Li+, Sr2+, and B+ were measured using inductively coupled plasm-ooptical emission spectrometry (ICP-OES; IPIS Dionex 120, Dionex, Sunnyvale, CA, USA) with an uncertainty of <±1%. Concentrations of Cl, SO42−, and Br were analysed by ion chromatography (IC; Dionex 120, Dionex, Sunnyvale, CA, USA) with an uncertainty of <±5%; HCO3− and CO32− concentrations were determined via hydrochloric acid titration with phenolphthalein and a mixed solution of methylene blue and methyl red as indicators (uncertainty <±1%).

The δ34O and δD analysis was performed on a MAT 253 stable isotope mass spectrometer (Thermo Fisher Scientific, USA) at the National Research Center for Geoanalysis (NRCGA, PRC), Chinese Academy of Geological Sciences. Values of δ34O and δD are reported relative to SMOW with standard deviations of ±0.2‰ and ±3‰, respectively.

Boron separation and isotopic ratio measurements were performed at the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. The analysis of B isotopic compositions and chemical separation of B followed the procedure described elsewhere (Fan et al., 2015; He et al.,...
Boron was isolated from solution sample via a two-column ion-exchange procedure. Firstly, these spring water samples, containing about 10 µg B and using 2 M NH$_4$OH to remove cations, were passed through a peristaltic pump coupled with a 0.8 mL Amberlite IRA 743 B-specific resin column. The Amberlite IRA 743 B-specific resin was regenerated by 10 mL of 2 M HCl, 20 mL of pure water and 10 mL of NH$_4$H$_2$O and washed to neutral pH prior to use. Then, 10 mL of 75ºC, 0.1 M HCl was used to elute the B from the resin. The eluant was evaporated to 0.5 mL at 60ºC. Secondly, the residue was diluted using pure water (low-B water) and passed through a 0.15 mL cation-anion mixed resin to eliminate HCl and further purify the sample. The eluate was again evaporated to 0.5 mL at 60ºC. Finally, the residue was digested with 6 M HNO$_3$ and 1 M HCl in a microwave oven and analyzed by inductively coupled plasma-mass spectrometry.

Fig. 1. Sedimentary formations and tectonic foundation of the Changdu-Lanping-Simao Basin (CD-LP-SM), China (Du et al., 1997; Jiao, 2013; Lin, 2007; Qu et al., 1998).
to 0.3 mL at 60°C for mass spectrometry analysis after adding an equal amount of mannitol to suppress volatilization of B. Boron isotopes were analysed using a Triton thermal ionization mass spectrometer (TIMS; Thermo Fisher Scientific Inc., U.S.A) and expressed as the δ¹¹B value according to the formula:
\[
\delta^{11}B (\‰) = \left[ \frac{^{11}B/^{10}B}_{\text{sample}} / \frac{^{11}B/^{10}B}_{\text{standard}} - 1 \right] \times 1000
\]
The measured ¹¹B/¹⁰B value of NIST SRM 951 was 4.00514±0.1‰ (2σ, n=6) with a precision of better than ±0.3‰ (2σ).

4 Results

According to the Schukalev and Kurllov (MGMR, 1983) classification, all saline springs in study area are of Na-Cl type; hot and cold springs are of various types, including Na-Cl, Na-Ca-Cl, and Na-Cl-HCO₃ (Fig. 3). On the basis the Valyashko (MGMR, 1983) classification, springs in study area are of chloride type, sodium sulphate subtype, magnesium sulphate subtype, and carbonate type. The springs in the study area have total dissolved solids (TDS) of 2.30–228.25 g/L, and pH of 6.52 to 8.44. There is a wide range of salinities, with mean values of 61.07 g/L for saline springs, 11.79 g/L for hot springs, and 7.30 g/L for cold springs. Cl and Na are the major constituents that generate overall salinity, followed by Ca and SO₄²⁻.

Outlet temperatures range from 40°C to 50°C for hot springs. Stable isotope (δD and δ¹⁸O) values range from −141.48‰ to −72.45‰ and from −17.54‰ to −7.44‰ V-SMOW, respectively (Table 2). The δ¹¹B values of springs show large variations, but can be systematically divided into two types: high δ¹¹B saline springs (+4.61‰ –
and low δ11B hot and cold springs (−4.37‰–+4.53‰ for hot springs and −3.47‰ and +14.84‰ for cold springs). Saline springs in the study area exhibit higher δ11B values than hot and cold spring waters. The chemical and isotopic values of springs in study area are summarized in Table 1 and Table 2.

5 Discussion

5.1 Recharge source

The linear relationship between the δD and δ18O of meteoric water can be used to identify the water source of springs (Clark et al, 1997; Fetter, 2000; Mook, 2006; Wang, 1991; Xun et al., 2008). Springs in the study area show a slight positive oxygen shift (Fig. 5), which may result from isotopic fractionation between deeply circulating meteoric waters and host rocks in geothermal systems, and may have experienced stronger evaporation before recharging the geothermal system. From Fig. 4, the regressed trend lines between the δ18O values and Cl concentration for saline springs from CD-LP-SM show a slight positive correlation or parallel...
Cold springs have not experienced strong evapo-concentration, which indicates that the recharge water of hot and cold springs from CD-LP-SM is dominated not only by δD values of saline springs are dominated not only by different sources of dissolved chemicals (e.g., Cl), but also by strong evapo-concentration. There is a negative correlation for most hot and cold springs from CD-LP-SM, which indicates that the recharge water of hot and cold springs have not experienced strong evapo-concentration or steam separation, but only absorbed dissolved chemicals from different sources. Recharge water may experience removal of isotopically light steam during evapo-concentration, resulting in chlorides enriched liquid and heavy δD, O values.

Fig. 5 shows δD, O vs. δD for all springs in the study area; all data points fall on or close to the global meteoric water line (δD=8δ18O+10; Craig, 1961), the Chinese meteoric water line (δD=7.74δ18O+6.48; Liu et al., 1997), and the southwest of China meteoric water line (δD=5.4δ18O+4.84; Liu et al., 1997), indicating their meteoric origin, which is similar to the geothermal waters in the Tengchong-Baoshan-Lincang Block. The δD and O values of meteoric waters decrease with increasing elevation, and from coastal areas to inland areas. The relationship with altitude and latitude should reflect the oxygen and hydrogen isotopic composition of meteoric water. The relationships between δD and δD, O and latitude can be expressed by the regression lines Y=−0.4X+12.24 (n=49, R²=0.72) and Y=−1.07X+13.02 (n=49, R²=0.82), respectively (Fig. 6b and 6d). Altitude
correlates well with both $\delta D$ and $\delta^{18}O$, with calculated regression lines of $Y=−48.33X−2984.81$ ($n=49$, $R^2=0.75$) and $Y=−377.61X−2694.82$ ($n=49$, $R^2=0.85$), respectively (Fig. 6a and 6c). With the gradual decline in altitude, $\delta^{18}O$ and $\delta D$ values increase gradually from north (Changdu) to south (Simao; Fig. 6). Generally speaking, spring waters from Changdu basin show obviously lower $\delta^{18}O$ and $\delta D$ values than those from the southern part of the research area. The Changdu basin is located in an inland area (northeastern Tibet) with high altitude; therefore, the $\delta^{18}O$ and $\delta D$ values of meteoric waters in Changdu basin are lower than those from the southern part of the research area. The springs in Changdu basin have much more depleted $\delta^{18}O$ and $\delta D$ values than do those in the southern area. Thus, springs in the CD-LP-SM appear to be meteoric in origin, which is reflected in the variation trends of $\delta^{18}O$ and $\delta D$ values.

The isotopic compositions of meteoric waters also exhibit obvious altitudinal effects. Yu et al. (1984) identified negative correlations between $\delta^{18}O$, $\delta D$, and elevation for eastern Tibet, western Sichuan, and Guizhou: $\delta^{18}O = 0.0031H$ (‰) + 6.19, and $\delta D = 0.026H$ (‰) + 30.2, respectively, where H refers to the recharge elevation in metres. It is evident that the $\delta^{18}O$ and $\delta D$ values for springs in CD-LP-SM exhibit obvious negative correlations to altitudinal (Fig. 6). From Fig. 4 and Fig. 5, spring waters from the CD-LP-SM mainly originate from leaching and deep circulation of meteoric water; slight positive oxygen shifts are primarily controlled by deep meteoric water circulation, water-rock interaction, and evapo-concentration. Hydrogen isotopic values can more accurately reflect primary sources of precipitation (Yu et al, 1987).

The mean recharge elevations of spring waters in the study area were calculated to be 3897.8 m for the Changdu Basin of eastern Tibet, 2841 m for Yanjing Town in eastern Tibet and for Lanping Basin in Yunnan, and 2139.1 m for the Simao Basin in Yunnan. The mean altitudes of the main mountains around the study area are >4000 m for the northern Hengduan Mountains, >3000 m for the central Hengduan Mountains, and >2000 m for the Ailao and Wuliang mountains. Thus, the mean recharge elevations of the spring waters are close to the mean altitudes of the surrounding mountains. By contrast, the sampled mean elevations of the spring waters in the study area were found to be ~3500 m for the Changdu Basin, ~2300 m for Yanjing Town, ~2000 m for the Lanping Basin, and ~1060 m for the Simao Basin. Thus, sampled elevations are nearly 400 m lower than the recharge elevations.
altitudes of spring waters in Changdu Basin, 540 m lower in Yanjing Town, 840 m lower in Lanping Basin, and 1080 m lower in the Simao Basin. This suggests that the differential water head from the recharge area to the discharge area for spring water circulation has a long vertical distance, which may be an important factor in driving rapid and deep circulation of spring waters under the action of gravity. Generally, river/lake water does not infiltrate deep geothermal reservoirs or circulate at great depths under the action of gravity; furthermore, it is not the main recharge source of spring waters in the study area. Therefore, the main recharge sources for spring waters in the study area are likely to be rainfall and/or ice-snow melt from the surrounding mountains. With collision of the Indian and Eurasian Plates and the on-going uplift of the Himalayas and Tibetan Plateau, many extension faults have developed, including the Lancangjiang fault, Jinshajiang-Ailaoshan fault, and many smaller scale faults. Ice-snow melt or rainfall water circulate into the deep crust via faults and also ascend back to the surface via faults.

5.2 Sources of dissolved solutes
5.2.1 Inference from hydrochemistry

All of the spring waters investigated in this study were collected from Jurassic-Palaeogene strata, which are characterized by red beds with interbedded evaporites (gypsum, argillaceous limestone, and halite). Springs consistently plot above the seawater evaporation trajectory (SET) on a graph of log Cl vs. log Na (Fig. 7a), with salt springs showing an approximate 1:1 molar ratio. This indicates that springs originate from the dissolution of halite by circulating groundwater, typically generating Cl-rich brines with a high ($\approx$1:1) Na:Cl molar ratio (Fontes et al., 1993); these waters are enriched in Na with respect to Br (Fig. 7b).

Dissolution of Ca-bearing minerals, which mainly include CaSO$_4$, CaCO$_3$, and MgCaCO$_3$, explains the enrichment of Ca relative to Cl and Br (Fig. 7d, 7e), because the dissolution of halite does not affect Ca content. Ion exchange reactions in the shales and sandstones surrounding carbonate reservoirs may also explain an excess of divalent cations. Cerling et al. (1989) noted that when clay minerals are weathered by meteoric water, there is a release of Na ions, previously held as exchangeable ions. On this basis, ankeritization of dolomite and calcite in the carbonate assemblages of the study area could provide a further explanation for the excess Ca.
Dissolution of Mg-bearing minerals, mainly CaMg(CO₃)₂ and MgCO₃, could lead to the enrichment of Mg in spring water, whereas clay mineral adsorption reactions result in Mg depletion. In the study area, Mg is depleted relative to Cl and Br (Fig. 7g, 7h), indicating that Mg is derived from clay mineral adsorption reactions rather than from the dissolution of Mg-bearing minerals.

The dissolution of Li-bearing silicates can lead to the enrichment of Li relative to Cl and Br (Fig. 7j, 7k), because Li has no contribution to diagenesis. Li is enriched in authigenetic magnesites, which are widely distributed in the salt-bearing clastic layer of the Lanping-Simao Basin. On this basis, Li may have derived from the dissolution of authigenetic magnesites when meteoric waters diluted the salt-bearing strata.

K is depleted relative to Cl, but enriched relative to Br; the ratios of K/Br and K/Cl are consistent with the SET (Fig. 7c, 7f). As such, the dissolution of halite and potassium feldspar may have impacted on the K content during water-rock interactions. The distribution of formation waters in a plot of log Cl vs. log Br (Fig. 7i) can indicate the different origins and processes that have affected hydrochemistry. The SET is constant until halite saturation is reached during evaporation of seawater.
Water affected by strong evaporation before halite precipitation can plot to the right and below the SET, because reverse partitioning of Br can cause an excess of Br relative to Cl during halite recrystallization (Land et al., 1981; Stoessell et al., 1986). In contrast, waters derived from halite dissolution and mixed with marine and meteoric waters experience an enrichment of Cl relative to Br and plot beneath the SET (Kharaka et al., 1987). Therefore, springs from the study area, which plot above and along the SET (Fig. 7i), are likely dominated by meteoric mixtures and halite dissolution.

The saturation indices of most springs in the study area with respect to common carbonate minerals (calcite, aragonite, and dolomite) are more than zero (Fig. 8a), estimated by use of PHREEQC, which confirms that the precipitation or dissolution of these three mineral phases should have occurred in study area. This calculation is consistent with the fact that carbonates exist extensively around the springs, and the magnesite saturation index for Leiwaqi is above zero, which is consistent with the existence of Baxia large-scale magnesites. Springs also plot in the calcite and dolomite dissolution field (Fig. 8b), which suggests that dissolution of calcite and dolomite is a minor source of salinity for springs in the study area.

Ternary Ca–SO4–HCO3 phase diagrams show how the chemical compositions of fluids change at the Earth’s surface. Risacher et al. (1996) and Risacher et al. (2003) suggested that Cl–SO4-rich brines may be result from three scenarios: (1) oxidation of sulphide minerals or native sulphur, (2) dissolution of windblown gypsum, or (3) dissolution and recycling of buried gypsum/anhydrite. The sedimentary lithologies of the study area are characterized by red beds with interbedded evaporates of gypsum, argillaceous limestone, and halite from the Jurassic to the Palaeogene; outcrops of gypsum ores are widely distributed in the Changdu-Simao Basin (Qin et al., 2017; Qu et al., 1998), and are characterized by marine origin according to Li (2015). Data for most of the saline springs in study area and all saline springs of Nangqian fall in the Cl-SO4 field (Fig. 9), which may indicate the dissolution and recycling of buried marine gypsum/anhydrite; this may be the main reason for the lack of alkaline HCO3-CO3-rich saline springs in the study area.

It can be seen that the dissolution of halite may be the main source of solutes in the springs, with the dissolution of marine gypsum/anhydrite and carbonatites being a relatively minor source. Lowenstein et al. (2009) noted that deep Ca–Cl brines form during deep circulation of diagenetic or hydrothermal waters, interaction with rocks and sediments at elevated temperatures, and passage of these waters back up to the surface along faults, where they then discharge. As shown in Fig. 9, the majority of saline springs in Yanjing fall into the Ca-Cl field, while some fall into the CI-SO4 field or plot near the chemical divide (the line from calcite to gypsum/anhydrite), which

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**Fig. 8.** (a) Saturation indices of spring waters with respect to calcite, aragonite, and dolomite. (b) Plots of SO4²⁻/Ca²⁺ vs. Mg²⁺/Ca²⁺ in spring waters from the Changdu-Lanping-Simao Basin (CD-LP-SM).

**Fig. 9.** Ternary Ca-SO4-HCO3 phase diagram of springs from the Changdu-Lanping-Simao Basin (CD-LP-SM), Yanjing, and Rehai of Tengchong. Data for Yanjing and Rehai are from Lin (2007) and Zhang et al. (2008), respectively. Data for Nangqian are from Han et al. (2016). Diagram modified from Lowenstein et al (2009).
may indicate that these saline springs mainly recharge from deep Ca–Cl-type waters mixed with meteoric water. Most hot and cold springs in the study area fall into the Na-HCO₃-SO₄ field; although, some fall into the Cl-SO₄ field (Fig. 9); this may reflect origination from meteoric water or from surface water recharge mixed with deep circulation waters (or stronger water-rock interaction). Data from geothermal waters in Tengchong fall into the Na–HCO₃–SO₄ field, very close to the HCO₃-end-member, which may reflect sedimentary lithologies characterized by SM rocks and carbonatites (Zhang et al., 2015; Zhang et al., 2016). It can be concluded that spring waters from the Nangqian-Changdu-Lanping-Simao basin share geochemical affinities, but are quite different from those of Tengchong.

5.2.2 Inference from boron isotopes

Carbonates and crustal-derived volcanic rocks are widely distributed in the CD-LP-SM (Qu et al., 1998); the δ¹¹⁷B values in the springs of the CD-LP-SM are all the same or similar as those of marine carbonates (−5.5% to +23%); Fig. 10; Hemmings et al., 1995; Spivack et al., 1997) and marine sulphate minerals are widely distributed in the CD-LP-SM (Li, 2015). Therefore, we speculate that B in study area springs is most likely derived from marine carbonates and crustal-derived volcanic rocks.

A simple isotopic model to estimate the impacts of water-rock interaction was calculated using the formula

\[ \delta^{11}B_{w,f} = \left( f \times \delta^{11}B_{w,i} + B_r/B_w \times \delta^{11}B_{r,i} + B_r/B_w \times \delta^{11}B_{w,r} \right) / \left( B_r/B_w + f \right) \]

Where \( \delta^{11}B_{w,i}, B_w, \delta^{11}B_{r,i}, \) and \( B_r \) are the initial B isotopic values and B concentrations of host rocks and meteoric waters, respectively; the fractionation factor (\( \delta^{11}B_{w,r} \)) is a constant factor through the water-rock interaction; \( f \), the only critical factor controlling the final isotopic values (\( \delta^{11}B_{w,f} \)), represents the water-rock ratio (W/R; Giggenbach, 1993).

As no B values for meteoric water in the study area are known, the composition of meteoric waters is represented by that of Himalayan rainwater with a B isotopic value of +5.4±1.4‰ and B concentration of 0.09 µmol/l (Rose et al., 2000). Chaussidon et al. (1991) systematically reported on the δ¹⁷B values of Himalayan leucogranites (crustal-derived volcanics), with values ranging from −16.6‰ to −10.3‰. The mean boron isotopic value (−14±3‰) of Himalayan leucogranites was used to represent the mean isotopic composition of crustal-derived volcanic rocks in the study area, and the mean value of 87 mg/L from both granite and silicate source rock can be regarded as the mean B content of crustal-derived volcanic rocks in study area (Rose et al., 2000). As there are no available δ¹¹B values for the carbonates in the study area (Hemmings et al., 1992), we assumed the values of modern marine carbonates (δ¹¹B of +22.1±3‰ and a B concentration of 11.9 mg/L). Fractionation factors of 1‰ (<200ºC), 0.5‰ (300ºC), and 0‰ (>500ºC) were proposed by several past studies (Kaliwoda et al., 2011; Palmer et al., 1992).

Variations in δ¹¹B and B concentrations during water-rock interactions and the results of modelling are shown in Fig. 11a. Modelled evolutionary paths based on two different host rocks (crustal-derived volcanic rocks and marine carbonates) are represented by reaction lines 1 (RL1) and 2 (RL2), respectively. The estimated δ¹¹Bw values of crustal-derived volcanic host rock is about −13, while that of marine carbonates is −23.1‰. Most saline springs fit the marine carbonate reaction line (RL2) remarkably well; most hot and cold springs are distributed in the area delimited by the two reaction lines, but dip closer to RL2, indicating that marine carbonates were the main source of B in the springs; crustal-derived volcanics may represent a minor source. Geothermal waters from the

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Western Yunnan geothermal belt are close to RL1, which indicates that their B mainly originates from the interaction of crustal-derived volcanics and marine carbonates. Thus, there are different B sources for the waters of CD-LP-SM and the Western Yunnan geothermal belt.

Two mixing curves were fitted according to the binary mixture equation and the value range of the terminal eigenvalue; the parameters of end-members are presented in Table 3. In the B concentrations vs. $\delta^{11}$B plot (Fig. 11b), all springs in the Changdu-Simao Basin fall on or around the marine carbonate end-member, indicating that the main B sources of springs are marine carbonates; crustal-derived volcanics are a minor source and there are no marine or deep mantle sources.

The lower $\delta^{11}$B values of hot spring waters in the Changdu-Simao Basin may reflect two factors: (a) weak water-rock interactions (Gonfiantini et al., 2006; Vengosh et al., 1998); and/or (2) dissolved carbonates resulting from CO$_2$ degassing in saline springs, which are more saturated than hot and cold springs.

With regards to weak water-rock interactions, the $\delta^{11}$B values of springs in the study area are mainly controlled by the leaching of reservoir host rocks (marine carbonates and volcanic rocks). According to Bo et al. (2015), the ranges of estimated reservoir temperatures for saline, cold, and hot springs are 65.1°C–109.0°C, 37.8°C–64.4°C, and 65.5°C–144.1°C, respectively. The circulation depths of hot (848.9–2833.8 m) and cold (1140.5–2468.7 m) springs are much shallower than those of saline springs (2505.3–4701.6 m). Furthermore, saline springs in the Lanping-Simao Basin have experienced more water-rock interactions than have the cold and hot springs; thus, the $\delta^{11}$B values of hot and cold springs are lower than those of saline springs.

With regards to dissolved carbonates caused by CO$_2$ degassing in saline springs, spring waters in the study area have high HCO$_3^-$ concentrations. When spring waters move upward to the surface, decreasing water pressure causes CO$_2$ degassing, which in turn determines the transformation of HCO$_3^-$ to CO$_3^{2-}$ at constant alkalinity:

$$2\text{HCO}_3^- = \text{CO}_3^{2-} + \text{CO}_2(g) + \text{H}_2\text{O}$$

With the emission of CO$_2$ from spring waters, a number of reactions should occur:

$$\text{CO}_3^{2-} + \text{Ca}^{2+} = \text{CaCO}_3(s)$$
$$\text{CO}_3^{2-} + \text{Ca}^{2+} + \text{Mg}^{2+} = \text{CaMg(CO}_3)^2(s)$$
$$\text{CO}_3^{2-} + \text{Mg}^{2+} = \text{MgCO}_3(s)$$

These reactions result in increasing CO$_3^{2-}$ concentration and decreasing Ca$^{2+}$ and Mg$^{2+}$ concentrations in the spring waters.

The saturation indices of springs in the study area with respect to common carbonate minerals (i.e., calcite, aragonite, dolomite, and magnesite), calculated by use of geochemical code PHREEQC, confirm that the precipitation of three mineral phases (calcite, aragonite, dolomite) should have occurred in the study area; magnesite likely precipitated in the Leiwuqi area. As saline springs have experienced a greater degree water-rock reactions, the $\delta^{11}$B values of saline springs are lower than those of hot and cold springs.

Fig. 11. Variations in $\delta^{11}$B (‰) and B concentrations for springs in the Changdu-Lanping-Simao Basin (CD-LP-SM) and Western Yunnan geothermal belt.

Water-rock reaction lines (RL1 and RL2) show the evolution of water-rock interactions with different host rocks (marine carbonates and crustal-derived volcanics, respectively).

Fig. 12. Relationship between HCO$_3^-$ concentrations and $\delta^{11}$B values in springs of the Changdu-Lanping-Simao Basin (CD-LP-SM).
Cl/B ratios and Chausidon et al., 1995). The positive correlation between $\delta^{11}\text{B}$ values and low HCO$_3^-$ contents, while cold and hot springs are characterized by lower $\delta^{11}\text{B}$ values and higher HCO$_3^-$ contents. These findings indicate that B isotope fractionation occurs to a greater degree in saline springs than it does in hot and cold springs; the $\delta^{11}\text{B}$ values of saline springs are greater than those of hot and cold springs.

5.3 Comparison with springs worldwide

Present-day seawater has a constant $\delta^{11}\text{B}$ value of $+39.5\%o$ and a B concentration of 4.5ppm (Spivack et al., 1987). The $\delta^{11}\text{B}$ values of continental crust range from $-20\%o$ to $-7\%o$, while those of the primitive mantle are also relatively low $-10+2\%o$ (Chausssidon et al., 1992; Chausssidion et al., 1995). The positive correlation between Cl/B ratios and $\delta^{11}\text{B}$ values in springs worldwide can be used to determine the origin of B. Marine sources have high $\delta^{11}\text{B}$ values and high Cl/B ratios, while terrestrial sources are characterized by lower $\delta^{11}\text{B}$ values and high Cl/B ratios (Lü et al., 2014). We compared our data to that of geothermal systems worldwide and found binary mixing between a continental end member and a marine end member (Fig. 13).

Thermal springs in India, the Dead Sea (Israel), the Izu Peninsula (central Japan), and northeastern Taiwan show different B concentrations (0.23ppm–0.25ppm for India, 20.54ppm–31.35ppm for the Dead Sea, 0.02ppm–2.01ppm for the Izu Peninsula, and 3.81ppm–4.64ppm for Taiwan) and $\delta^{11}\text{B}$ values ($+34\%o$ to $+41\%o$ for India, $+52.2\%o$ to $+55.7\%o$ for the Dead Sea, $+36.2\%o$ to $+42.6\%o$ for the Izu Peninsula, and $+33.27\%o$–$+36.94\%o$ for Taiwan). The $\delta^{11}\text{B}$ values in these areas are all higher, reflecting the influence of seawater. Thus, we can easily differentiate B sources in springs of the study area, which are of terrestrial origin.

There are several factors affecting the discrete distribution of $\delta^{11}\text{B}$-Cl/B relationships in non-marine spring waters worldwide, including rock type, tectonic structures, and geological setting. However, although springs in study area have similar $\delta^{11}\text{B}$ values to those seen in most no-marine thermal waters worldwide (Fig. 13), their origins are not identical. A large amount of Cl is caused by salt solution and leads to high Cl/B ratios; high Cl/B ratios are seen in springs of the study area, exceeding those of other geothermal systems worldwide.

The $\delta^{11}\text{B}$ values ($-6.7\%o$–$+25.0\%o$) and Cl/B systematics of geothermal waters from Iceland are primarily dominated by the composition of the local basalt (i.e., a mantle source; Aggarwal et al., 2000). The $\delta^{11}\text{B}$ values ($-3.1\%o$–$+3.9\%o$) of the Ngawha geothermal system, New Zealand, can be accounted for by low water-rock interaction, with B being derived from B-enriched basement (i.e., mantle origin); no seawater sources are involved (Aggarwal et al., 2003; Romain Millot, 2011). The B concentrations (17.5ppm–82.1ppm) and $\delta^{11}\text{B}$ values ($-6.7\%o$ to $-1.9\%o$) of geothermal waters from the Taupo Volcanic Zone, New Zealand, are in agreement with those of Ngawha geothermal field, and are mainly derived from water-rock interaction involving magmatic rocks with no seawater input (Romain Millot, 2011). The B in geothermal fluids of Yellowstone National Park (Wyoming) primarily originate from rhyolitic wall rocks supplied by a mantle plume (Palmer et al., 1990). Although these examples show similar data to the CD-LP-SM springs, the B origin in springs of the study area is different, reflecting a unique geological background and wall-rock type. In addition, the wide distribution of crustal -derived He indicates that water circulation in the Laping -Simao Basin and northern Laos may be limited above the upper mantle (Bo et al., 2015). Thus, B in springs from the study area is unlikely to have a deep mantle source; instead, a primarily crustal source (volcanic rocks and marine carbonates) is more likely.

Hot springs in Indonesia and France have shown similar $\delta^{11}\text{B}$ values but different Cl/B values to the thermal springs in our study area; this reflects different water-rock interactions and wall-rock types. The $\delta^{11}\text{B}$ values ($-2.4\%o$–$+28.7\%o$) and Cl/B values of most geothermal hot springs on Java, Indonesia, are dominantly affected by groundwater mixing (Purnomo et al., 2016). For thermal waters in the Limagne Basin, France, B is mostly derived from a granitic reservoir (Millot et al., 2007). The $\delta^{11}\text{B}$ values in thermal springs from the northern Rift Valley, Israel, are similar to the saline springs in our study area. Previous studies have indicated that B is derived from
three sources: (1) dilution of deep-seated trapped CaCl$_2$ brines, consistent with the springs from Yanjing in the study area; (2) meteoric cyclic salts; and (3) interactions of groundwater with carbonate and/or clay minerals in aquifer rocks (Vengosh et al., 1994), consistent with the water-rock interactions in the study area. Consequently, we speculate that B in the study area comes from B-enriched host rocks of a shallow crustal source. Seawater and mantle processes cannot provide abundant B for these thermal waters.

Springs in the Tibet geothermal belt, Western Yunnan geothermal belt, and Nangqen Basin exhibit varying thermal waters. We speculate that B in the study area comes from B-water-rock interactions in the study area. Consequently, reflecting weak water-rock interactions and weak cold springs are lower than those of saline springs, springs in the CD-LP-SM. The mantle sources, which differs from the B sources of magma (Zhang et al., 2016). Thus, the B in springs from reservoir host rocks (large granitic batholiths and metamorphic rocks) and by magmatic fluids from shallow magma (Zhang et al., 2016). Thus, the B in springs from the Western Yunnan geothermal belt has both crustal and mantle sources, which differs from the B sources of springs in the CD-LP-SM. The $\delta^{11}$B values of springs in marine carbonates range from +10‰ to +30‰ (Ishikawa et al., 1993; Vengosh et al., 1991a), higher than those of primitive mantle (-12‰ to -8‰), springs in metamorphic rocks (-9.0‰ to -7.4‰), and igneous rocks (-17‰ to -2‰; Barth, 1993; Jiang, 2000).

6 Conclusions

(1) According to their chemical characteristics, springs in the CD-LP-SM are leached brines. Dissolution of halite, carbonates, and gypsum/anhydrite are the principle sources of solutes, and $\delta^{18}$O and $\delta^{13}$C values indicate that springs waters are mainly derived from meteoric water or ice-snow melt water from surrounding mountains combined with water-rock interactions and deep meteoric water circulation.

(2) The B contents and $\delta^{11}$B values (+4.61‰~+32.39‰ for saline springs, -4.37‰~+4.53‰ for hot springs, and -3.47‰~+14.84‰ for cold springs) of springs in the CD-LP-SM vary significantly, confirming their terrestrial origin. However, both values are similar to those of the Tibetan geothermal area and the Nangqen Basin, indicating the same B source. The $\delta^{11}$B values of hot and cold springs are lower than those of saline springs, reflecting weak water-rock interactions and weak saturation of dissolved carbonates.

(3) The $\delta^{11}$B-Cl/B and $\delta^{11}$B-B binary mixing relationship suggest that B in the spring waters may originate from interaction with marine carbonates and volcanic rocks. These characteristics are similar to those of other geothermal waters of crustal origin, but quite different from geothermal waters with marine and deep mantle sources. The mixing process between marine and non-marine sources can be illustrated in a $\delta^{11}$B-B/Cl/B diagram of thermal waters around the world, on which springs in the CD-LP-SM are differentiated from those with mantle and marine sources. In summary, we conclude that B in the springs of the CD-LP-SM are primarily of a crustal source (marine carbonates and volcanic rocks); they do not have marine or deep mantle sources. Interestingly, springs of the CD-LP-SM have the largest ranges in B contents and $\delta^{11}$B values, which could reflect the unique tectonic history of the CD-LP-SM.

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