# 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/SO<sub>4</sub> ratios of ~1 suggest that halite, sulphate, and carbonate are the solute sources. Integration of geochemical,  $\delta^{18}$ O, and  $\delta D$  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  $\delta^{11}$ B values of -4.37% to +32.39%, indicating a terrestrial source. The  $\delta^{11}$ B-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  $\delta^{11}$ B 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  $\delta^{11}$ B-Cl/B relationship suggests mixing of marine and non-marine sources. The  $\delta^{11}$ B-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,  $\delta^{18}$ O,  $\delta$ D,  $\delta^{11}$ B, Boron, spring water origin

Citation: Qin et al., 2019. Geochemical Constraints on the Origin and Evolution of Spring Waters in the Changdu-Lanping-Simao Basin, Southwestern China. Acta Geologica Sinica (English Edition), 93(4): 1097–1112. DOI: 10.1111/1755-6724.13853

# **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  $\delta D$  and  $\delta^{18}O$  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  $({}^{10}B$  and  ${}^{11}B$ ). 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 (Kaliwoda et al., 2011). The  $\delta^{11}$ B 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 isotope characteristics and Cl/B ratios in the springs of the CD-LP-SM, the surrounding area, and other geothermal fields is needed to explain the large-scale characteristics of B isotope in springs of the CD-LP-SM.

# 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 Paleotethys 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-P<sub>1</sub>), subduction stage (P<sub>2</sub>-P<sub>3</sub>), collision stage ( $T_1$ -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), bibbey-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, to the east by the Jinshajiang-Ailaoshan 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  $(T_3-J_1)$ ; (2) a depression basin  $(J_2-J_1)$  $K_1$ ; (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  $(J-E_2)$  strata, and upper Cretaceous– Paleocene strata are characterized by salt-bearing deposits (Qu et al., 1998).

Our study area included the Nanggen 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 (Lü et al., 2014). From east to west, the Western Yunnan geothermal belt (21°00'-26°00' N, 96°  $00'-102^{\circ}00'$  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 Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, Sr<sup>2+</sup> and B<sup>3+</sup> were measured using inductively coupled plasmaoptical emission spectrometry (ICP-OES; IPIS Intrepid II XSP, Thermo Elemental, Madison, WI, USA) with an uncertainty of <±1%. Concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Br<sup>-</sup> were analysed by using ion chromatography (IC; Dionex 120, Dionex, Sunnyvale, CA, USA) with an uncertainty of <±5%; HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> concentrations were determined via hydrochloric acid titration with phenolphthalein and a mixed solution of methylene blue and methyl red as indicators (uncertainty <±1%).

The  $\delta^{18}$ O and  $\delta$ D analysis was performed on a MAT 253 stable isotope ratio mass spectrometer (Thermo Fisher Scientific, USA) at the National Research Center for Geoanalysis (NRCGA, PRC), Chinese Academy of Geologecal Sciences. Values of  $\delta^{18}$ O and  $\delta$ D are reported relative to SMOW with standard deviations of  $\pm 0.2\%$  and  $\pm 3\%$ , 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.,

Study area										
	Lanping-Simao Block									
period	Changdu Block	Western Margin	Middle Par	Eastern Margin						
Е <sub>2-3</sub> Е <sub>2</sub>	f.Gongjue red sandy and muddy(SM)rocks, bibbey-rocks with		f.Mengla light grey and claret-colored sandstone with interbedded siltstone f.Denghei violet and brown red sandstone and mud rocks							
E <sub>1</sub>	(gypsum, argillaceous limestone and halite)		f.Mengyejing gypsum and salt-bearing mudstone and sandstone, salt-bearing formation in the top and bottom							
К2	f.Hutousi f.Nanxin brick-red and brown-red medium-grained calcareous sandstone and quartzy sandstone		f.Pashahe light grey feldspar-quartz sandstone with interbedded feldspar-quartz sandstone f.ManGang red quartz sandstone with interbedded siltstone and mudstone							
к <sub>1</sub>	f.Jingxing mallve quartz sandstone, mud rocks and argillaceous siltstone		f.Jingxing light-o sandstone with inte variegated mud							
J <sub>3</sub>	f.Xiaosuoka quartzy sandstone, lithic quartz sandstone, siltite and shale	f.Bazhulu claret-colored mudstone, silty mudstone, siltstone and fine grain quartz sandstone								
J <sub>2</sub>	f.Dongdaqiao Quartz fine sandstone with interbedded siltite f.Tutuo shale with interbedded lithic quartz sandstone and siltite	f.Hepingxiang(western basin) f.Huakaizuo (eastern basin) claret-colored and greyish-purple fine sandstone in the middle and bottom, variegated mudstone in the top								
J <sub>1</sub>	f.Chalangga lithic quartz sandstone and quartzy sandstone	f.Zhangkezhai(western basin) f.Yangjiang (eastern basin) red mudstone and silty mudstone with interbedded fine grain quartz sandstone								
T <sub>3</sub>	f.Bagong shale, feldspar-quartz sandstone and siltite with interbedded carbonaceous shale and coal series f.Bolila calcarenitic dolomite, silty-fine dolomite and bioclastic limestone f.Jiapeila amaranthine conglomerate, sandstone and silty mudstone	odingxi f.Manghuai h sandy and muddy (SM) led in the bottom	f.Dapingzhang yellow and purple siltstone f.Weiyuanjiang greyish-green mudstone with interbedded argillaceous limestone	f.Waluba ash black shale with interbedded siltstone and fine sandstone f.Sanhedong limestone, gray and black shale f.Waigucun variegated sand-mudstone with interbedded evaporates	uiyibi f.Pantiange nterbedding SM rocks ate silicalites					
T <sub>2</sub>	f.Walasi sandstone, slate and conglomerates dominate and volcanics in the bottom	f.Manghuihe f.Xia volcanics dominate, wit rocks interbed	f.Choushui gray calcareous mudstone with interbedded limestone and argillaceous limestone f.Huangzhulin limestone with interbedded mudstone in the top, gray purple sandstone and siltstone with interbedded limestone in the bottom		f.Gaoshanzhai f.C volcanics dominate, ii and radioloc					
T <sub>1</sub>	f.Malasongduo volcanic tuff, rhyolite with interbedded sandstone and shale	P	Р	P,D	Р					
	oceanic crust	divers	zent unconformity	<ul> <li>parallel unconformity</li> </ul>						

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).

2013; Wei et al., 2014). Boron was isolated from solution sample via a two-column ion-exchange procedure. Firstly, these spring water samples, containing about 10  $\mu$ g B and using 2 M NH<sub>4</sub>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  $NH_3$ · $H_2O$  and washed to neutral pH prior to use. Then, 10 mL of 75°C, 0.1 M HCl was used to elute the B from the resin. The eluant was evaporated to 0.5 mL at 60°C. 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



Fig. 2. Geological sketch map and sampling sites in the Changdu-Lanping-Simao Basin (CD-LP-SM). A, denotes the Changdu Basin; B, denotes the Lanping Basin; C, denotes the Simao Basin; D, denotes the Tengchong-Baoshan-Lincang blocks.

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  $\delta^{11}$ B value according to the formula:

 $\delta^{11}B$  (‰) =[(<sup>11</sup>B/<sup>10</sup>B)<sub>sample</sub>/((<sup>11</sup>B/<sup>10</sup>B)<sub>standard</sub>-1]×1000 The measured <sup>11</sup>B/<sup>10</sup>B value of NIST SRM 951 was 4.00514±0.1‰ (2 $\delta$ , n=6) with a precision of better than ±0.3‰ (2 $\sigma$ ).

#### 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-HCO<sub>3</sub> (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  $SO_4^{2-}$ . Outlet temperatures range from 40°C to 50°C for hot springs. Stable isotope ( $\delta D$  and  $\delta^{18}O$ ) values range from -141.48‰ to -72.45‰ and from -17.54‰ to -7.44‰ V-SMOW, respectively (Table 2). The  $\delta^{11}$ B values of springs show large variations, but can be systematically divided into two types: high  $\delta^{11}B$  saline springs (+4.61‰-

Sample ID	Sample type	Sample site	TDS(mg/L)	nH	Water type	Water type
Sample ID	Sample type	Sample site	TDS(IIIg/L)	pm	(Valyashko's classification)	(Schukalev's classification)
CD 01	Saline spring	Jiya Village, Leiwugi, Changdu	167557.49	7.56	Chloride type	Na-Cl
CD 02	Saline spring	viju (mage, Dernadi, Changad	228645.99	7.25	Chloride type	Na-Cl
CD 03	Saline spring	Zaochi Village, Leiwugi, Changdu	71123.49	7.49	Chloride type	Na-Cl
CD 04	Saline spring		69629.9	7.67	Chloride type	Na-Cl
CD 05	Saline spring		36682.99	7.1	Chloride type	Na-Cl
CD 06	Saline spring	Chatuo Village, Gongjue, Changdu	36738.03	7.1	Chloride type	Na-Cl
CD 07	Cold spring		9840.61	7.63	Chloride type	Na-Ca-Cl
CD 08	Saline spring	Youzha Village, Gongiue, Changdu	38155.91	7.31	Chloride type	Na-Cl
CD 09	Saline spring	Touzha vinage, Gongjue, Enanguu	38165.73	7.34	Chloride type	Na-Cl
CD 10	Hot spring		30866.71	7.51	Chloride type	Na-Cl
CD 11	Hot spring	Yanjing Village, Naxi, Changdu	30568.03	7.58	Chloride type	Na-Cl
CD 12	Hot spring		30254.73	7.49	Chloride type	Na-Cl
LP 01	Saline spring	Shangjing Lapping	133493.52	6.93	Chloride type	Na-Cl
LP 02	Saline spring	Shangjing, Lanping	131285.53	7.28	Chloride type	Na-Cl
LP 03	Saline spring	Viging Lanning	8218.85	8.05	Chloride type	Na-Cl
LP 04	Saline spring	Alajing, Lanping	23104.31	7.69	Chloride type	Na-Cl
LP 05	Saline spring	Leomuijng Leoping	8859.21	7.76	Chloride type	Na-Cl
LP 06	Saline spring	Laomujing, Lanping	8664.95	7.5	Chloride type	Na-Cl
LP 07	Saline spring	Shundangjing, Yunlong	165728.16	6.89	Chloride type	Na-Cl
LP 08	Saline spring	Shijing, Yunlong	81235.55	7.24	Chloride type	Na-Cl
LP 09	Cold spring	Tangdeng Village, Vunlong	6381.99	7.32	Sodium sulfate subtype	Na-Cl
LP 10	Cold spring	Tangueng vinage, Tuniong	6494.59	6.77	Sodium sulfate subtype	Na-Cl
LP 11	Saline spring	Nuodeng Village, Yunlong	20315.2	7.12	Chloride type	Na-Cl
LP 12	Saline spring	Daiing Yunlong	58433.24	7.81	Chloride type	Na-Cl
LP 13	Cold spring	Dajing, Tuniong	2883.53	8.44	Magnesium sulfate subtype	Na-Cl
LP 14	Saline spring	Shangxiaojing, Yunlong	141182.5	7.31	Sodium sulfate subtype	Na-Cl
LP 15	Saline spring	Tianeriing Vunlong	15267.02	7.54	Magnesium sulfate subtype	Na-Cl
LP 16	Saline spring	Thanorjing, Tuniong	14813.73	7.56	Magnesium sulfate subtype	Na-Cl
LP 17	Hot spring	Chatingsi Yunlong	6869.6	6.52	Sodium sulfate subtype	Na-Cl
LP 18	Hot spring	Chullingsi, Fullong	7966	6.68	Sodium sulfate subtype	Na-Cl
SM 01	Saline spring	Xiaojing Village Zhenvuan	60746.66	7.23	Magnesium sulfate subtype	Na-Cl
SM 02	Saline spring	inacjing (inage, zhen) aan	66189.56	7.25	Magnesium sulfate subtype	Na-Cl
SM 03	Saline spring		63147.87	7.03	Magnesium sulfate subtype	Na-Cl
SM 04	Saline spring	Dajing Village, Zhenyuan	50435.48	6.93	Chloride type	Na-Cl
SM 05	Saline spring		48242.15	7	Chloride type	Na-Cl
SM 06	Saline spring	Naguohe Village Zhenvuan	13642.77	7.15	Chloride type	Na-Cl
SM 07	Saline spring	Tugaone Thuge, Zhenyuun	13348.4	6.89	Chloride type	Na-Cl
SM 08	Saline spring	Dahebian Village Zhenvuan	22020.66	6.78	Chloride type	Na-Cl
SM 09	Saline spring	Buileolair Vinage, Ellenyaan	15339.28	6.93	Chloride type	Na-Cl
SM 10	Saline spring	Moging Village Zhenvuan	34308.9	7.4	Chloride type	Na-Cl
SM 11	Saline spring	woqing vinage, Zhenyuan	34350.4	7.57	Chloride type	Na-Cl
SM 12	Hot spring	Mangka Village Tinggu	9874.81	7.1	Chloride type	Na-Cl
SM 13	Hot spring	Wangka Vinage, Jinggu	10542.45	7.17	Chloride type	Na-Cl
SM 14	Hot spring		2296.57	7.06	Magnesium sulfate subtype	Na-Cl
SM 15	Hot spring	Huanle Village Jinggu	5115.51	6.7	Magnesium sulfate subtype	Na-Cl
SM 16	Hot spring	Traume (muge, singgu	6439.69	6.56	Magnesium sulfate subtype	Na-Cl
SM 17	Hot spring		6461.08	6.65	Magnesium sulfate subtype	Na-Cl
SM 18	Saline spring	Xiangyan Village, Jinggu	96324.59	7.38	Chloride type	Na-Cl
SM 19	Hot spring	Manzhongtian Zhengdong	3401.6	6.82	Carbonate type	Na-Cl-HCO <sub>3</sub>
SM 20	Hot spring	munzhonguun, zhonguong	2615.92	6.84	Carbonate type	Na-Cl-HCO <sub>3</sub>
SM 21	Cold spring	Mantan, Zhengdong	10894.62	7.44	Magnesium sulfate subtype	Na-Cl

Table 1 Field observations, TDS, pH, and water type of spring waters in the CD-LP-SM

+32.39‰) and low  $\delta^{11}$ B 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  $\delta^{11}$ B 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  $\delta D$  and  $\delta^{18}O$  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 evapo-concentration before recharging the geothermal system. From Fig. 4, the regressed trend lines between the  $\delta^{18}$ O values and Cl concentration for saline springs from CD-LP-SM show a slight positive correlation or parallel

Table 2 Chemical and isotopic data of spring waters in the CD-LP-SM Basin

	Na	Ca	К	Mg	Li	Sr	Br	В	Cl	SO4	HCO <sub>2</sub>	$\delta^{18}$ O	$\delta D$	$\delta^{11}B$
Samples	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰	‰	‰
CD 01	64230	750	410	200	3.7	16.65	17.75	2.99	99590	2050	290	-15.33	-120.93	30.21
CD 02	87650	1030	560	270	4.74	22.87	29.86	3.86	135970	2810	290	-15.98	-125.83	32.39
CD 03	25900	1110	240	230	1.45	22.47	8.53	3.05	40760	2460	360	-15.23	-119.19	24.96
CD 04	25360	1090	240	230	1.33	22.48	8.12	2.28	39990	2330	350	-15.05	-137.78	25.6
CD 05	10940	1820	80	750	0.92	33.75	0.06	1.14	20460	2430	160	-17.3	-134.7	10.21
CD 06	10860	1810	90	820	0.99	36.75	0.08	1.53	20470	2470	170	-17.24	-134.26	10.71
CD 07	2470	900	40	140	0.41	28.45	0.01	0.68	4850	1190	210	-16.96	-129.17	9.48
CD 08	12710	1250	90	340	0.57	22.77	0.06	1.89	20630	2890	190	-17.33	-134.94	4.99
CD 09	12750	1260	90	320	0.56	22.02	0.04	1.87	20720	2790	200	-17.54	-141.48	4.61
CD 10	10330	900	630	120	11.84	34.48	2.02	11.5	17730	690	330	-12.76	-107.61	-3.88
CD 11	9410	940	630	590	12.11	34.85	1.88	11.9	17710	730	410	-13.22	-105.12	-4.37
CD 12	9580	840	590	520	10.26	29.98	1.99	10.21	17660	610	330	-12.87	-99.47	-3.65
LP 01	47870	1640	900	510	1.91	15.74	31.57	6.56	76250	5270	180	-12.99	-110.38	23.95
LP 02	47940	1610	1120	490	2.68	15.42	29.25	6.64	75030	5030	200	-12.18	-110.6	21.29
LP 03	2990	110	50	20	0.07	1.51	2.69	0.25	4650	270	110	-12.45	-104.73	28.09
LP 04	8390	270	130	50	0.27	4.15	3.61	0.46	13210	760	150	-12.61	-101.8	28.31
LP 05	3240	180	40	30	0.1	2.09	1.36	0.18	4980	320	140	-12.59	-101.68	26.63
LP 06	3010	170	40	30	0.1	1.94	1.3	0.19	4870	310	140	-12.26	-100.8	26.05
LP 07	61340	1980	430	90	0.88	19.36	23.6	2.65	96500	4400	180	-13.24	-110.63	22.84
LP 08	29180	1330	400	270	2.91	22.69	5.66	2.68	46440	3110	210	-12.75	-104.44	23.61
LP 09	2110	170	120	50	3.12	2.38	0.54	6.52	2670	710	660	-11.74	-97.32	-3.37
LP 10	1930	370	100	50	2.71	2.82	0.5	6.29	2440	730	1020	-12.43	-102.49	-3.47
LP 11	6760	690	150	80	0.12	7.29	1.2	0.79	10560	1640	400	-12.01	-99.31	5.81
LP 12	20760	460	310	120	0.54	8.87	8.29	1.61	34260	1010	340	-10.43	-85.49	28.13
LP 13	1110	80	20	30	0.04	2.74	0.62	0.26	1420	120	270	-12.49	-100.94	14.84
LP 14	50520	1690	610	530	3.52	33.6	13.04	7.64	80030	6280	240	-12.12	-118.67	14.21
LP 15	5820	210	120	60	0.2	1.92	1.71	0.52	8660	270	440	-12.21	-99.98	28.22
LP 16	5590	210	110	60	0.19	1.82	2.08	0.35	8370	270	470	-12.2	-89.22	27.67
LP 17	2290	160	60	30	1.17	1.64	0.66	2.71	2830	760	750	-13.21	-126.8	-1.27
LP 18	2670	190	70	30	13.88	1.94	0.72	3.06	3330	900	820	-13.25	-107.85	-1.34
SM 01	21120	1430	220	320	2.21	27.37	5.99	5.33	33590	3700	160	-9.53	-82.85	28.53
SM 02	22290	1410	190	320	2.58	27.3	7.31	4.16	37090	3380	220	-10.15	-87.45	25.94
SM 03	23130	1400	110	200	2.28	29.86	3.87	1.5	35400	3310	130	-10.33	-81.59	16.5
SM 04	19520	1160	110	140	1.84	24.98	3.03	1.28	28210	2620	180	-10.22	-82.63	16.39
SM 05	17890	1330	100	210	1.71	28.61	2.77	1.53	26310	3370	130	-10.6	-92.47	14.77
SM 06	4140	620	90	120	1.27	11.28	2.26	0.55	6810	1410	330	-9.77	-81.73	10.03
SM 07	4060	600	80	130	1.2	10.91	2.22	0.79	6710	1310	350	-10.73	-84.59	10.01
SM 08	7230	1000	120	70	2.16	17.47	2.47	0.83	11270	2110	320	-11.12	-99.77	10.67
SM 09	4980	740	80	100	1.4	12.85	1.11	0.53	7640	1670	300	-10.5	-88	11.48
SM 10	12500	740	50	170	0.67	10.56	3.6	0.5	18680	2290	250	-10	-83.47	17.09
SM 11	12060	740	50	180	0.75	10.13	3.57	1	18710	2290	240	-9.91	-78.45	18.83
SM 12	3200	450	40	50	1.45	10.35	1.89	1.27	4920	900	340	-10.88	-89.31	1.35
SM 13	3340	480	40	40	1.47	10.57	1.76	1.37	5300	940	330	-10.88	-85.72	1.67
SM 14	590	140	10	30	0.17	1.72	0.13	0.25	880	180	430	-11.81	-97.83	3.4
SM 15	1570	200	20	30	0.44	4.23	0.39	0.68	2230	450	570	-10.83	-85.35	3.09
SM 16	2010	240	30	30	0.56	5.65	0.5	0.85	2880	570	630	-11.09	-96.4	1.97
SM 17	2000	240	30	30	0.6	5.64	0.55	0.94	2890	570	630	-11	-97.72	1.77
SM 18	35940	780	220	20	0.51	8.83	15.51	2.51	57040	1470	80	-7.44	-74.67	18.77
SM 19	990	110	20	10	0.42	2.08	0.24	0.96	1140	310	740	-9.23	-73.38	4.53
SM 20	740	100	20	10	0.31	1.61	0.23	0.72	830	220	650	-9.78	-86.31	4.4
SM 21	3810	200	40	50	0.6	3.69	1.69	0.78	5760	430	570	-7.94	-72.45	0.86

relationship, which indicates that the variations in  $\delta^{18}$ O and  $\delta$ D 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 chloride enriched liquid and heavy  $\delta^{18}$ O values.

Fig. 5 shows  $\delta^{18}$ O vs.  $\delta$ D for all springs in the study area; all data points fall on or close around the global

meteoric water line ( $\delta D=8\delta^{18}O+10$ ; Craig, 1961), the Chinese meteoric water line ( $\delta D=7.74\delta^{18}O+6.48$ ; Liu et al., 1997), and the southwest of China meteoric water line ( $\delta D=7.54\delta^{18}O+4.84$ ; Liu et al., 1997), indicating their meteoric origin, which is similar to the geothermal waters in the Tengchong-Baoshan-Lincang Block. The  $\delta^{18}O$  and  $\delta D$  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  $\delta D \& \delta^{18}O$  and latitude can be expressed by the regression lines Y=-0.14X+12.24 (n=49, R<sup>2</sup>=0.72) and Y=-1.07X+13.02 (n=49, R<sup>2</sup>=0.82), respectively (Fig. 6b and 6d). Altitude



Fig. 3. Piper diagram of spring water and geothermal water samples from the Changdu-Lanping-Simao (CD-LP-SM) Basin and Tengchong-Baoshan-Lincang Blocks.

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  $-\delta^{18}O \approx = 0.0031$ H (m)+6.19, and  $-\delta D \approx = 0.026$ H(m) +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



Fig. 4. Plots of  $\delta^{18}$ O (‰ VSMOW) vs. Cl(mg/L) for spring waters from the Changdu-Lanping-Simao Basin (CD-LP-SM) and geothermal springs of western Yunnan



Fig. 5. Relationship between  $\delta D$  and  $\delta^{18}O$  for spring waters of the Changdu-Lanping-Simao Basin (CD-LP-SM) and other sites in Yunnan and Tibet.

GMWL, Global meteoric water line; CMWL, China meteoric water line; SW CMWL, Southwest of China meteoric water line.

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



Fig. 6. Relationships between  $\delta^{18}$ O and latitude,  $\delta$ D and latitude,  $\delta^{18}$ O and altitude, and  $\delta$ D and altitude in spring waters in the Changdu-Lanping-Simao basin (CD-LP-SM).

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 icesnow 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 Clrich 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<sub>4</sub>, CaCO<sub>3</sub>, and MgCaCO<sub>3</sub>, 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.



Fig. 7. Plots of log Cl vs. log Ca (a), log Br vs. log Na (b), log Cl vs. log K (c), log Cl vs. log Ca (d), log Br vs. log Ca (e), log Br vs. log K (f), log Cl vs. log Mg (g), log Br vs. log Mg (h), log Br vs. log Cl (i), log Cl vs. log Li (j), and log Br vs. log Li (k) in spring waters from the Changdu-Lanping-Simao Basin (CD-LP-SM). All concentrations are in mg/L.

Dissolution of Mg-bearing minerals, mainly CaMg  $(CO_3)_2$  and MgCO<sub>3</sub>, 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 LanpingSimao 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.



Fig. 8. (a) Saturation indices of spring waters with respect to calcite, aragonite, and dolomite. (b) Plots of  $SO_4^{2-}/Ca^{2+}$  vs.  $Mg^{2+}/Ca^{2+}$  in spring waters from the Changdu-Lanping-Simao Basin (CD-LP-SM).

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 Leiwuqi 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-SO<sub>4</sub>-HCO<sub>3</sub> 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-SO<sub>4</sub>-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-SO<sub>4</sub> 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



Fig. 9. Ternary Ca-SO<sub>4</sub>-HCO<sub>3</sub> 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).

alkaline HCO<sub>3</sub>-CO<sub>3</sub>-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 Cl-SO<sub>4</sub> field or plot near the chemical divide (the line from calcite to gypsum/anhydrite), which



Fig. 10. Boron (B) isotopic compositions in nature (Han et al., 2016; Lü et al., 2014; Xiao et al., 2012; Zhang et al., 2016).

may indicate that theses 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 -HCO<sub>3</sub>-SO<sub>4</sub> field; although, some fall into the Cl-SO<sub>4</sub> 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–HCO<sub>3</sub>–SO<sub>4</sub> field, very close to the HCO<sub>3</sub>-endmember, 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  $\delta^{11}$ B values in the springs of the CD-LP-SM are all the same or similar as those of marine carbonates (-5.5‰-+23‰; Fig. 10; Hemming 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  $\delta^{11}B_{w,f}$ =(f× $\delta^{11}B_{w,i}$ +B<sub>r</sub>/B<sub>w</sub>× $\delta^{11}B_{r,i}$ + B<sub>r</sub>/B<sub>w</sub>× $\Delta_{w-r}$ ) / (B<sub>r</sub>/B<sub>w</sub>+f). Where  $\delta^{11}B_{w,I}$ , B<sub>w</sub>,  $\delta^{11}B_{rI}$ , and B<sub>r</sub> are the initial B isotopic values and B concentrations of host rocks and meteoric waters, respectively; the fractionation factor ( $\Delta_{w-r}$ ) 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  $\delta^{11}$ B 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  $\delta^{11}$ B values for the carbonates in the study area (Hemming et al, 1992), we assumed the values of modern marine carbonates ( $\delta^{11}B$  of +22.1±3‰ and a B concentration of 11.9 mg/L). Fractionation factors of 1‰ (<200°C), 0.5‰ (300°C), and 0‰ (>500°C) were proposed by several past studies (Kaliwoda et al., 2011; Palmer et al., 1992).

Variations in  $\delta^{11}$ B and B concentrations during waterrock 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  $\delta^{11}$ Bw f value 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

Table 3 Fitting curve parameters for springs in the Changdu-Lanping-Simao Basin (CD-LP-SM)

Carial number	Marine carbona	tes end-member	Crust-derived volcanic end-member		
Senai number	B (mg/L)	$\delta^{11}\mathrm{B}$ (‰)	B (mg/L)	$\delta^{11}\mathrm{B}$ (‰)	
Mixing curve 1	25.0	20.0	688	-10.3	
Mixing curve 2	3.71	-5.5	688	-16.3	

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<sub>2</sub> 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



Fig. 12. Relationship between  $\text{HCO}_3^-$  concentrations and  $\delta^{11}\text{B}$  values in springs of the Changdu-Lanping-Simao Basin (CD-LP-SM).

causes  $CO_2$  degassing, which in turn determines the transformation of  $HCO_3^-$  to  $CO_3^{2-}$  at constant alkalinity:

$$2HCO_3 = CO_3^2 + CO_2(g) + H_2O$$

With the emission of  $CO_2$  from spring waters, a number of reactions should occur:

$$CO_{3}^{2-}+Ca^{2+}=CaCO_{3}(s)$$
  

$$CO_{3}^{2-}+Ca^{2+}+Mg^{2+}=CaMg(CO_{3})^{2}(s)$$
  

$$CO_{3}^{2-}+Mg^{2+}=MgCO_{3}(s)$$

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-



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 crustalderived volcanics, respectively). rock interaction than cold and hot springs, they are more saturated in dissolved carbonate minerals. Furthermore, the precipitated carbonate minerals in saline springs can adsorb more <sup>10</sup>B from the liquid phase, resulting in  $\delta^{11}$ B enrichment in the aqueous phase. As carbonates are deposited, HCO<sub>3</sub><sup>-</sup> in the solution is converted into CO<sub>3</sub><sup>2-</sup>, which results in HCO<sub>3</sub><sup>-</sup> depletion. Fig. 12 shows saline springs have high  $\delta^{11}$ B values and low HCO<sub>3</sub><sup>-</sup> contents, while cold and hot springs are characterized by lower  $\delta^{11}$ B values and higher HCO<sub>3</sub><sup>-</sup> 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  $\delta^{11}$ 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  $\delta^{11}$ B value of +39.5‰ and a B concentration of 4.5ppm (Spivack et al, 1987). The  $\delta^{11}$ B values of continental crust range from -20‰ to -7‰, while those of the primitive mantle are also relatively low -10±2‰ (Chaussidon et al, 1992; Chaussidon et al, 1995). The positive correlation between Cl/B ratios and  $\delta^{11}$ B values in springs worldwide can be used to determine the origin of B. Marine sources have high  $\delta^{11}$ B values and high Cl/B ratios, while terrestrial sources are characterized by lower  $\delta^{11}$ 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  $\delta^{11}$ B values (+34‰ to +41‰ for India, +52.2‰ to +55.7‰ for the Dead Sea, +36.2‰ to +42.6‰ for the Izu Peninsula, and +33.27‰–+36.84‰ for Taiwan) to the springs in our study area. Seawater and rock dissolution are the main sources of B in the thermal springs of India;



• Tibet geothermal belt(China)  $\square$  western Yunnan geothermal belt(China)  $\triangle$  Nangqen Basin(China) Fig. 13. Correlations between  $\delta^{11}$  B-Cl/B for springs of ma-

jor geothermal systems around the world.

involved (Aggarwal et al., 2003; Romain Millot, 2011). d Sea (Israel), the Izu eastern Taiwan show h-0.25ppm for India, ea, 0.02ppm-2.01ppm 4 64ppm for Taiwan) involved (Aggarwal et al., 2003; Romain Millot, 2011). The B concentrations (17.5ppm-82.1ppm) and  $\delta^{11}$ B values (-6.7‰ to -1.9‰) 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

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 Lanping -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  $\delta^{11}$ 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  $\delta^{11}$ B values (-2.4‰-+28.7‰) 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  $\delta^{11}$ 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

hot springs from the Dead Sea are the products of interaction between evaporated seawater and detrital sediments (Chatterjee et al., 2017; Vengosh et al., 1991b); hot springs on the Izu Peninsula are strongly influenced by seawater, which is enriched in <sup>11</sup>B; hydrothermal fluids in northeastern Taiwan are also mainly from seawater (Oi et al., 2008; Zeng et al., 2013). Compared with our study area, the  $\delta^{11}$ 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  $\delta^{11}$ 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  $\delta^{11}$ 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  $\delta^{11}$ B values (-6.7‰ -+25.0‰) 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  $\delta^{11}B$ 

values (-3.1‰-+3.9‰) of the Ngawha geothermal

system, New Zealand, can be accounted for by low waterrock interaction, with B being derived from B-enriched

basement (i.e., mantle origin): no seawater sources are

three sources: (1) dilution of deep-seated trapped  $CaCI_2$  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  $\delta^{11}B$ values, ranging from -16.0% to +13.1%, -9.45% to +1.54‰, and +3.55‰ to +29.59‰, respectively; their corresponding B contents range from 0.36ppm to 472.4ppm, 0.02ppm to 10.44ppm, and 1ppm to 174.77ppm (Lü et al., 2014; Zhang et al., 2016). These values indicate terrestrial B similar to those of springs in the Changdu-Simao Basin. Marine carbonate rocks and Benriched volcanic rocks are the main sources of the B in the springs from the Tibet geothermal belt and Nanggen Basin, similar to the springs of the Changdu-Simao Basin. The B in thermal waters from the Western Yunnan geothermal belt is mainly controlled by the leaching of 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  $\delta$ D 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-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.

#### Acknowledgments

This work was funded by the National Key Basic Research Project of China (973 program, No.2011CB403004). We thank Ma Yunqi, associate research fellow, for providing valuable suggestions and help during lab experiments.

> Manuscript received Aug. 1, 2018 accepted Dec. 20, 2018 associate EIC LIU Lian edited by LIU Lian

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