



# Boron geochemistry from some typical Tibetan hydrothermal systems: Origin and isotopic fractionation



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## ABSTRACT

The Tibetan plateau is characterized by intense hydrothermal activity and abnormal enrichment of trace elements in geothermal waters. Hydrochemistry and B isotope samples from geothermal waters in Tibet were systematically measured to describe the fractionation mechanisms and provide constraints on potential B reservoirs. B concentrations range from 0.35 to 171.90 mg/L, and isotopic values vary between  $-16.57\%$  and  $+0.52\%$ . Geothermal fields along the Indus-Yarlung Zangbo suture zone and N–S rifts are observed with high B concentrations and temperatures. The similar hydrochemical compositions of high-B geothermal waters with magmatic fluid and consistent modeling of B isotopic compositions with present  $\delta^{11}\text{B}$  values imply that the B in high-B geothermal waters is mainly contributed by magmatic sources, probably through magma degassing. In contrast, geothermal fields in other regions of the Lhasa block have relatively low B concentrations and temperatures. After considering the small fractionation factor and representative indicators of Na/Ca, Cl/HCO<sub>3</sub>, Na + K and Si, the conformity between modeling results and the isotopic compositions of host rocks suggests that the B in low-temperature geothermal fields is mainly sourced from host rocks. According to simulated results, the B in some shallow geothermal waters not only originated from mixing of cold groundwater with deep thermal waters, but it was also contributed by equilibration with marine sedimentary rocks with an estimated proportion of 10%. It was anticipated that this study would provide useful insight into the sources and fractionation of B as well as further understanding of the relationships between B-rich salt lakes and geothermal activities in the Tibetan plateau.

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## 1. Introduction

B is a ubiquitous trace element with high geochemical reactivity and a single oxidation state. Its two natural stable isotopes, <sup>11</sup>B and <sup>10</sup>B, have relative abundances of 19.8% and 80.2%, respectively. In light of its significant isotopic fractionation with relatively large mass differences and its participation in most geochemical processes, B has unique advantages in providing information on origins and tracing geochemical processes (Jiang, 2001). Due to their soluble and incompatible nature (Chaussidon and Marty, 1995; Barth, 1998; Ellis and Mahon, 1967; Ellis, 1970), B isotopes are excellent for tracing endogenic geochemical processes such as dehydration and metamorphism during slab subduction (Ishikawa and Tera, 1997; Nakano and Nakamura, 2001; Rosner et al., 2003; Agostini et al., 2008), magmatism (Kaliwoda et al., 2011; Arnórsson and

Andrésdóttir, 1995; Trumbull and Chaussidon, 1999) and hydrothermal ore deposits (Jiang, 2001, 2004, 2008; Yang and Jiang, 2012; Zhao et al., 2011). Moreover, strong fractionation during transfer in seawater or crust makes B a sensitive indicator of supergene geochemical processes, including supergene weathering (Rose, 2000; Chetelat et al., 2009). Although an extensive isotopic range is to be expected, abundant compositions have been reported in different reservoirs (Barth, 1993; Chaussidon and Marty, 1995; Jiang and Palmer, 1998; Vengosh et al., 1992, 1995, 1999). These supplements to the isotopic database and research on fractionation mechanisms have contributed to the establishment of B isotopic geochemistry and have enriched its applications in geological studies.

The Tibetan Plateau is one of the most prominent regions with intensive hydrothermal activities in the world. Special trace elements (B, As, Li, Cs) are unusually enriched in geothermal waters and are concentrated in salt lakes. The observed B concentrations are as high as 568 mg/L, which is remarkably higher than the

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concentration of 29.08 mg/L in the Yellowstone geothermal system (Palmer and Sturchio, 1990). The estimated Cs discharge of the Zhumosha geothermal spring into the Yaluzangbu River is more than 100 times that of the world's total demand for Cs every year (Zheng and Duo, 1996). B mainly migrates in the dissolved and/or absorbed phase by fluid due to its high solubility and ability to migrate easily in solution. It is expected that B isotopes do not fractionate significantly at magmatic temperatures, and they may record valuable information related to high-temperature fluid-related processes (Rosner et al., 2003; Ishikawa and Tera, 1997; Nakano and Nakamura, 2001; Kaliwoda et al., 2011). Thus, B isotopes are significant for recording the geochemical evolution of B and for understanding the genesis of geothermal fields and related hydrothermal activities. However, sources of B and mechanisms of the isotopic fractionation of B in geothermal waters in Tibet have not been well established due to the complex geological setting. It is unclear whether the unusual enrichment is related to magmatism and how isotopic compositions are influenced by different geochemical processes. In terms of the geochemistry of major resource elements, Grimaud et al. (1985) indicated that such a rich resource in some high temperature geothermal waters could not have been caused only by water–rock interaction, and they suggested that the magma may be the dominant source. In particular, isotope hydrology studies have confirmed that the large-scale and high-hydraulic-pressure geothermal systems in the Tibetan Plateau are developed and maintained by rapid groundwater circulation (Wei et al., 1983; Tan et al., 2014). Therefore, in some geothermal fields with higher temperatures and hydraulic pressures that occur along the Indus-Yarlung Zangbo suture zone, there does not seem to be enough time to trigger strong water–rock interactions to cause unusual enrichment in B and other mineral elements. However, all of these conclusions seem to lack solid evidence at present, and new direct confirmation needs to be introduced. This study first introduces and compares many new B isotopic data of the geothermal waters in the Tibetan Plateau. New insights into the origin and evolutionary enrichment mechanism of the B mineral resources of geothermal waters are provided. The B distribution and isotopic variation and fractionation mechanisms during potential geochemical processes have also been modeled. It is expected that this work will be very significant for understanding hydrothermal activities and for developing applications of B isotopes to uncover the origin of B resources in geothermal water.

## 2. Geologic setting

The Tibetan plateau is generally regarded as the product of continental accretion accompanied by the closing of the Tethys Ocean and by the India-Asia collision which contributed to the uplifting of the Plateau (Yin and Harrison, 2000; Tapponnier, 2001). The Plateau is adjacent to the Himalayas to the south, and they are separated from each other by the Indus-Yarlung Zangbo suture zone (IYSZ). From north to south, the Tibetan Plateau tectonic units are composed of a series of east-west-trending continental blocks: Songpan-Ganzi, Qiangtang and Lhasa. Bounded by three north-dipping Late Cenozoic fault systems, the Himalayas consist of three tectonic slices: the Tethyan Himalaya, the High Himalaya and the Lesser Himalaya. Collectively, the present hydrothermal activity in the Tibetan-Himalayan Plateau is regionally distributed and occurs in the Lhasa block and the Himalayas. The Lhasa block is bounded by the Bangong-Nujiang suture zone (BNSZ) to the north and by the Indus-Yarlung Zangbo suture zone (IYSZ) to the south. Magmatism in the Southern Lhasa block has been characterized by four epochs from the early Jurassic subduction of the Neo-Tethyan ocean to the Cenozoic India-Asia continental collision (Zheng et al., 2014 and references therein). In particularly, the voluminous

Gangdese batholiths and Linzizong volcanic units formed during the Cretaceous–Early Tertiary are widespread (Mo et al., 2007; Gao et al., 2010; Wen et al., 2008). The Himalayas are separated from the Tibetan Plateau by the Indus-Yarlung Zangbo suture, and they mainly consist of late Precambrian to early Paleozoic sediments and meta-sedimentary rocks (Yin and Harrison, 2000).

North-south-trending rifts attributed to east-west extension are prominent features in the Southern Tibet (Tapponnier et al., 1981; Armijo et al., 1986). From west to east, the chronology indicates that the rift ages become younger from 24 Mpa to 8 Mpa (Chung et al., 2005). Geothermal fields, especially for high temperature systems, are mainly distributed along these rifts, which may provide channels for the rise of geothermal fluids. This indicates that intensive hydrothermal activities in Tibet are not only controlled by magmatism but are also associated with rift structures. Moreover, east-west-trending sutures, especially for the BNSZ and the IYSZ, between different accreted blocks also provide important constraints on the development of geothermal systems. Typically high-temperature springs enriched in some incompatible elements are often discovered along the IYSZ. Those springs with large-scale sinters are located roughly along the BNSZ and have relatively low temperature. These differences in geographical location and corresponding chemical composition appear to imply an order of time and extent of activities.

## 3. Sampling and analytical methods

The selection of samples in this study is based on tectonics, lithologies and hydrochemical features of geothermal springs. Finally, 21 thermal water samples were collected from typical thermal fields in 2012. The sampling sites are distributed in the Lhasa block and the Tethyan Himalayas, including hot springs, boiling springs and geysers (Fig. 1). Specifically, almost all of the samples were collected along the east-west suture zones or the south-north-trending rifts. Lithologies of host rocks around selected geothermal springs broadly contain volcanic and sedimentary rocks. During sampling, a temperature-resistant glass flask was inserted as deep as possible into the spring (or well head or hole) and was filled with boiling or hot water. After that, the flask was immediately sealed with a plug to prevent vapor–water separation. When the hot water cooled, it was filtered on site through 0.45- $\mu\text{m}$  MF-Millipore membrane filters. The water bottles were washed with distilled water in the laboratory and then with raw water three times in the field. Samples for analysis of chemical compositions were collected in two 500-mL high-density polyethylene bottles. One bottle was acidified with ultrapure  $\text{HNO}_3$  to pH < 2.0 for cation analysis, and the other was for anion analysis and was not acidified. Samples for B isotopic analysis were collected in a separate bottle.

Physicochemical parameters such as temperature (T), pH and total dissolved solids (TDS) were measured on site with a calibrated portable Multi-Parameter Analyzer. The concentration of  $\text{HCO}_3^-$  was also analyzed at sites by titration for precise values. Major chemical compositions were determined at the State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering (Nanjing). Cation concentrations were measured using ICP-AES with uncertainties of less than 5%, and anion concentrations were measured by ion chromatography with uncertainties of less than 2%. The chemical separation of B and analysis of the B isotopic composition followed the procedure described by Wei et al. (2014). A two-column procedure was established for B separation/purification: a column with 5 mL of mixed cation–anion resin was used first, followed by a peristaltic pump coupled with an Amberlite IRA 743 B-specific resin column. The Amberlite IRA 743 B-specific resin was conditioned by 10 mL of 2 M HCl, 20 mL of pure water and

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