

Geothermal-type Lithium Resources in Southern Xizang, China



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Abstract: High-temperature geothermal water has abundant lithium (Li) resources, and research on the development and utilization of geothermal-type lithium resources around the world are increasing. The Qinghai–Tibetan Plateau contains huge geothermal resources; especially, Li-rich geothermal resources in southern Xizang, southwestern China, are widely developed. The Li-rich geothermal spots in Xizang are mainly distributed on both sides and to the south of the Yarlung Zangbo suture zone. Such resources are often found in the intensely active high-temperature Li-rich geothermal fields and, compared with other Li-rich geothermal fields around the world, the Li-rich geothermal fluid in the Xizang Plateau, southern Xizang is characterized by good quality: the highest reported Li concentration is up to 239 mg/L; the Mg/Li ratio is extremely low and ranges from 0.03 to 1.48 for most of the Li-rich geothermal fluid; the Li/TDS value is relatively high and ranges from 0.25–1.14% compared to Zhabuye Li-rich salt lake (0.19%) and Salar de Uyuni (Bolivia) (0.08–0.31%). Continuous discharge has been stable for at least several decades, and some of them reach industrial grades of salt lake brine (32.74 mg/L). In addition, elements such as boron (B), caesium (Cs), and rubidium (Rb) are rich and can be comprehensively utilized. Based on still-incomplete statistics, there are at least 16 large-scale Li-rich hot springs with lithium concentration of 20 mg/L or more. The total discharge of lithium metal is about 4300 tons per year, equivalent to 25,686 tons of lithium carbonate. Drilling data has shown that the depth is promising and there is a lack of volcanism (non-volcanic geothermal system). With a background of the partial-melting lower crust caused by the collision of the Indo-Asia continent and based on a comprehensive analysis of the tectonic background of southern Xizang and previous geological, geophysical, and geothermal research, deep molten magma seems to provide a stable heat source for the high-temperature Li-rich geothermal field. The Li-rich parent geothermal fluid rushes to the surface to form hot springs along the extensively developed tectonic fault zones in southern Xizang; some of the Li-rich fluid flows in to form Li-rich salt lakes. However, most of the Li-rich geothermal fluid is remitted to seasonal rivers and has not been effectively exploited, resulting in great waste. With the continuous advance of lithium extraction technologies in Li-rich geothermal fluid, the lithium resource in geothermal water is promising as a new geothermal type of mineral deposit, which can be effectively exploited. This is the first study to undertake a longitudinal analysis on the characteristics, distribution and scale, origin and utilization prospects of Li-rich geothermal resources in southern Xizang, research that will contribute to a deeper understanding of Li-rich geothermal resources in the area and attract attention to these resources in China.

Key words: geothermal resources, lithium, Xizang (Tibet)

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1 Introduction

In recent years, with the promotion and popularization of electric vehicles, the demand for lithium resources around the world has been continuously increasing (Park,

2012; Martin et al., 2016). Facing the rising price of the metal, the exploration for lithium and increase in mines has continued to be active worldwide (Liu L J et al., 2019). There are many geothermal fields worldwide, such as the Puga Valley in Kashmir (Chowdhury et al., 1974),

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the Puna Plateau in Argentina (Kasemann et al., 2004), and the Chilean Lahsen geothermal (Cortecchi et al., 2005), revealing the presence of high concentrations of some rare and precious alkali metals such as lithium, rubidium, and caesium (Li, Rb, Cs) and dispersed elements such as arsenic, boron, and bromine (As, B, Br). In particular, the unusual enrichment of lithium in geothermal water is generally accepted as one type of significant and potentially valuable mineral resource for future exploration. Considering that geothermal resources also have huge potential to be green energy, the lithium resources in Li-rich geothermal fluid are receiving increasing attention (Campbell, 2009; Tomaszewska and Szczepański, 2014), and some scholars even point out that lithium resources in geothermal water can reach 2 Mt (Gruber et al., 2011; Kesler et al., 2012).

Lithium resources in salt lakes contribute three-quarters of the world's lithium demand and many scholars consider that geothermal water in Li-rich brine lakes is an important source of lithium (Shcherbakov and Dvorov, 1970; Zheng et al., 1983, 1989, 1990; Campbell, 2009; Munk et al., 2011; Tan et al., 2012; Yu et al., 2013; Ericksen et al., 1978; Luo et al., 2017). Therefore, much research work has been carried out on extracting and utilizing lithium raw materials from Li-rich geothermal water, and several studies have asserted that Li-rich

geothermal water will become an effective way to meet the rising demand for the resource (Yanagase et al., 1983; Hano et al., 1992; Jeongeon et al., 2012; Krotscheck and Smith, 2012; Cetiner et al., 2015) because certain high-temperature geothermal waters have unusually high and important economic concentrations of lithium (Campbell, 2009). This is a particularly important lithium resource replenishment considering the current world shortage (Tan et al., 2012).

The Tibetan Plateau, as an eastern extension of the Mediterranean–Himalayan geothermal zone that belongs to one of the world significant representative geothermal zones, has very rich geothermal resources (Fig. 1) and a long history of research process. Most geothermal springs in this region show an unusual enrichment of lithium and other typical resources (e.g. B, Rb, Cs) dissolved in hot water or as geothermal deposits (Tan et al., 2018). Research on Li-rich geothermal resources in China started early when Zheng et al. (1983) discovered a hot spring with high lithium concentration in the southern part of the Bangkog Co in Xizang. They conducted preliminary research on its genesis as early as 1960. In addition, a preliminary estimate of the lithium resources in the Yangbajing geothermal field was also reported, with a resource of 390,000 tons (Zheng and Liu, 1982).

In recent decades, the huge geothermal energy in

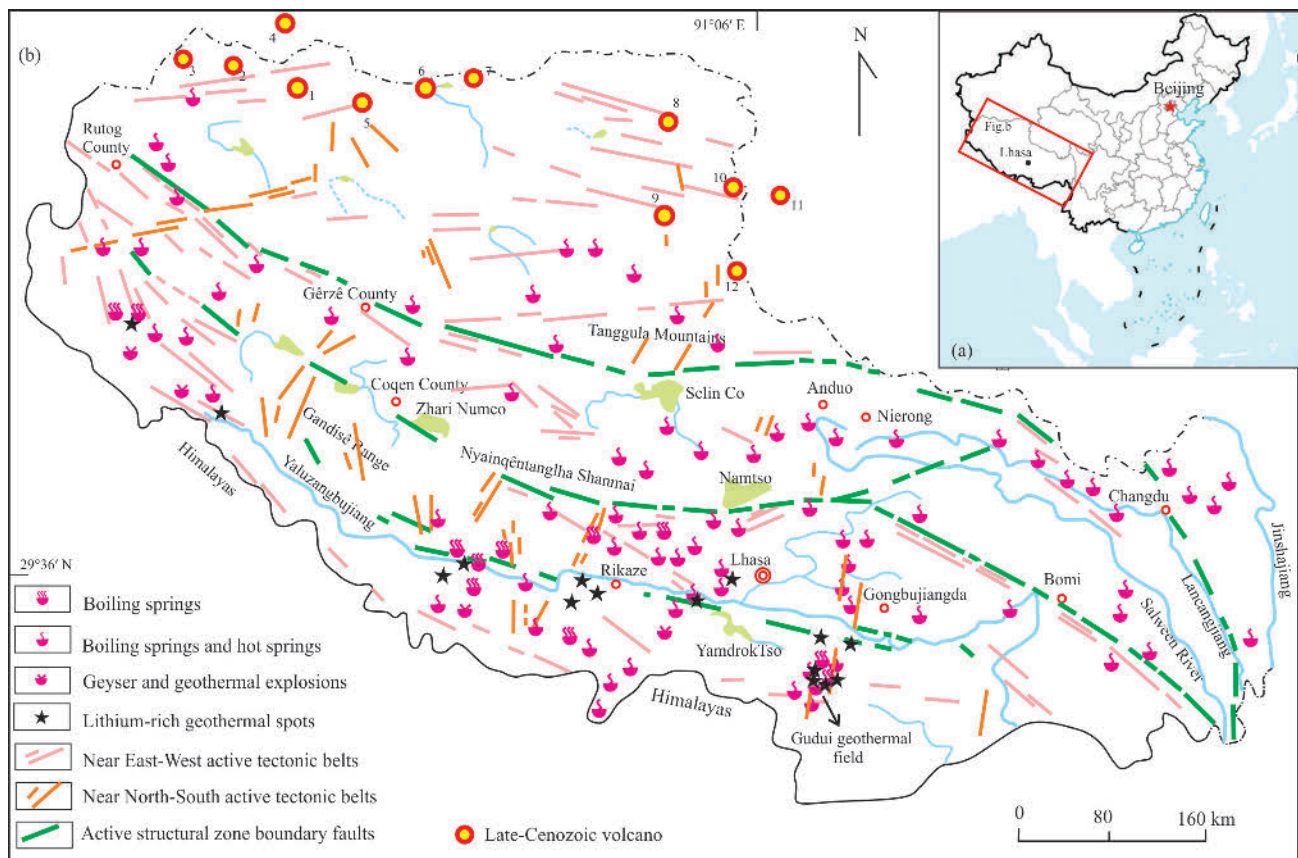


Fig. 1. Distribution of hot spring sites, active tectonics, and Late Cenozoic volcanoes in the Xizangan Plateau (modified from Zheng et al., 1995; Li Z Q, 2002; Guo et al., 2014; Luo et al., 2017) and lithium-rich geothermal spots in southern Xizang (after Tong et al., 2000; Wang and Zheng, 2019).

The 12 Late Cenozoic volcanoes are: 1, Shenglidaban; 2, Quanshuigou; 3, Liuhuangdaban; 4, Kaerdaxi; 5, Heishibeihu; 6, Dujiانشan; 7, Huangyangling; 8, Yongbohu; 9, Bamaoqiongzong; 10, Kushuihuanbei; 11, Heiguoshan; and 12, Yuyehu (according to Guo et al., 2014). China basemap after China National Bureau of Surveying and Mapping Geographical Information.

Xizang's geothermal resources has been effectively exploited (Pang et al., 2013). However, the degree of research on, and exploitation and utilization of the lithium resources are still very low, and they have not attracted their due attention and should be given more attention. With the rapid transformation of China's economy and industrial base, the high-tech industries are developing quickly. China's demand for lithium resources is increasing rapidly year by year, coupled with the continuous expansion of the international lithium demand market and the shortage of Li-rich mineral raw materials, so that any Li-rich water that can be used to extract lithium is an effective solution (Tan et al., 2018). Therefore, in the context of the exploration, exploitation and market dynamics of lithium resources at home and abroad in recent years, in order to improve the current situation of research and utilization of lithium resources in the high-temperature Li-rich geothermal field in Xizang, based on our team's rich field and other research experiences in the Qinghai-Tibetan Plateau (Zheng and Liu, 1987; Zheng et al., 1983, 1990, 1995) and understanding of the development and utilization status of other high-temperature Li-rich geothermal fields around the world, we propose that Li-rich geothermal water is an important kind of lithium mine. Targeted field and indoor research work have been carried out in response to this concept. Based on this, we consider that with the continuous advancement of extraction technologies, geothermal-type lithium resources have the potential to become a new genetic type of lithium ore deposit.

This article absorbs and summarizes previous relevant research materials (Zheng and Liu, 1982, 1987, 2007; Zheng et al., 1983, 1989, 1990, 1995; Tong et al., 1981, 2000; Zheng S H et al., 1982; Duo, 2003; Luo et al., 2017; Guo and Wang, 2012; Pang et al., 2013; Tan et al., 2014, 2018; Zheng W et al., 2015; Wang R C, et al., 2017; Mao, 2018; Guo et al., 2007, 2009, 2010, 2012, 2017, 2019a, 2019b; Wang and Zheng, 2019; Wang et al., 2019; Xia and Zhang, 2019; Zhang et al., 2019). Together with field investigations and research on the key areas in southern Xizang (e.g., the Gudui geothermal field), we aim to report the characteristics, distribution and scale, origin and utilization prospects of geothermal-type lithium resources in southern Xizang. We also aim to attract attention to Li-rich geothermal systems, strengthen exploration investment and basic research of geothermal-type lithium resources, to find out the accurate lithium resources retained in geothermal water in China, and ultimately, implement rational extraction and utilization of the geothermal-type lithium in the near future.

2 Characteristics of High-Temperature Lithium-Rich Hot Water in Southern Xizang

The collision between India and Eurasia plates that occurred since the Eocene has been resulting in the uplift of the Tibetan Plateau and formation of the Himalayan geothermal belt (Blisniuk et al., 2001; Williams et al., 2001; Duo, 2003; Zhu et al., 2004; Taylor and Yin, 2009; Pan et al., 2012). Many geothermal-active regions occur in the central and southern parts of the Tibetan Plateau (Fig.

1). The high-temperature Li-rich geothermal resources in southern Xizang are mostly distributed on both sides of the Yarlung Zangbo suture zone and associated N-S trending rifts, especially at the intersection of the main and secondary faults (Han, 1990; Wang and Zheng, 2019; Fig. 1). Compared with other high-temperature Li-rich geothermal fields around the world, such as the El Tatio geothermal field in Chile (Cortecchi et al., 2006), Clayton Valley (Munk et al., 2011), Rehai geothermal field in SW China (Wang et al., 2016), some active volcanic hydrothermal systems in Yellowstone geothermal field, USA (Guo et al., 2014), and those around Salar de Uyuni, Bolivia (Ericksen et al., 1978), the Li-rich geothermal fields in southern Xizang lack Quaternary volcanic eruptions and even volcanic rocks in the surrounding strata (Fig. 1). In fact, almost all the Late Cenozoic volcanoes in Tibet are located in the north of the country, as shown in Figure 1. Therefore, the southern Xizang Li-rich geothermal fields all belong to high-temperature non-volcanic geothermal fields. The temperatures of the surface springs are more than 70°C, close to the boiling temperature of local water (83°C), and the location of the high-temperature hot springs are strongly controlled by small-scale secondary faults, such as Yangbajing geothermal field (Duo, 2003), Yangyi geothermal field (Yuan et al., 2014), Gudui Geothermal field (Fig. 2; Wang and Zheng, 2019) and the Mapamyum geothermal system (Wang et al., 2016). The fluid of the Li-rich hydrothermal systems is almost all pH neutral, and most contain Cl⁻ as predominant anions and Na⁺ as predominant cation, whereas their Ca and Mg concentrations are generally low. The hydrochemical types are mainly Na-Cl type, with surrounding surface water mainly Ca-Mg-SO₄-HCO₃ and Na-Ca-Mg-SO₄-Cl-HCO₃ types (Guo and Wang, 2012; Guo et al., 2014; Wang et al., 2016; Wang and Zheng, 2019; Supplementary data 1).

Lithium concentration in the natural water is extremely low, with less than 0.01 ppm of lithium in the world's major rivers (Morozov, 1969) and most seawater contains no more than 1 ppm lithium (Schwochau, 1984; Kesler et al., 2012). In comparison, the Gudui cold spring water in Xizang only contains 0.017 ppm lithium (Wang, 2017).

The minimum industrial grade of salt-lake brines is LiCl 200 mg/L (equivalent to Li ion 32.74 mg/L), and the cut-off grade is LiCl 150 mg/L (equivalent to Li ion 24.56 mg/L), according to the specifications for salt-lake, salt mineral exploration DZT 0212-2002 issued by the Chinese government. In contrast, the lithium concentration in some geothermal fluid in southern Xizang is extremely high, and some of them reach the available industrial grades. For example, the lithium ion concentration of Jianhaizi hot spring is as high as 239 mg/L (Supplementary data 1). The lithium ion concentration of Zhumosha hot spring is as high as 65.40 mg/L and field investigation found that it develops on the Yarlung Zangbo River. The Moluojiang boiling spring has a lithium ion concentration of 50 mg/L (Supplementary data 1).

In addition, it is reported that more than 60% of the total lithium reserves (about 26.9 Mt) exist in brine, especially in those located in Bolivia, Chile, North America, and China (Cha et al., 2017). However, high concentrations of

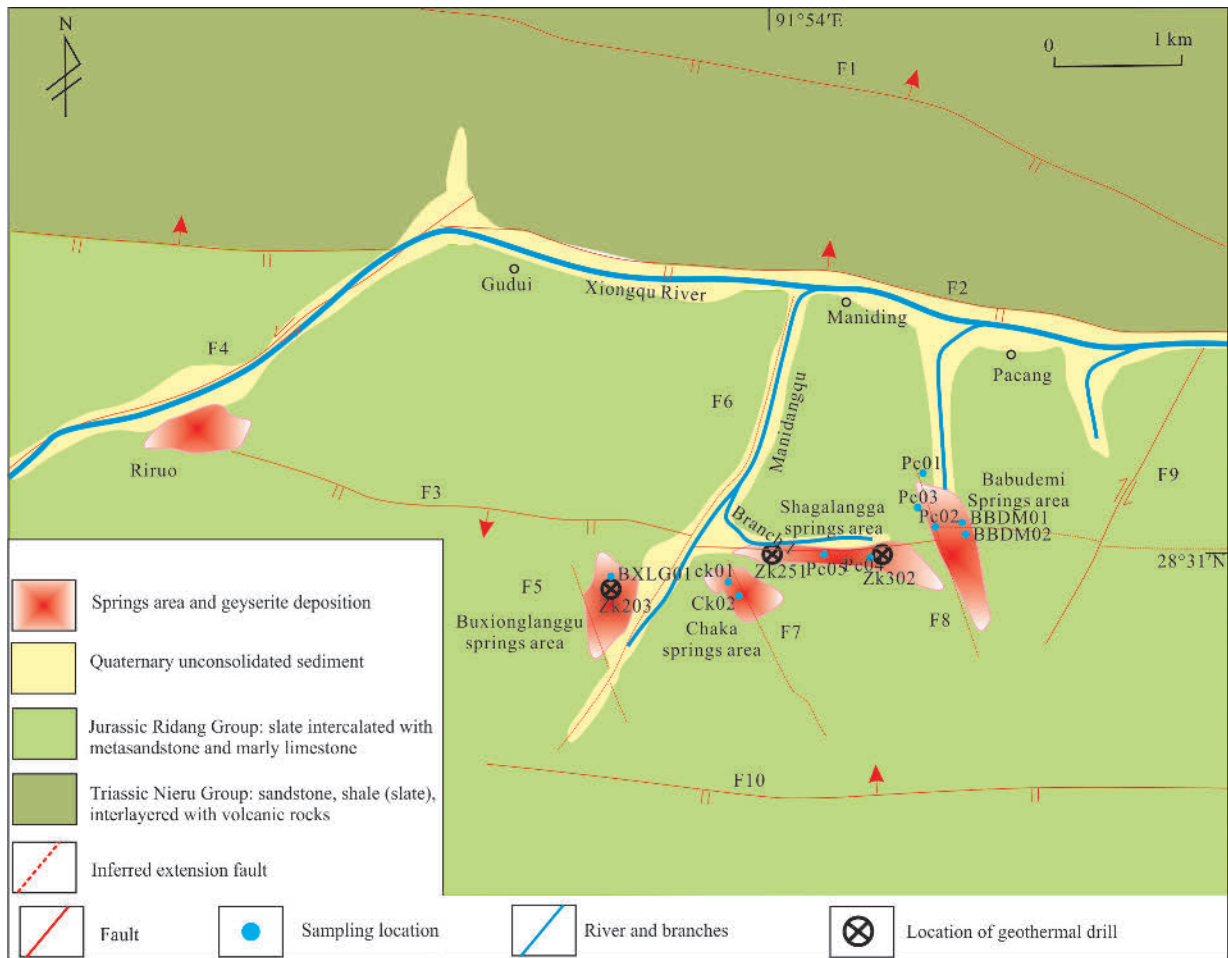


Fig. 2. Simplified geological map and sampling locations of the Gudui Geothermal Field.

F5, F6, F7, F8 are extension faults; other properties unknown (modified from Liu et al., 2017; Wang, 2017; Wang and Zheng, 2019).

Mg^{2+} usually coexist with Li^+ in brine, by which the high cost and technical complexity for the recovery of Li^+ from the high Mg/Li ratio brine have led to the situation of lithium resources failing to meet market demands (Zhao et al., 2017). It is noted that there are plentiful geothermal water resources with high Li/TDS value and low Mg/Li ratio properties in the world (Sun et al., 2019). China's high-temperature Li -rich hot water in southern Xizang has a very low Mg/Li ratio, between 0.03–1.48 (average 0.43; Supplementary data 1); this feature is highly conducive to industrial exploitation. Although the TDS values of most of the Li -rich hot waters are not high, the Li/TDS values are quite high, some as high as 1.14% (Supplementary data 1), which is even higher than Zhabuye (0.19%; communication data from Prof. Liu Xifang), the most Li -rich salt lake in the Qinghai–Tibet Plateau, and at Salar de Uyuni (0.08–0.31%; Schmidt, 2010), the richest Li -bearing salt lake in the world. Moreover, according to Zheng et al. (1983) and Tong et al. (2000), most of the Li -rich geothermal water in southern Xizang has been stably discharged for decades (e.g., Gudui geothermal field for at least 42 years; Fig. 3), and possess stable heat source and lithium source. Nevertheless, so far, most of the Li -rich

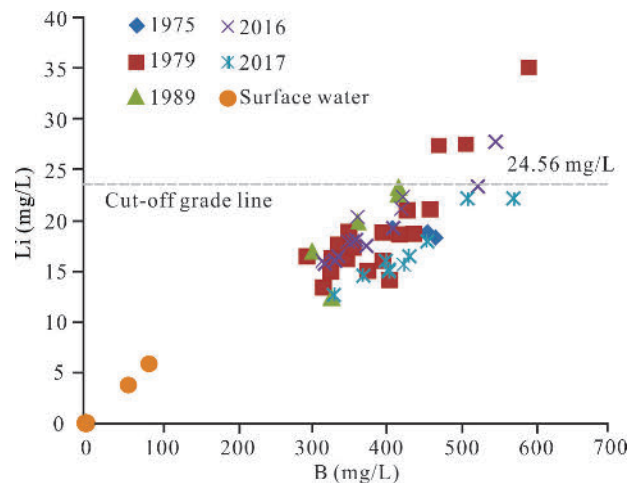


Fig. 3. Trends and relationships of boron and lithium concentration in the Gudui geothermal field from 1975 to 2017 (data from Tong et al., 2000; Wang, 2017; Wang and Zheng, 2019).

geothermal water resources have flowed into the surface runoff, causing great waste. In recent years, many boreholes have uncovered the deep geothermal water of

different geothermal fields, such as Yangbajing and Gudui, which has even higher lithium concentration than the surface hot springs (personal communication between academicians Zheng Mianping and Duoji), indicating that there is hope for finding more Li-rich geothermal resources in the deep high-temperature Li-rich geothermal field.

Since 1956, extensive geothermal geological surveys have been carried out in Xizang, finding that the hot waters in the Yarlung Zangbo geothermal belt are rich in elements such as B, Li, Cs, and Rb (Zheng et al., 1995). In 1995, during the field investigation in Xizang geothermal fields, Zheng M P discovered the anomalous enrichment of Cs in the sinters, and then proposed a new type of hydrothermal deposit—Cesium-bearing geyserite. The Li-rich hot waters reported in this paper are also developed with high concentrations of B (Fig. 3), Cs, Rb and other resources that can be comprehensively utilized, which can undoubtedly increase the development and utilization value of the high-temperature Li-rich geothermal water in Xizang. In addition, we noticed that some high-temperature Li-rich hot water in Xizang also discharged massive As (approximately 6.6 mg/L in the south bank of the Semi; Zheng et al., 1995); the highest record is 126 mg/L of the Moluojiang hot spring in southern Xizang (Tong et al., 2000), Sb (Semi 1.40 mg/L, Zheng et al., 1995), W (tungsten concentration of Daggyai, Semi and Gudui varies from 289.1 to 1103 $\mu\text{g/L}$, Guo et al., 2019a), Hg (0.006 mg/L; Zheng et al., 1995) and other harmful elements.

Through the study of the geochemical characteristics and distribution of these harmful elements in high-temperature Li-rich geothermal fields, we can not only effectively control pollution by harmful elements in the Xizang Plateau, but also comprehensively make use of them in the future. In the near future, the value of the exploitation of these metal elements from the high-temperature Li-rich geothermal field will be comparable to that generated by the utilization of geothermal heat.

3 Distribution and Scale of High-Temperature Lithium-Rich Geothermal Resources in Southern Xizang

According to genetic type, China's lithium deposits can be divided into endogenous and exogenous. Zheng M P (personal communication) classified Li-containing geothermal fluid into one of the ten kinds of lithium resources according to output background, distribution range, research, typical deposit characteristics and exploited degree. Here we focus on a brief introduction to geothermal-type lithium resources in southern Xizang, China.

China's high-temperature Li-rich geothermal fluid is mainly distributed in Xizang, especially in the south (Fig. 1). Since 1956, after successive large-scale investigations of the geology and geothermal deposits conducted by the Xizang Geology and Mineral Bureau, a Comprehensive Investigation Team of the Chinese Academy of Sciences (CAGS) and the Institute of Mineral Geology of CAGS, the extensive geothermal activities have received increasing attention. The survey found that recent medium

- and high-temperature geothermal resources are mainly distributed in the southern part of the Qinghai–Tibetan Plateau, with deposits dominated by siliceous sinter, and the water-chemical type dominated by Na-Cl (Supplementary data 1). Nearly 700 geothermal display areas (points) have been discovered (Zheng et al., 1982; Zhang et al., 1989; Tong et al., 1981, 2000), among which 57 areas are high-temperature geothermal systems (temperature $\geq 150^\circ\text{C}$). The medium-high temperature geothermal systems generally have a high lithium concentration, especially the hot springs on both sides of the Yarlung Zangbo River, which are rich in B, Cs, Li, Rb and other elements (Zheng et al., 1995). During an in-depth study of the Daggyai geothermal field, Zheng et al. (1990) conducted a preliminary estimate of its resources and pointed out for the first time that the concentration of Cs, Li, Rb and B in many geothermal waters in Xizang reached a single comprehensive utilization index, such as the hot spring in the Semi geothermal field where Li concentration is as high as 35 mg/L. Grimaud et al. (1985) conducted a detailed studied of nearly 300 hot springs in Xizang and found that many geothermal fields produce geothermal water rich in B, Li and Cs. Although many waters in geothermal fields worldwide are enriched with a large amount of Li, many on the Xizangan Plateau show that the anomalous enrichment of elements such as B, Rb, and Cs has reached economic utilization grade (Grimaud et al., 1985). Li Z Q (2002) and Luo Y B et al. (2017) thought that the geothermal fluid activities in Xizang are basically consistent with corresponding activity tectonics. The high-temperature geothermal fluid activity areas in southern Xizang can be divided from west to east into: (1) the Dangreyongco–Dingri; (2) Shenza–Xietongmen; (3) Yadong–Gulu; and (4) Sangri–Cuona geothermal belts (Zheng W et al., 2015; Wang, 2017; Wang and Zheng, 2019), which is basically consistent with Zheng et al.'s (1983) conclusions about the Xizang Quaternary basin and linear structural sketches. As noted above, when researching the Li-containing hot springs in southern Bangkog Co, Zheng et al. (1983) thought that there was still a large amount of B, Li, potassium (K) and fluorine (F) that were carried out from the ground. On this basis, Zheng et al. (1983) discussed the relationship between Li-rich hot springs and volcanic, epithelial magma.

Based on data from the book *Thermal Springs in Xizang* (Tong et al., 2000), Li-rich geothermal fluid in Xizang was counted, as shown in Supplementary data 1. According to its now-out of date statistics, the total annual Li and B emissions of some high-temperature Li-rich hot springs with flow reports were calculated. The results show that the annual lithium discharge is 4,281 tons, equivalent to 25,686 tons of lithium carbonate, and boron emissions are as high as 91,882 tons (Supplementary data 2), which is enough to illustrate the huge utilization potential. Therefore, the lithium resources carried by geothermal systems can be used to meet the demand in the international market (Tan et al., 2012). Besides, the consensus is that lithium in the Li-rich salt lakes originated from geothermal water (Grimaud et al., 1985; Zheng et al., 1995; Tan et al., 2012), which further illustrates the importance of lithium resources in

geothermal water and the urgency of promoting research, extraction and utilization of geothermal lithium resources.

In addition, most of the Xizang Li-rich geothermal water is often accompanied by high-concentration Rb, Cs, and B resources (Supplementary data 1), which further improves the utilization value of the geothermal-type lithium resources. Comprehensive analysis of previous research data, at the boundary condition of about 24.56 mg/L of lithium ion (equivalent to salt lake brine ore), yielded many high-temperature Li-rich hot (boiling) spring areas (screened out from Tan et al., 2000), including Moluojiang, Duoguoqu, Semi, Labulang, the water chemistry characteristics of which are shown in Supplementary data 1 and 2. Through field investigations and research at Buxionglangu, Shagalangga and Babudemi boiling springs, we found in addition that the Chaka and Riruo hot springs in the Gudui geothermal field are all under the control of tectonic structures being found at the intersection areas of faults (Fig. 2). Plotting the lithium and boron concentration data in geothermal water from the past 42-year history of the Gudui geothermal field (Fig. 3), we found that it has remained basically stable, and that the surface water concentration is significantly lower than that of geothermal water. In addition, we also found that the relationship of boron and lithium concentration between the Gudui geothermal water and surface water is basically linear, indicating the characteristics of binary mixing; this shows that the surface hot spring is the result of mixing between deep Li- and B-rich geothermal fluid and surface water, which is further explained by the existence of a deep parent geothermal fluid (Wang and Zheng, 2019). Generally speaking, the potential of the high-temperature Li-rich geothermal resources further increases its development and utilization value.

4 Origin of High-Temperature Li-Rich Geothermal Resources in Southern Xizang

Two-thirds of the world's supply of lithium resources relies on extraction from Li-rich salt-lake brines. Most Li-rich hot springs are distributed around the periphery of these salt lake brines, and they play an important role in the formation of continental Li-rich salt lakes, such as the tentatively listed World Heritage Atacama in Chile, Uyuni in Bolivia, Hombre Muerto in Argentina, Silver Peak and Searles in America. Bradley et al. (2013) highlighted the important role of geothermal activity in the basic characteristics of the continental Li-rich brine mineralization model. Munk et al. (2016) further summarized the control effect of geothermal activity on the continental Li-rich salt lake brine as follows: (1) it provides a geothermal fluid source for enhanced leaching of Li from source rocks; (2) it is also likely a direct source of Li from shallow magmatic brines and/or magmatic activity; (3) it may play a role in the concentration of Li through distillation or 'steaming' of thermal waters in the shallow subsurface; (4) thermally driven circulation may be an effective means for advecting Li from source areas. Probably the highly fractionated granites developed in southern Xizang are closely relative to the mineralization

of W, Sn, Nb, Ta, Li, Be, Rb, Cs and REEs etc. (Wang R C et al., 2017) to regions of brine accumulation; and (5) it can result in the formation of the Li-rich clay mineral hectorite, which can in turn be a potential source of Li to brines if leaching and transport occur from the clay source. It can be seen that geothermal activity plays an important role in the mineralization of Li-rich salt lake brine. Therefore, in recent years, much research has been conducted on the formation of high-temperature Li-rich geothermal fluids; from the literature, we found that the key factors that control the formation of geothermal fields are the heat source and the passage that allow geothermal water to circulate from depth to the surface.

Geothermal heat has two sources: one is recent active volcanoes. For example, active volcanoes in the Andes of South America have many surrounding geothermal fields; another source is deep molten magma. These geothermal fields are widely developed, such as Salton Sea, California, USA (Brothers et al., 2009; Lachenbruch et al., 1985; Schmitt and Hulen, 2008; Karakas et al., 2017), Mapamyum non-volcanic field (Wang et al., 2016), Yangbajing (Guo et al., 2007), Yangyi (Yuan et al., 2014), and Gudui (Guo et al., 2019a, b). The regional deep faults caused by strong tectonic activities through time constitute mass heat migration channels, which cause the deep heat energy to migrate to shallower strata, forming the geothermal fields and display areas, especially those areas the fractures in different directions cut each other (Wang, 2017). Tectonic and volcanic activities provide channel systems and heat that drive groundwater convective cycles and are necessary for leaching lithium from source rocks (Ericksen et al., 1978). Large geothermal fields are often distributed along large deep fault zones, especially at fault intersections, as noted above, as at Salton Sea, located on the active San Andreas faults (Brothers et al., 2009), superimposed with the subsequent SAF-IF strike-slip fault (Karakas et al., 2017), which is as rich in lithium as Bolivia and Chile's most productive salt lakes (Campbell, 2009); The high-temperature Li-rich geothermal display areas in Xizang are mostly distributed near a deep fault, especially at the intersections of near E–W and N–S deep faults, as shown in Figure 1. In addition, geothermal fields such as Lake Taupo, New Zealand, Yellowstone, and Geysir in Iceland (Elderfield and Greaves, 1981; Jones et al., 2007; Geilert et al., 2015) also have the above features.

Given suitable heat sources and tectonic conditions, there are two paths for the formation of a high temperature geothermal fluid. One is that atmospheric precipitation or glacial melt water seeps along fault zones. As the depth of infiltration increases, it is closer and closer to the deep molten magma body and then is gradually heated. With buoyancy, the heated water increases and rises constantly along the faults and at last forms hot springs, and finally, densely developed hot springs form geothermal fields; The other way is that atmospheric precipitation or glacial meltwater infiltrates along faults to a certain depth and then mixes with rising hot magmatic fluid to form a deep high-temperature geothermal reservoir. The mixed geothermal reservoir fluid then rises along the fault to the surface to form a hot spring or geothermal field. The geothermal water formed by these two processes has clear

differences in water chemistry characteristics.

Chowdury et al. (1974) pointed out that B, F, As, Li, and Cs are closely related to the final stage of magma crystallization evolution. Based on experimental studies (Fuge, 1977; Webster and Holloway, 1980) and analysis of trace elements in granite (Grimaud et al., 1985), it has been pointed out that magma fluid that is rich in K, Rb, Cs, B, Li, F and Cl can be released in the final stages of granite evolution. From the characteristics of high-temperature Li-rich geothermal water in southern Xizang, most are neutral or alkaline Na-Cl type waters rich in characteristic elements such as B, Li, Rb, Cs and F. What's more, acidic geothermal water is often developed and rich in SO_4^{2-} , which was considered typical for steam-heated acid waters (Guo et al., 2019b). In addition, Cl ion concentration has a good linear relationship with other characteristic ions, as at Gudui (Wang and Zheng, 2019), which indicates that there, deep magmatic fluids are mixed in (Guo et al., 2019a, b). Similarly, other southern Xizang high-temperature Li-rich geothermal fields could also have mixing with deep magma fluids. Many geophysical studies have shown that the existence of a large number of melts in the deep part of southern Xizang (Nelson et al., 1996; Brown et al., 1996; Makovsky et al., 1996; Kind et al., 1996; Chen et al., 1996; Tan et al., 2004; Wei et al., 2010) further supports the above conclusions. All the geothermal fields and hot springs around the world are basically controlled by the above factors, but not all can produce large amounts of Li-rich geothermal water.

Each Li-rich geothermal field has its unique characteristics; the only difference is the source of lithium. Despite in-depth studies, there is still controversy, but basically the consensus supports two sources: (1) water-rock reaction between high temperature geothermal fluid and Li-rich rocks (mostly in volcanic rocks such as tuff, e.g. Vide salt lake, South America, Silver Peak Lake, USA; Bradley, 2013); in southern Xizang, highly fractionated granites, such as Ramba leucogranite (Li: 226 ppm; Liu Z C et al., 2014), and Xiaru leucogranite (Li: 2000 ppm; Wang R C et al., 2017) might be examples, which dissolve and bring out lithium from the source rock. Other examples include the Uyuni salt pans in Bolivia, which are surrounded by hot springs containing unusually high lithium concentration associated with Quaternary rhyolite volcanic rocks (Ericksen et al., 1978). Water-rock reaction is considered to be the main source of lithium in brines (Campbell, 2009; Shcherbakov and Dvorov, 1970; Ericksen et al., 1978). Zheng et al. (1983) mentioned the origin of the Li-containing hot springs in Bangkog Co, noticing that water in the volcanic sedimentary beds has a high concentration of lithium and boron and, therefore, considered that the Cenozoic acid volcanic rocks in central and southern Xizang are important sources of boron and lithium in this region (Zheng et al., 1983). Araoka et al. (2014) discovered that the enrichment of lithium in the Nevada Basin was mainly through reactions between high-temperature geothermal fluid associated and Li-rich tuff or volcanic glass using a systematic lithium isotope study of several Li-rich playas (Clayton Valley brine field; Alkali Lake; Columbus Salt Marsh) in Nevada. The lithium concentration of the surrounding geothermal water is as

high as 36 ppm (Davis et al., 1986), which indicates the importance of the water-rock reaction (Araoka et al., 2014). (2) High-temperature steam aqueous solution carrying lithium from the late stage of deep molten magma differentiation; because lithium is a moderately incompatible element in the magma system, it usually accumulates in the residual melt during the magma differentiation process (Zhang et al., 1998). Although high-temperature Li-rich geothermal fields are widely developed in southern Xizang, so far there is no related volcanic rock reported, rather they might be related to the intrusive rocks reported by Francheteau et al. (1984) leading to the high heat flow values in southern Xizang (Grimaud et al., 1985). Tan et al. (2014) explained the circulation process of underground geothermal fluid in Xizang's main high-temperature geothermal system through hydrogen and oxygen stable isotope data, the results showing that the formation of the high-temperature geothermal system is mainly due to rapid circulation of groundwater and upwelling of residual magma fluid. And in most cases, the granite outcrops can be observed not far from the hot springs (Grimaud et al., 1985), for example, the Cuonadong tourmaline granite (Liu M L et al., 2019) is developed not far from the Gudui geothermal field to the southeast. Although many studies have shown the relationship between southern Xizang geothermal fields and deep molten magma, such as Yangbajing, Mapamyum, Daggyai, Semi (Guo et al., 2019a, b), Gudui (Wang and Zheng, 2019) etc., still the accurate source of high lithium concentration is rarely mentioned. Guo et al., (2019a, b) proved that the magma sources contribute to the extraordinary high concentration of As and W in some Li-rich geothermal water. The host rock leaching alone cannot explain the observed lithium anomaly in the Li-rich geothermal systems that have had continuous outflow for decades or longer because a fixed volume of surrounding rock cannot have such a huge amount of metal for hot water leaching. Based on the same considerations, Guo et al.'s (2019b) estimates of the As discharge flux and the total amount of available As in the Yangbajain system reservoir rocks supporting the existence of a magma chamber have been validated by geophysical and geochemical studies (Brown et al., 1996; Zhao et al., 1998a, b; Zhao et al., 2002). Overall, the results indicate that the estimate of the available As in reservoir rocks is more than two orders of magnitude lower than the estimated total flux, and therefore the As in the Yangbajain geothermal waters cannot be derived exclusively from host rock leaching but should be primarily from the input of magmatic fluid.

Further evidence can be offered by taking the Gudui Li-rich geothermal system as an example, for we consider that the metal lithium in the Gudui geothermal field mainly comes from the deep magmatic hydrothermal system. Therefore, substantial contribution of lithium from underlying magma chambers below southern Xizang is postulated, which are likely attributable to partial melting of the subcontinental lithospheric mantle that has undergone metasomatism by Li-rich fluids derived from subducted oceanic crust and marine sediments (Tian et al., 2018). Therefore, we consider that lithium in geothermal

fields is closely related to deep molten magma. It is also easy to capture the direct source with the contribution of magmatic fluid input not being ruled out. Of course, in-depth research on this issue is necessary.

The strongly active high-temperature geothermal fluid in southern Xizang extracts lithium by water-rock reaction when it flows through felsic Li-rich rock such as granite or mixes directly with Li-rich magma fluid. Research has shown that high-temperature geothermal fluid dissolves lithium in rocks more than conventional cryogenic fluids (Chagnes and Światowska, 2015). Through the analysis of the trend of lake water composition, Zheng et al. (1990) discovered that the abundances of B, Li, K and Cs in the modern lakes of the Qinghai–Tibetan Plateau are characterized by the outward decline from the Gangdese–Yaluzang as a high value center, which also constitutes the geochemical anomaly areas of B, Li and Cs on the plateau. The origin there is contributed to the diffusion of volcanic geothermal fluid to the surface from deep melts in the western part of the Bangur and Yarlung Zangbo (Zheng et al., 1990). Based on recent researches, we accept that the formation of the Li-rich salt lakes in Xizang has undergone many ‘pre-enrichment’ processes in the early Li-rich oceanic crust (Zheng M P, unpublished) that partially melted to form Li-rich magma during subduction to complete the initial lithium enrichment. The Li-rich magma gradually cooled and crystallized along the deep and large fractures during the continuous ascending process. In the late stage of crystallization differentiation, lithium was further enriched in the magma hydrothermal fluid. With the further collision of the Indo-Asian continent, under different geological conditions, some of the Li-rich magmatic hydrothermal fluid formed rich tourmaline-spodumene granites or highly fractionated granites, which distribute surrounding the Xizang Semi geothermal field, while part of the Li-rich magmatic hydrothermal fluid can form Li-rich geothermal fluid by mixing with infiltrated surface water and then the mixed fluid rises along the fault zone to reach the surface (Figs. 4, 5). Some of the geothermal fluid is sent to the salt lakes, and further concentrated by evaporation and enrichment to form the Li-rich salt lakes brines, whereas most flows into surface runoff.

To illustrate the above conclusions, we take Yangbajain and Gudui geothermal fields as examples. Yangbajain is chosen because, among all the hydrothermal areas in Tibet, it has been investigated systematically in the past three decades (Tong et al., 1981; Zhao et al., 1998b; Duo, 2003; Guo et al., 2007, 2009), and the existence of a magmatic heat source and high-temperature reservoir (over 200°C) has also been confirmed (Guo et al., 2014). Guo et al. (2010) showed that the deep geothermal fluid is the mixing product of both magmatic and infiltrating snow-melt water, whereas the shallow geothermal fluid is formed by the mixing of deep geothermal fluid with cold groundwater (mixing process and ratios are shown in the Fig. 4). In addition, two groups of high-angle normal NNE–SSW and NE–SW stretching/extensional faults are distributed in front of the Nyenchen Tonglha and Tang mountains near to the geothermal field. These faults were active until the Quaternary and are crucial structures for

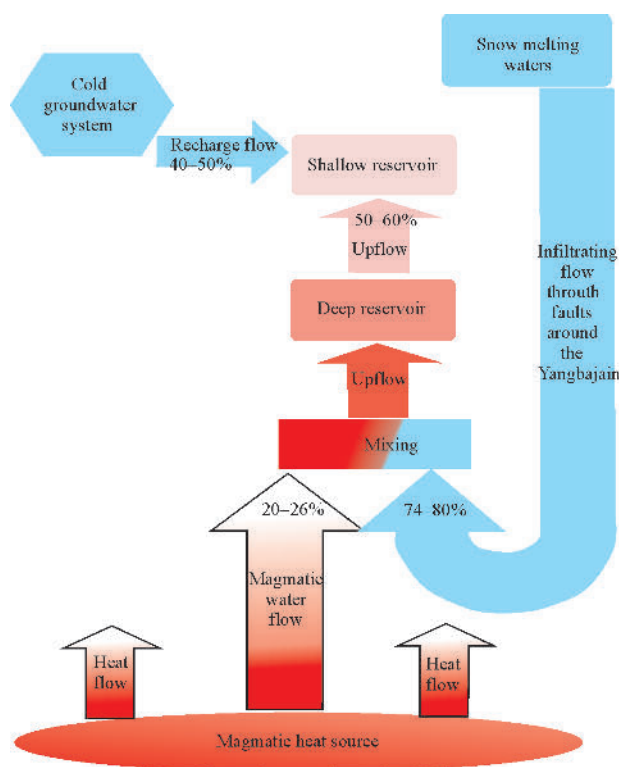


Fig. 4. Conceptual model of the Yangbajain geothermal water system (modified according to Guo et al., 2010).

the occurrence of the field because they provided favorable permeability for the migration and storage of the geothermal fluids at depth. What's more, the deep geothermal fluid is richer in lithium (personal communication with academician Duoji).

The reason to select the Gudui geothermal field is that it is characterized by the most intensive hydrothermal activity among all Tibet geothermal areas (Guo et al., 2014), although it is not as well known or systematically researched. Based on its hydrochemistry, Gudui is very likely to be a magmatic hydrothermal system similar to Yangbajain (Guo et al., 2014). In addition, Wang et al. (2019), through hydrogen and oxygen isotope research, suggested that the deep reservoir at Gudui also definitely mixed with magmatic fluid and then, together with strontium isotope data, proposed the 6th-Class Reservoirs Evolution Conceptual Model (6-CRECM) for the geothermal system (Fig. 5). They also found that the lithium concentration is decreasing gradually from deep geothermal fluid, which is mixing more magmatic fluid to shallow fluid, which might provide further clues to prove that lithium comes from deep magmatic fluids (Wang et al., 2019). The geological characteristics of the Gudui area (Fig. 2) and previous studies also show that the strongly developed faults had an important role in the formation of the Gudui Li-rich high-temperature geothermal system (Liu et al., 2017; Wang, 2017; Wang and Zheng, 2019).

Taking these two examples into consideration, we think that the deep molten magma of the lower crust provided a stable heat source and lithium source for the high-temperature Li-rich geothermal fields developed in

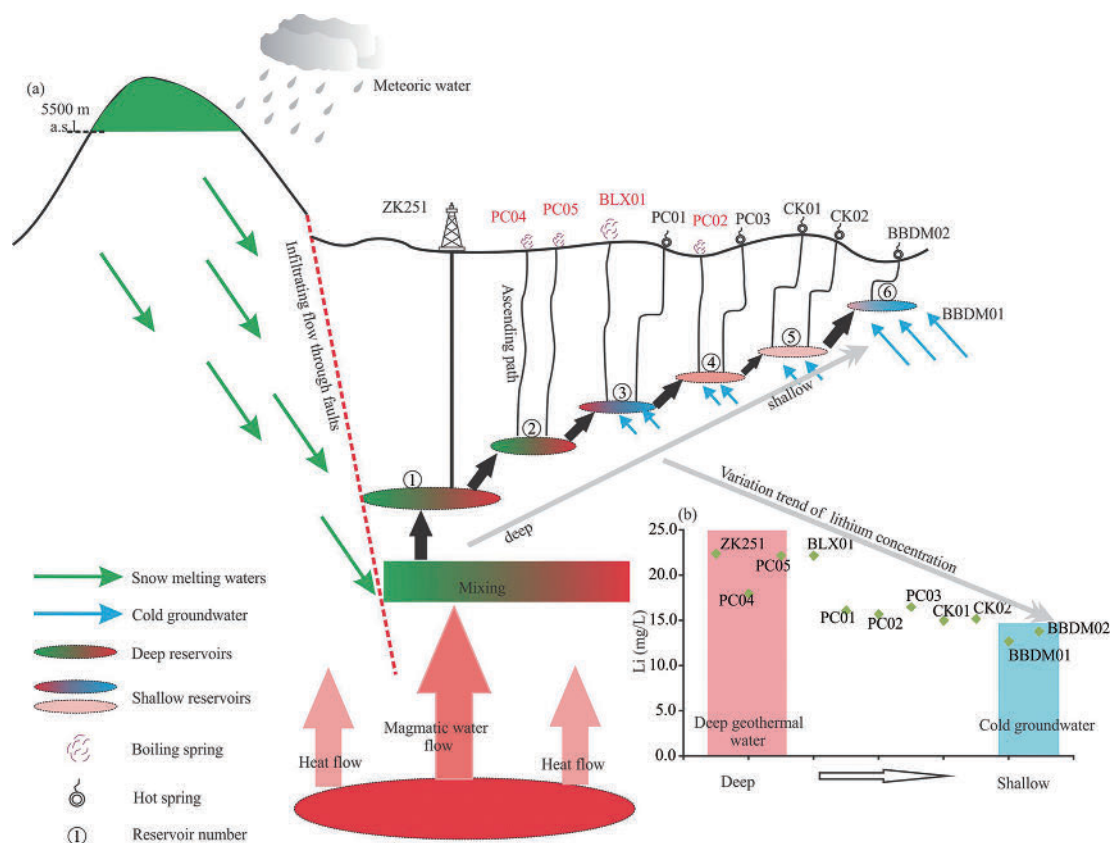


Fig. 5. (a) The 6th-Class Reservoirs Evolution Conceptual Model (6-CRECM) for the Gudui geothermal system; (b) changing trend of lithium concentration from deep geothermal fluid to shallow geothermal fluid of the Gudui geothermal field (modified from Wang et al., 2019).

southern Xizang. Li (2002) also thought that the melting layers in the crust in southern Xizang not only provide heat energy for the shallow hydrothermal system, but also supply liquid and metallogenic elements. The upper fractional melting layer has driven amplified area's hydrothermal activities in southern Tibet, whereas the near-surface upwelling emplaced melting masses from the lower crust to promote the presenting of some high-temperature geothermal fields (Li, 2002). The deep-produced Li-rich parent geothermal fluid rushes to the surface to form hot springs along the extensively developed tectonic fault zones in southern Xizang, and some of the Li-rich fluid flows into the lakes to form Li-rich salt lakes; however, most of the Li-rich fluid is wasted, flowing into different rivers. More investigations on Li-rich high-temperature geothermal fields are needed to further verify the conclusions reached here.

5 Prospects for the Utilization of High Temperature Li-Rich Geothermal Resources in Southern Xizang

Many worldwide researches have been done on extraction of lithium from liquid minerals, and numerous methods have been proposed, such as solvent extraction, evaporative crystallization, precipitation, ion exchange adsorption, or a combination of methods (Flexer et al.,

2018; An et al., 2012; Song et al., 2017), among which the solvent extraction and ion exchange adsorption have received the most attention (Sun et al., 2019), but the recovery of lithium from geothermal fluid resources has rarely been reported to date. Based on the experiences of extracting caesium in the Cs-bearing geyserite deposit in Xizang and the changes in concentration of lithium and other chemical constituents during Li-rich geothermal fluid evaporation and concentration experiments, combined consideration of the topography and geology of the high-temperature Li-rich geothermal area in southern Xizang, we consider the efficiency of simple evaporation concentration is too low to meet current development and utilization needs. Through preliminary exploration and research, we thought that membrane and adsorption methods are still very promising and worth considering, especially with natural non-polluting adsorbents such as aluminum-based or zeolite-based, and even those that combine natural substances and synthetic substances together can be considered. Not only can they be green and pollution-free, but this method can also increase man-made controllability. According to the chemical composition and type of geothermal fluid, appropriate adjustments can be made to improve the efficiency of lithium extraction while reducing energy consumption. So far, our team is still conducting research on the use of

different adsorbents to extract lithium resources in Li-rich geothermal water. We are confident that, in the near future, exploitation of high-temperature Li-rich geothermal water in southern Xizang will be enhanced.

Fortunately, Chinese scholars have begun to pay attention to this problem and achieved results. Sun et al. (2019) proposed a green recovery method of lithium from geothermal water based on a novel Li–Fe phosphate electrochemical technique. The recovery rate of Li^+ is up to 90.65% after eight adsorption-desorption cycles. In addition, only electrical energy is consumed and no organic solvents or other toxic reagents used or produced during the recovery process. All these properties make the above method a green and promising candidate for the recovery of Li^+ from geothermal water. In addition, Zheng (1999) thought that low-salinity geothermal fluids are also a special ore-forming fluid through a comparative study of the fluids rich in Li, B, Cs and Rb from the Salton Sea, Puga, Taupo and high-temperature geothermal fields developed in Xizang. The study of the low-temperature mineralization that is developing in Xizang will be helpful to improve metallogenic theory and increase ore-forming target areas. Therefore, it is necessary to enhance research on high-temperature Li-rich geothermal resources in southern Xizang.

6 Conclusions

Geothermal-type lithium resources are a new type of lithium resources, which are widely distributed worldwide and have huge potential reserves. Scholars from different countries have carried out research on these resources, which should also be given due attention by Chinese scholars. Our research has discovered geothermal-type lithium reserves in China but further relevant exploration investment and basic research is needed, to realize industrial extraction and utilization of geothermal-type lithium resources. We consider that there will be more efficient and portable methods to extract lithium resources from geothermal water in the near future.

China's geothermal-type lithium resources are mainly distributed in southern Xizang, and strongly controlled by E–W extension structures and the Yarlung Zangbo suture zone. The Cenozoic volcanic activities on both sides of the suture zone and in the southern part of Xizang have not been reported previously, and the magmatism caused by the melting of the upper crust is essential for the development of high-temperature Li-rich geothermal systems. China's high-temperature Li-rich geothermal water is characterised by low Mg/Li ratio, high Li/TDS ratio, and has been continuously and stably discharged for decades; some waters reach industrial grades, and all are associated with high-quality accompanying elements such as B, Cs, Rb that can be comprehensively utilized.

The current high-temperature Li-rich geothermal water in southern Xizang has a large scale of metal lithium emission per year, and the deep potential resources are even more abundant, which has great exploitation and utilization value. With the advancement of technology, methods for extracting lithium from Li-rich geothermal water are gradually diversifying, and will gradually

mature. In the near future, utilization of lithium and other resources from the high-temperature Li-rich geothermal water will not only produce its due economic value, but also help to reduce environmental pollution of harmful elements.

In summary, the high-temperature Li-rich geothermal resources widely developed in southern Xizang are a valuable asset worth exploiting, and the near-surface Li-rich geothermal fluid with rare alkali metals is also a modern low-salt hydrothermal ore-forming fluid. The study of its mineralization will help deepen our understanding of low-temperature mineralization and regional prospecting.

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