Enrichment mechanism of Li, B and K in the geothermal water and associated deposits from the Kawu area of the Tibetan plateau: Constraints from geochemical experimental data

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ARTICLE INFO

Handling Editor: Marcello Liotta.
Keywords:
Geothermal water
Evapo-concentration
Phase separation
Distribution and enrichment of elements

ABSTRACT

In the Tibetan Plateau, most geothermal springs show an unusual enrichment of boron and lithium and other typical resources dissolved in hot water or geothermal deposits. The evolution of the geothermal water and the distribution of elements during the phase separation of residual liquid and associated deposits remain unclear. Through a chemical analysis of the deposits and geothermal water in the Kawu area during primary discharge and later evaporation, the elemental distribution and enrichment processes between the two phases of deposits and the mother water are discussed. Basic results show that the elements Li, B and K are preferentially enriched in the geothermal water rather than distributed into the geothermal deposits of travertine during the primary phase separation of geothermal water discharge. The elements B and K, as a whole, are enriched in the late residual mother water in the later stages during evapoconcentration. However, Li shows a distinctly depleted trend in the residual mother water at the stage when the lithium carbonate precipitates in the deposits. The most important finding of the evapoconcentration experiment is that the zabuyelite, an unusual lithium carbonate mineral, is firstly detected in the mineral association of geothermal deposits. It is only precipitated within a very small interval during an intermediate stage with a very high concentration of Li while there are very low concentrations of Ca and Mg and an unusually high Li/Mg ratio in the mother geothermal water. The zabuyelite is a trademark mineral in the salt lake deposits in the Tibetan Plateau. This is the first time it has been found in the mineral association of deposits of evapoconcentrated geothermal water. This indicates that geothermal water discharge may be the main source for Li, B and K accumulation in the salt lakes. In addition, the typical elements of Li, B and K are extremely enriched during the late stage of the residual mother water or precipitate as zabuyelite or sylvite within a very concentrative stage. They are also very promising mineral resources for development and utilization.

1. Introduction

There are some geothermal fields in the world with an enrichment of useful mineral resources, i.e., Chilean Lahnge geothermal resources developed in the Andes Mountains (Alfredo, 1988; Fernandez-Turiel et al., 2005; Gianni et al., 2005), the Puna Plateau in Argentina (Alonso, 1999; Simone et al., 2004) and the Puga Valley in Kashmir, India (Chowdhury et al., 1974). All of these geothermal waters reveal the presence of high concentrations of some rare and higher alkali metals (Li, Rb and Cs) and dispersed elements (As, B and Br). In particular, the unusual enrichment of lithium in the geothermal water is generally accepted as a type of significant and potentially valuable mineral resource for future exploration. The Tibetan Plateau, as an eastern extension of the Mediterranean-Himalayan geothermal zone that belongs to one of the world famous representative geothermal zones, has very rich geothermal resources. In addition to their energy significance, most geothermal waters also have an unusual enrichment of boron and lithium and other typical mineral resources dissolved in the hot water or deposited with siliceous sinters and calcic travertines. Magmatic fluids upward intrusion and water-rock interactions have been concluded for the geological origin and enrichment mechanism of these elements in the geothermal system (Tan et al., 2014; Zhang et al., 2015; b). According to previous observations and statistics for the geothermal resources in the Tibetan Plateau, 58 geothermal fields with an enrichment of B (> 100 mg/l) and 20 large hot springs with Li concentrations over 10 mg/l have already been found (Tong et al., 1981). With increasing international market demands and the scarcity of mineral materials for lithium resources, it seems to be an effective way to extract Li from any...
Li-rich waters. In this aspect, scientists have already conducted a number of studies on lithium extraction and utilization from geo-
thermal water with Li enrichment and concluded that it should be a
solution to satisfy the increasing demands for lithium resources
(Yanagase et al., 1983; Hano et al., 1992; Jeongeon et al., 2012; Krotscheck and Smith, 2012; Cetiner et al., 2015).

Previously, geologists realized and observed that some rare and
alkali elements are enriched in geothermal deposits during the phase
separation of silica sinters deposited from residual fluids (Milorad
and Milorad, 1969). Similarly, Chowdhury et al. (1974) found higher concentrations of Li, Rb, and Cs present in both geo-
thermal water and related deposits through observing a geothermal system in the Puga Valley, India. There are many types of waters (geothermal water, salt lake brine, and oilfield water) with unusual enrichments of some rare and dispersed elements in the Tibetan Pla-
ateau, which are very unique. Among these waters, the geothermal water seems to be more significant because it is believed to be the source of the salt lake resources while it also hosts valuable extractable Li and other elements (Grimaud et al., 1985; Zheng, 1995; Li et al., 2006; Tan et al., 2012). In addition, during geothermal water discharge, some rare alkali elements enriched in the hot water can stimulate silica colloids to rapidly condense because of their high property of electrolytes. This can possibly lead to an enrichment of some elements in the silica deposits and evolve into a new type of hydrothermal deposit. Zheng (1995) first found and assessed a new type of cesium-bearing geyserite in many geothermal fields in the Tibetan Plateau in the 1980s. The unusual enrichment of Cs in silica sinters has proven to be an important and prospective resource for the extraction of cesium. Moreover, the unu-
usally high concentration of Li, Rb, Cs and B present in the residual geothermal water after silica deposition may be used in the future. In addition to silica sinters, there have also travertine deposits distributed in some geothermal fields in the Tibet. Until now, the unusual enrich-
ment of Li, B and K and other elements in the geothermal water on the Tibetan Plateau was not exploited and utilized. With a sharp reduction of salt lake resources for large-scale development over the past several decades, it is an urgent task to find more mines to replace them. The large-scale distribution of geothermal water and deposits are con-
idered to be significant potential mines for future exploration to re-
place the diminishing salt lake resources. Thus, it is significant to track the movement and distribution of typical elements during the phase separation of geothermal water. Zheng (1995) previously studied silica sinter-type geothermal fields and found that some elements are preferentially enriched in silica deposits when the spring water discharges at the surface. In contrast, there are very few studies on the elements’ distribution and enrichment between liquids and solids during phase separation for travertine-type geothermal waters, in the Tibetan Plateau and around the world.

In this study, an unusual enrichment of Li, B, and K in the geo-
thermal waters with large-scale travertine deposits distributed around the springs in the Kawu area were investigated. The main research objectives are to uncover the movement, distribution and enrichment relationships of Li, B and K during the primary phase separation of travertine deposits/thermal water and evapoconcentrated residual water/deposits during the processes of isothermal evaporation. The study will have important theoretical significance for tracking the geochemical enrichment processes of some mineral elements enriched in geothermal water. It can also provide new evidence to affirm the source relationships between geothermal water and salt lakes in the Tibetan Plateau. More importantly, this study will provide basic data for future technological designs to synthetically extract the valuable mineral elements Li, B and K enriched in geothermal water.

2. Geothermal systems in the Tibet and Kawu area

2.1. Overview of geothermal geology in the Tibet

The Indian and Eurasian Plates collided during the Cenozoic, re-
sulting in the uplift of the Tibetan Plateau. Simultaneously, the Indian Plate was subducted and thrust beneath the Tibetan Plateau, causing the crust to melt and providing the tectonic background and heat conditions for the formation of geothermal resources in the Tibetan Plateau (Nelson et al., 1996; Brown et al., 1996; Bai et al., 2006; Feng et al., 2012; Guo, 2012). The Tibet geothermal zone is the eastern ex-
tension of the Mediterranean–Himalayan geothermal belt. Many boiling or hot springs and geysers with high reserve temperatures (> 150 °C) are distributed along the transmeridional Yaluzhangbo suture (YS) and Bangong suture (BS). The most intense geothermal activities are mainly distributed along the Yaluzhangbo suture and many geothermal springs with high temperatures occur on both sides of the Yaluzangbo River as well as in the riverbed. Field observations suggest that large-scale silica sinters or travertines are widely deposited in almost all geothermal springs in the Tibetan Plateau, particularly in northern Tibet along the BS, where thick and old geothermal deposit terraces are distributed despite small-scale present-day geothermal activities (Zheng, 1995). Therefore, the geothermal abnormalities should be more active and larger during the geologic past than at present in some geothermal fields of the BS. The geothermal activities in Tibet have a long geo-
ological history, and many hot or boiling springs and geysers are still flowing at high temperatures and pressures. The geothermal deposits of most boiling springs are dominated by silica sinters and are called si-
lica-type geothermal fields in the Tibetan Plateau. The unique char-
acteristics of the silica deposits include an unusual enrichment of Cs, which has huge potential economic value if extracted (Zheng, 1995). However, there are also large-scale travertine deposits in some geo-
thermal fields. The most typical geothermal system with travertine-type deposits is the Kawu geothermal field distributed in the southern Yal-
uzangbo River (Fig. 1).

2.2. Introduction about geothermal system in Kawu area

In Kawu area, like the other geothermal fields along Yaluzangbo River, the modern geothermal activities are still very strong and many boiling springs, fumaroles, mud pots and geysers are densely distributed along both sides of the Chongqu River. The temperature of the spring mouth is over the local boiling point (> 80 °C). The Kawu geothermal system is mainly controlled by a northeastern trending strike-slip fault (Fig. 1). The main outcrops of strata around the geothermal springs from north to south are Gangdise magmatic rocks, Cretaceous sedi-
mentary rocks, ophiolite group rocks (mainly ultrabasic rocks), Late Jurassic and early Cretaceous complex rocks, Triassic sedimentary and metamorphic rocks, Neogene leucogranites and High-Himalaya meta-
morphic and granite rocks. There are also large-scale travertine deposits around the mouth of the present-day geothermal springs, as well as areas of ancient geothermal activities far away from the modern springs. As for the formation mechanism of large-scale travertines, it remains unclear at present. It may be mainly attributed to geothermal water with rich bicarbonates discharging from the surface and boiling and then precipitating as calcium carbonate with water vapor and carbon dioxide being released as following chemical reaction:

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Ca^{2+} + 2HCO_3^- \rightarrow CO_2 + H_2O + CaCO_3
\]

In the field, the intense bubbling of dioxide can be observed. It can be concluded that geothermal fluids at depth in the high-temperature zone is relatively rich in gaseous components originated from the heat source. The thermodynamic equilibrium constant decreases with in-
creasing temperature, resulting in increasing saturation index. That is
to say, the geothermal fluids should be super-saturated with respect to
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