Boron circulation and recharge pattern in Zabuye drainage basin, Tibetan plateau

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Abstract. Zabuye salt lake is famous for abundance of B and Li resource, especially for natural product of lithium carbonate mineral. Based on systematic measurement of chemical compositions and boron isotope, the fractionation mechanisms of boron were discussed to constrain possible boron cycle among different reservoirs. The excellent consistency of borax isotopic composition on the basis of fractionation between hydroboracite and borax and basicboron structure indicates that boron isotopic fractionation occurred during lake water evolution, such as crystallization, adsorption, and alteration processes. The increase of $\delta^{11}\text{B}$ values in brine with corresponding pH varying from 9.86 to 9.01 suggests that pH has predominant control over the separation because $\text{B(OH)}_3$ will preferentially concentrated in trigonal (B(OH)$_3$) species. Very low $\delta^{11}\text{B}$ values of brine in Zabuye salt lake imply a negative origin as almost all natural geochemical processes will result in positive values without any other extra boron input. Similar fractionation factor between carbonate-rich clay and brine to that between sediment and brine in other salt lakes in Tibetan Plateau also strongly support the accumulation of boron from the input of carbonate-rich clay. Unlike the consecutive evaporation in Bange salt lake with relatively positive $\delta^{11}\text{B}$ values, Zabuye salt lake has experienced crystallization from initial brine and subsequent redissolution of carbonate-rich clay processes and the extracted boron is carried into the lake by river water and rising springs.

1. Introduction
Zabuye salt lake is located in the interior of the Tibetan Plateau and famous for abundant resources of boron and lithium [1,2]. It is unique in the world for natural product of lithium carbonate mineral. In the drainage basin, previous research on sedimentology, biochronology, and mineral deposits have been conducted and evolution history has also been well established since Late Pleistocene. However, the source of extremely enriched boron is still unclear and formation of depleted isotopic value is unknown. Specifically, geological and geochemical studies in the drainage basin show that developed rocks has relatively high boron content, especially for travertine widely developed around the lake [2,3]. In addition, a large area of sinters that deposited from intensive geothermal activities in ancient period has also been observed with abundant boron. Thus, it is interesting to figure out where the ultra-large-scale boron sourced from and how the boron ore forms. In this paper, boron and boron isotopes of different water in Zabuye drainage basin were discussed to reveal boron isotopic fractionation and sedimentary process. The special circulation of boron element is expected to be helpful for understanding evolution and mineralization of Zabuye salt lake.
2. Sampling and analysis

Around the Zabuye salt lake, lake water, marsh water, groundwater, and river water were sampled with polyethylene bottles. During the field sampling, water was filtered through 0.45 μm Millipore membrane filters before collecting and sealing. Samples for cation analysis were acidified with ultrapure HNO$_3$ to pH < 2.0. After sampling and sealing, water samples were refrigerated at 4°C and then transported to laboratory for measurement.

The rock bulk composition and mineral constituent was performed by X–Ray diffraction (XRD) analyses. Temperature (T), pH and total dissolved solids (TDS) were measured using a calibrated portable Multi-Parameter Analyzer (WTW Multi 340i). In the laboratory, cations of samples were measured by ICP-AES with errors < 5.0% and anions by ion chromatography with errors < 2.0%. As to boron isotope, it was measured by Neptune Plus MC-ICP-MS with isotopic standard ($^{11}$B/$^{10}$B)$_{\text{standard}}$ NIST 951 = 4.04362.

3. Result

Borax and hydroboracite are two of the main borate minerals in Zabuye salt lake area. The former is mainly distributed in the periphery of lake while the latter is close to the catchment area. Lacustrine carbonatite was measured with extremely low isotopic value of -28.06‰ and the mineral is mainly composed of hydroboracite. With respect to water samples, they were collected in different area of Zabuye salt lake and the TDS is varied from 115.4mg/L to 10.22g/L. The isotopic values are varied from -18.06‰ to -8.82‰ and decreased from -4.84‰ in the upstream to -10.51‰ in the downstream. Predominant hydrochemical compositions of most fresh water are Na$^+$ and HCO$_3$ and saline water are mainly controlled by Na$^+$ and Cl$^-$. One special case needed mentioning is that spring water around the lake has relatively higher Ca and Mg concentrations compared with fresh water.

4. Discussion

4.1. Boron isotopic fractionation occurred during lake evolution

The carbonate sample that is mainly composed of hydroboracite can be used as representative sample with $\delta^{11}$B value of -28.06‰. Unfortunately, isotopic composition of borax has not been successfully detected as insufficient sample quantity. The isotopic fractionation between solution and borax has not been reported possibly because borates did not maintain boron isotope equilibrium with the coexisting brine after precipitation from solution [4]. Experimental and empirical studies reveal that borate minerals that have the same boron coordinates and atomic structures show similar isotopic values due to conservative behaviors, such as hydroboracite, colemanite, and inyoite [5]. This means boron isotope of borax can be indirectly calculated in terms of fractionation between borax and inyoite. Considering that difference between the bond strength of $^{11}$B and $^{10}$B with oxygen yield isotopic fractionation of 3.3‰ for borax and inyoite [5,6], the corresponding $\delta^{11}$B value of borax should be restricted in -24.76‰ based on borax precipitated in equilibrium. Alternatively, according to basic boron structure and theoretical fractionation factor of $^{11}$B and $^{10}$B (table 1), separate values of atomic

| Boron Mineral    | Chemical Formula | Basic boron structure |
|------------------|------------------|-----------------------|
| borax            | Na$_2$B$_4$O$_7$(OH)$_4$·8H$_2$O | 2BO$_3$+2BO$_4$ |
| Tincalconite     | Na$_2$B$_4$O$_7$(OH)$_4$·3H$_2$O | 2BO$_3$+2BO$_4$ |
| kernite          | Na$_2$B$_4$O$_7$(OH)$_4$·3H$_2$O | 2BO$_3$+2BO$_4$ |
| colemanite       | CaB$_4$O$_7$(OH)$_4$·H$_2$O | BO$_3$+2BO$_4$ |
| meyerhoffertite  | Ca$_3$B$_4$O$_7$(OH)$_{10}$·2H$_2$O | 2BO$_3$+4BO$_4$ |
| inderite         | MgB$_4$O$_7$(OH)$_2$·5H$_2$O | BO$_3$+2BO$_4$ |
| inyoite          | Ca$_3$B$_4$O$_7$(OH)$_{10}$·8H$_2$O | 2BO$_3$+4BO$_4$ |
| hydroboracite    | CaMg[B$_4$O$_7$(OH)$_2$]·3H$_2$O | BO$_3$+2BO$_4$ |
groups in borate minerals can be obtained, simply assuming that almost all the $^{11}$B and $^{10}$B exists in the form of trigonal and tetrahedral, respectively. In combination with basic boron structure of borax $2\text{BO}_3 + 2\text{BO}_4$, isotopic value is expected to be -24.85‰. This value is quite consistent with fractionation result of borate minerals, evidently suggesting that borax and hydroboracite in Zabuye salt lake were not co-precipitated from brine but obviously deposited in a given differential sequence and significant boron isotopic fractionation occurred during evaporation and crystallization processes.

With respect to the water samples, variations of B and $\delta^{11}$B display a linear relation when the compositions in water change from intercrystalline water to lacustrine silty water. This linear variation pattern explicitly reflects boron adsorption by solid sediments from brine of Zabuye salt lake, during which $^{11}$B is concentrated in the remaining liquid and $^{10}$B is preferentially incorporated into solid phase. Simultaneously, during this adsorption process, brine pH decreases from 9.9 to 9.0 as corresponding $\delta^{11}$B values increase from -18.06‰ to -13.63‰, implying the potential influence of pH. The effect of pH on B element behaviors is more visual in the plot of B/Ca vs pH (figure 1). In fact, boron isotopic variation in brine is mainly controlled by isotopic composition and pH under a certain temperature since fractionation depends on the distribution of boron species in solution [9]. Therefore, the consistent variation of $\delta^{11}$B values and pH suggests that pH have important influences on isotopic composition of remaining brine in Zabuye salt lake after adsorption process as heavy isotope prefers acidic specie($\text{B(OH)}_3$) rather than tetrahedral ($\text{B(OH)}_4^-$) species.

![Figure 1. pH and B/Ca variations of different water in Zabuye drainage basin. Lake water of Bange were also displayed for comparison.](image)

4.2. Possible recharge pattern and special boron cycle in Zabuye salt lake

As shown by hydrochemistry of rivers around the salt lake, chemical compositions rapidly become saline with the river flowing from the upstream to the downstream, especially for boron concentration. Simultaneously, a better correlation has been observed between river water and brine. This phenomenon exactly reflects that significant amount of boron was leached from carbonate-rich clay and accumulates in the lake. According to simple mixing calculation among marsh water, river water, and lake water, marsh and river water was identified as intermediate during water changing from smelt snow to brine. Thus, it can be concluded that river water is infiltrated into ground gradually after flowing across debouchure and emerged again as rising cold spring at the lake front. Rising spring
should be another important recharge pattern of boron to the salt lake.

Figure 2. Diagram of boron isotopes and Cl concentrations of waters in Zabuye drainage basin. Evolutionary paths are restricted by spring water and surface river water.

According to isotopic fractionation, $\delta^{11}$B of brine in salt lake will become heavier without any other extra input in natural geochemical processes. In regard to hydrochemical compositions in waters from Tibetan lakes, Zabuye has the most concentrated B and Cl concentrations, indicating strong evaporation compared with other lakes. Consequently, the corresponding $\delta^{11}$B values of brine should be more positive than that of most salt lake. However, this variation has not been observed in Zabuye salt lake because the subsequent redissolution of carbonate-rich clay has significantly decreased the isotopic composition of brine (figure 2). Meanwhile, given the annual boron gross accumulation of 295 tons [2], the accumulation time of liquid boron resources in the salt lake is possibly less than 3.2 ka years, which is apparently imbalance with the long history of Zabuye Salt Lake. In fact, a large amount of boron has been discovered in lacustrine sediment in the form of borate or carbonate minerals as a result of variations of local hydrogeological conditions in response to climate fluctuation. The positive carbon and oxygen stable isotopes in sediment cores since 10.6 kyr B.P. suggest that Zabuye lake probably closed its surface outflow due to a strong evaporation environment accompanied by drastic drop of lake level [10,11]. Thus, it is reasonable to deduced that boron in coexisting brine is stored subsequently in sediment and isotopic values of the borate minerals are expected to be higher and increased with burying depth. During the recession and evolution of salt lake, depositional boron has been dissolved again and carried to the center of drainage basin. This evolutionary process can also be reflected by isotopic fractionation. If we calculate the fractionation factor between carbonate-rich clay and brine according to definition, the result of 0.982 is similar to the range of salt lakes in Qaidam basin, 0.982 ~ 0.998 (Zhinu), 0.982 ~ 1.011 (Daqaidam), and 0.984 ~ 1.009 (Mahai) [12], strongly suggesting the accumulation of boron from the input of carbonate-rich clay. These multi processes of deposition and redissolution not only contribute to the enrichment and mineralization of boron resources, but also cause the variations of boron isotope. Therefore, unlike the consecutive evaporation in Bange salt lake with relatively positive isotopic values, Zabuye salt lake has experienced crystallization from initial brine and subsequent redissolution of carbonate-rich clay and
the latter is mainly responsible for present negative brine isotopic compositions.

5. Conclusions
- The excellent consistency of borax isotopic composition on the basis of fractionation between hydroboracite and borax and basic boron structure indicates that boron isotopic fractionation occurred during lake evolution.
- The increase of $\delta^{11}B$ values in brine with corresponding pH decreasing suggests that pH plays an important influence on boron isotopic composition of brine in Zabuye salt lake.
- The hydrochemical variations and isotopic fractionation indicate that very negative $\delta^{11}B$ values of brine in Zabuye salt lake is mainly related with redissolution of carbonate-rich clay and the main transportation pattern of boron into Zabuye salt lake is by river and cold spring.

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