

# Boron isotope geochemistry of Zigetang Co saline lake sediments, Tibetan Plateau

Xiaodan Wang<sup>1,2</sup> · Congqiang Liu<sup>1</sup> · Zhiqi Zhao<sup>1</sup> · Shijie Li<sup>1</sup> · Gangjian Wei<sup>3</sup>

Received: 14 April 2017/Revised: 22 May 2017/Accepted: 7 June 2017/Published online: 17 July 2017  
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**Abstract** The origin of boron in boron-rich salt lakes in the Tibetan Plateau is highly controversial. In this study, we carried out a detailed study on boron geochemistry and isotope composition of lake sediments collected in Zigetang Co, central Tibet. Evaporites had high boron concentrations of 172.3–418.6  $\mu\text{g/g}$  and  $\delta^{11}\text{B}$  values of  $-8.2\%$  to  $-3.3\%$ , suggesting a non-marine origin for the saline lake. The boron isotopic fractionation factor,  $\alpha$ , between evaporite and brackish water ( $\alpha_{\text{evaporite-brackish}}$ ) decreased systematically with depth, from 0.9942 at the top of the drill core to 0.9893 at the bottom; the linear variation between  $\alpha_{\text{evaporite-brackish}}$  and depth reflects boron isotopic fractionation associated with progressive crystallization. The positive correlation between  $\delta^{11}\text{B}$  versus [B] and  $\delta^{11}\text{B}$  versus depth in the evaporite phase reflects pH and boron speciation in the solution control on the adsorption of boron, and  $\text{B}(\text{OH})_3$  species incorporated preferentially into  $\text{Mg}(\text{OH})_2$  precipitation at high pH.

**Keywords** Boron isotopes · Zigetang Co · Equilibrium isotopic fractionation · Boron concentration

## 1 Introduction

Elements in lake sediments can be used to investigate the contributions of different forcing mechanisms to changes in sedimentary environments. Boron's highly soluble character and the large relative mass difference between  $^{10}\text{B}$  and  $^{11}\text{B}$  lead to significant isotopic fractionation (Wei et al. 2014). Hence, boron concentration and isotopic composition have been used as proxies for tracing mass transfer processes and reconstructing depositional environments (Chetelat et al. 2009). Experimental research of inorganic carbonate precipitation has been carried out to determine the dependence of boron isotopic composition of carbonate under different conditions (Xiao and Wang 2006). In this study, we explored evolution processes of Zigetang Co by studying boron isotopic composition of the evaporite phase in sediments collected from a drill core. This research will deepen understanding of the environmental evolution of salt lakes of the Tibetan Plateau.

11th International Symposium on Geochemistry of the Earth's Surface.

✉ Congqiang Liu  
liucongqiang@vip.skleg.cn

✉ Zhiqi Zhao  
zhaozhiqi@vip.skleg.cn

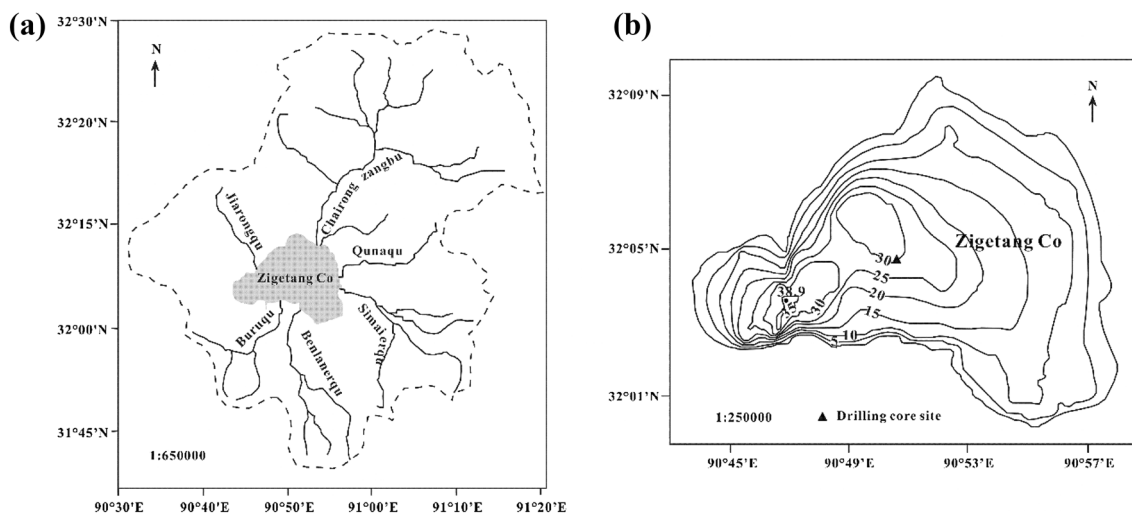
<sup>1</sup> State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, Guizhou, China

<sup>2</sup> University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup> State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

## 2 Geology of the study area

Zigetang Co (altitude 4561 m a.s.l.; in Tibetan, “Co” means “lake”) is in the central Tibetan Plateau, southern Tanggula Mountains, and belongs to Amdo County, Xizang Autonomous Region, China (Fig. 1). Zigetang Co is a meromictic saline endorheic lake with an area of 191.4  $\text{km}^2$ , formed along the Bangong Lake–Dongqiao–Nujiang River fault zone in the late Pliocene (Jin et al. 2016). No longer receiving glacial meltwater input, the water supply depends



**Fig. 1** Overview map of **a** the Zigetang Co catchment and **b** drilling core site within the lake in August 2012

on seasonal inflows, precipitation, and springs at the southwestern edge of the lake. The average water depth is 19.2 m with a maximum of 38.9 m. Oxygen content at 15–22 m depleted rapidly to 0 at 22 m with pH values between 9.9 and 10.2 (measured with Yellow Spring Instrument 6600 V2 multisensor sonde in 2012).

### 3 Methods and results

Around 0.2 g of solid sediment was weighed and dissolved by the following procedure: sediment samples were placed in a 50-ml centrifuge tube and repeatedly soaked for 24 h with boron-free water (20 mL) until all the adsorbed boron had been removed (concentration of boron was less than 10 ng/g). The dissolved part from each step was collected as the evaporite phase. The minerals in the sediment samples were identified by X-ray diffraction and found to consist of mixed layers of aragonite and calcite with lesser amounts of quartz, illite, dolomite, and kaolinite. Boron isotopic composition of lake water samples varied from +2.3‰ to +2.9‰, with a mean value of +2.5‰. Samples from Zigetang Co sediments had relatively high boron concentrations from 172.3 to 418.6 μg/g;  $\delta^{11}\text{B}$  values varied from −3.3‰ to −8.2‰, indicating a non-marine origin for the saline lake.

## 4 Discussion

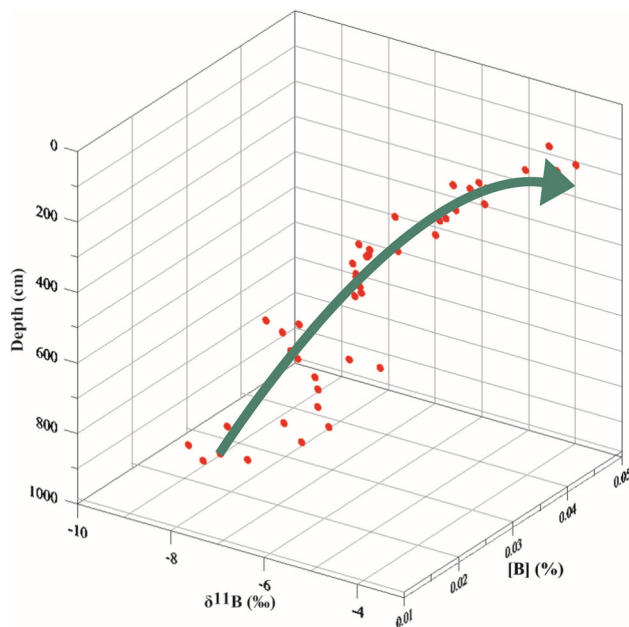
### 4.1 Boron isotopic fractionation occurred during crystallization of salts in evaporite phase

Boron contents and isotopic compositions varied systematically along the depth of the drill core in the evaporite phase:  $\delta^{11}\text{B}$  values decreased from −3.3‰ at the top to

−8.2‰ at the bottom of the drill core at 8.9 m in depth. Similar trends have been observed in the sediments from DSDP Hole 477 in the Guaymas Basin (Spivack et al. 1987). Calculated isotopic fractionation factors between evaporite and brackish water ( $\alpha_{\text{evaporite-brackish}}$ ) ranged from 0.9893 to 0.9942. Since boron isotopic fractionation was found to be controlled by speciation of boron in both the solution and mineralogy, and to vary with pH in the brine, the linear correlations of  $\alpha_{\text{evaporite-brackish}}$  values and depth should reflect the boron isotopic fractionation associated with progressive crystallization.

### 4.2 Isotopic composition of boron in lake sediments

Hobbs and Reardon (1999) suggested that the change in boron speciation could cause increased incorporation of boron at higher pH values. Palmer (1987) showed that the amount of adsorbed boron by sediment is determined by the activities of  $\text{B}(\text{OH})_3$ ,  $\text{B}(\text{OH})_4^-$ , and  $\text{OH}^-$ , and their affinity coefficients. Due to the low affinity coefficient of  $\text{B}(\text{OH})_3$  at low pH, the amount of adsorbed boron is also lower at low pH, and increases with the increase of  $\text{B}(\text{OH})_4^-$  that comes with increasing pH (Keren et al. 1981). The amount of adsorbed boron increased rapidly due to the relatively strong affinity of clays for  $\text{B}(\text{OH})_4^-$ . However, boron adsorption decreased rapidly due to competition by  $\text{OH}^-$  for the adsorption sites, since  $\text{OH}^-$  concentration increases with increasing pH (Umeda et al. 1981). Zigetang Co is a typical saline lake dominated by  $\text{Na}^+$  and  $\text{HCO}_3^-$ , with pH between 9.9 and 10.2. Mg precipitates may have low solubility as  $\text{Mg}(\text{OH})_2$  at higher parent solution pH. Xiao (2006) proposed that during synthetic carbonate precipitation, the incorporation of  $\text{B}(\text{OH})_3$  is attributed to the formation of  $\text{Mg}(\text{OH})_2$  at the higher pH of a calcifying microenvironment. In this study, the boron concentration



**Fig. 2** Spatial distribution of  $\delta^{11}\text{B}$  and  $[\text{B}]$  in evaporite phase along the depth of the drill core in the stereograph

increased from 172.3  $\mu\text{g/g}$  at the bottom layer to 418.6  $\mu\text{g/g}$  at the top layer, and  $\delta^{11}\text{B}$  also increased, from  $-8.2\text{‰}$  to  $-3.3\text{‰}$ . Linear correlations of  $\delta^{11}\text{B}$  versus  $[\text{B}]$  and  $\delta^{11}\text{B}$  versus depth were observed (Fig. 2). The increase of boron uptake into the Zigetang Co sediments is likely due to the coprecipitation of borate-boron with calcium carbonate or the adsorption of boron by  $\text{Mg}(\text{OH})_2$  precipitation. Adsorption of  $\text{B}(\text{OH})_3$  is accompanied by greater fractionation than is  $\text{B}(\text{OH})_4^-$  (e.g.  $\alpha_{\text{evaporite-brackish}}$  of 0.9893 in the bottom of the drill core and 0.9942 at the top), which is consistent with the formation of a tetrahedrally coordinated adsorbed species (Palmer et al. 1987). The activity of borate ions is important to the coprecipitation of borate-boron with calcium carbonate; the activity coefficient of  $\text{B}(\text{OH})_3$  increases and that of  $\text{B}(\text{OH})_4^-$  decreases with increasing concentration of dissolved chemical species, as the coprecipitation of  $\text{B}(\text{OH})_4^-$  is dominant for aragonite and that of  $\text{B}(\text{OH})_3$  for calcite. So, the amount of borate-boron coprecipitated with calcite increases with increasing salinity and pH, while it decreases with aragonite. Consequently, the  $\delta^{11}\text{B}$  of adsorbed boron is dependent on pH, and controlled by the speciation of boron—the different complexes formed at the solid surface—and by the chemical compositions of the brackish water.

## 5 Conclusions

Boron isotope geochemistry in evaporite sediments collected from Zigetang Co was investigated. The  $\delta^{11}\text{B}$  values and boron concentrations in the evaporite phase varied from  $-8.2\text{‰}$  to  $-3.3\text{‰}$ , and 172.3–418.6  $\mu\text{g/g}$ , respectively, indicating a non-marine origin of the saline lake. The geochemical information recorded in the evaporite phase of the sediments was interpreted as following: (1) Values of  $\alpha_{\text{evaporite-brackish}}$  decreased from 0.9942 to 0.9893 along the depth of the drill core. The linear correlations of the  $\alpha_{\text{evaporite-brackish}}$  values and depth suggest that boron isotopic fractionation occurred during progressive crystallization; and (2) The positive correlation between  $\delta^{11}\text{B}$  and  $[\text{B}]$  in the evaporite phase suggests pH and boron speciation in the solution control the adsorption of boron by clay, and the incorporation of  $\text{B}(\text{OH})_3$  into  $\text{Mg}(\text{OH})_2$  precipitation mainly depends on the pH of the solution.

**Acknowledgements** This work was jointly supported by the National Basic Research Program (973 project) of China (2013CB956401), and the National Natural Science Foundation of China (Grant Nos. 41210004, 41661144042).

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