Geochemical and hydroclimatic constraints on the formation of borate deposits in Da Qaidam Salt Lake of Qaidam Basin, northern Tibetan Plateau

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Abstract. The pinnoite deposit occurred in the lakebed of Da Qaidam Salt Lake in Qaidam Basin is rare in the world. This study focused on the pinnoite, ulexite and hydroboracite from Da Qaidam Salt Lake, through multi-index methods including mineralogy and geochemistry, aiming to interpret the mechanism of pinnoite and other borate minerals. The results showed that pinnoite as well as ulexite and hydroboracite in lakeside are formed in the lake environment with specific hydrogeochemical conditions (e.g., alkaline brine, hydrochemical types, boron concentration, boron ions, Mg/Ca ratio, dilution and mixing mechanism). The borate formation was controlled by a coupling mechanism, i.e., the inherent geochemical characteristics and the external conditions.

1. Introduction
Qaidam Basin is a larger hyper-arid basin on the northern Tibetan Plateau, where the evaporite deposition and associated potassium-rich brines are the most important salt-lake resources of China. In addition, borate deposits and boron-bearing brine are formed in Da Qaidam Salt Lake. Previous study on the Da Qaidam borate deposits using geochemical, solution chemical and mineralogical methods were focused on the so-called eastern high-grade mineral zone [1-2]. The pinnoite deposit beneath the bottom of saline lake is not yet studied though its formation is of distinguishing characteristic [3-4]. Here we report the mineralogical and geochemical results of pinnoite deposit in the lakebed as well as ulexite and hydroboracite in the lakeside, aiming to demonstrate the ore-forming environment and mechanism of borate deposits, as well as the inherent origin relationship between pinnoite and other borate minerals.

2. Study area
Da Qaidam (37°46'-37°55'N, 95°02'-95°22'E) is now a shallower salt lake that varies seasonally in surface area ranged from 23 to 36 km\textsuperscript{2}, and the depth rises less than 1 m during the summer flood season [4]. In lake region, the average annual E/P ratio is 24.3, and the average annual temperature is 1.4 °C [4]. The lake shows magnesium sulfate type of hyper-saline brine with TDS up to 375 g/L [3], and the average salinity is about 325 g/L. The thermal springs, melt water, rainfall and recharged
rivers flowed into Da Qaidam Salt Lake. The lake level and hydrochemistry are mainly controlled by the intensified summer evaporation and concentration.

3. Materials and methods

3.1. Sample descriptions
The pinnoite, ulexite and hydroboracite minerals, as well as several profile sections were collected from Da Qaidam Salt Lake (figure 1), and all the sediment samples were stored in cool rooms at 4 °C in the laboratory. All borate samples are prepared for XRD and SEM-EDS analysis.

3.2. Analytical methods
All samples for XRD analysis are referenced to the study of Da Qaidam Salt Lake [4]. The selected borate samples for SEM-EDS analysis were sprayed by gold, using a JSM-5610LV/INCA low vacuum scanning electron microscope coupled with an energy dispersive X-ray spectrometer. The high resolution and low resolution is HV3.5 nm and LV5.0 nm, respectively.

4. Results and discussion

4.1. Mineralogical records
Based on investigation in fieldwork and mineralogical results in the laboratory, the types of borate mineral can be divided into cemented massive pinnoite in the lakebed, grey nodular ulexite and earthy hydroboracite in the lakeside.

4.1.1. Pinnoite ore
The pinnoite mineral is off-white, with the characteristics of well developed bedding and cemented massive structure (figure 2a). XRD results showed that the main components of pinnoite deposit in the lakebed are pinnoite, hydromagnesite, halite and detrital minerals (figure 2c). SEM-EDS analysis for the pinnoite layer found that pinnoite crystals are euhedral (figure 2b, 2d), suggesting that the pinnoite ore is primary in origin [3]. In addition, three layer of pinnoite deposits emerged in the profile section, with no more than 16% B₂O₃ content [4].
4.1.2. Ulexite ore
The pure ulexite is white with soft texture, but appeared off-white due to coming from gray black or black silt (figure 3a). The ulexite can be dissolved partly in water, with the characteristics of spherical or nodular structure. XRD results showed that the main components of ulexite ore in the lakeside are ulexite, halite and calcite (figure 3c). SEM-EDS results showed that the ulexite is a fibrous or acicular crystal (figure 3b, 3d).

4.1.3. Hydroboracite ore
The hydroboracite is earthy with thin stratified structure (figure 4a). XRD results showed that the main components of hydroboracite ore in the lakeside are hydroboracite, halite, gypsum, quartz and muscovite (figure 4c). SEM-EDS results showed that the hydroboracite is an off-white slight oolitic crystal, with diameter varies from 0.5 to 2 mm (figure 4b, 4d). Especially, the average B₂O₃ content of ulexite and hydroboracite in the lakeside ranged from 3 to 9%, which belongs to low-grade borate deposit.
4.2. Ore-forming Conditions and Mechanism

In previous studies, the boron in lake brine occurred as B(OH)$_3$ and B(OH)$_4$ in Qaidam Basin [5]. However, the proportional relation of various boron concentrations cannot be determined accurately by the reliable experimental methods. Therefore, the comprehensive statistical form (B$_4$O$_7^{2-}$) can represent boron compositions in the equilibrium solution [2].

4.2.1. Pinnoite

The pinnoite deposits were controlled by alkaline conditions, sufficient Mg$^{2+}$ and B$_2$O$_3$ contents as well as the hyper-arid climate conditions [3]. Especially, the dilution and mixing mechanism plays an important role, i.e., the hydrolyzation of CO$_3^{2-}$ into OH$^{-}$ caused the lake brine more alkaline, under this hydrochemical condition, the reaction of B$_4$O$_7^{2-}$ with OH$^{-}$ produced BO$_2^{-}$, most of Mg$^{2+}$ reacted with BO$_2^{-}$ to produce the colloid pinnoite, and finally converted into the cemented pinnoite ore later due to the diagenetic compression[4]. Therefore, the chemical reaction process of pinnoite was concluded as follows:

1. $2\text{B(OH)}_3 + 2\text{B(OH)}_4^- = \text{B}_4\text{O}_7^{2-} + 7\text{H}_2\text{O}$
2. $\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$
3. $2\text{OH}^- + \text{B}_4\text{O}_7^{2-} + \text{H}_2\text{O} = 4\text{BO}_2^- + 2\text{H}_2\text{O}$
4. $\text{BO}_2^- + \text{Mg}^{2+} + 3\text{H}_2\text{O} = \text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ (pinnoite)

4.2.2. Ulexite

Based on the XRD results and actual profile section, we concluded that ulexite spheroids were nucleated directly from the sediment pore water in the near-shore marsh as a result of dilution of saturated NaCl brine rich in B$_4$O$_7^{2-}$ by Ca$^{2+}$-bearing spring water, and then grew gradually with sediment solidification, but appeared offwhite due to coming from gray black clay or black silt. Therefore, the chemical reaction process of ulexite was concluded as follows:

1. $2\text{B(OH)}_3 + 2\text{B(OH)}_4^- = \text{B}_4\text{O}_7^{2-} + 7\text{H}_2\text{O}$
2. $\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$
3. $\text{OH}^- + \text{B}_4\text{O}_7^{2-} + \text{H}_2\text{O} = 4\text{BO}_2^- + 2\text{H}_2\text{O}$
4. $\text{B}_4\text{O}_7^{2-} + \text{BO}_2^- + \text{Na}^+ + \text{Ca}^{2+} + 8\text{H}_2\text{O} = \text{NaCaB}_3\text{O}_5 \cdot 8\text{H}_2\text{O}$ (ulexite)

4.2.3. Hydroboracite

XRD results showed that the main components of hydroboracite ore in the lakeside are hydroboracite, also including a certain amount of halite, gypsum, quartz and muscovite. While SEM-EDS results
showed that the hydroboracite is a homogeneous oolitic crystal. From the above, we considered that earthy hydroboracite was produced at the lake shore locations where subsurface boron-bearing water mixed with the brines characterized by alkaline, Mg$^{2+}$-bearing and low sulfate, and where water table was subject to frequent fluctuations. Therefore, the chemical reaction process of hydroboracite was concluded as follows:

1. $2\text{B(OH)}_3 + 2\text{B(OH)}_4^+ = \text{B}_2\text{O}_7^{2-} + 7\text{H}_2\text{O}$
2. $\text{CO}_3^{2-} + \text{H}_2\text{O} = \text{HCO}_3^- + \text{OH}^-$
3. $\text{OH}^- + \text{B}_2\text{O}_7^{2-} + \text{H}_2\text{O} = 4\text{BO}_4^2^- + 2\text{H}_2\text{O}$
4. $\text{B}_2\text{O}_7^{2-} + 2\text{BO}_4^2^- + \text{Mg}^{2+} + \text{Ca}^{2+} + 6\text{H}_2\text{O} = \text{CaMgB}_6\text{O}_{11}·6\text{H}_2\text{O}$ (hydroboracite)

As a result, (a) an alkaline brine was crucial in creating chemical conditions favorable for borate precipitation; (b) hydrochemical types, boron concentration, boron ions, Mg$^{2+}$ concentration and Mg/Ca ratio in lake brine played a leading role in borate formation; and (c) dilution and mixing mechanism was a driving factor [4]. For instance, the carbonate-type salt lake such as Bangkog Co in Tibet, borax is the main borate mineral [6]; the magnesium-sulfate type salt lakes such as Xiao Qaidam Salt Lake in Qaidam Basin and Zhacang Chaka in Tibet, ulexite–pinnoite assemblage [7] and kurnakovite–pinnoite–ulexite assemblage [8] occurred in the sediment, respectively. Furthermore, compared to other borate deposits in the world, the ore-forming ages, mineral species and assemblages are also different [9-15].

As shown in Table 1, the $^{11}\text{B}/^{10}\text{B}$ value of pinnoite, ulexite, hydroboracite and borate earth ranged from 3.9962 to 4.0251, suggesting that the different borate minerals formed in the different brine concentration stages with different hydrochemical compositions. The previous study also found that the hydrological response to climate warming in high altitude mountain catchments contrasts strikingly to that in the hyper-arid Qaidam Basin [16], which is the key hydroclimatic driving factor. Consequently, due to the favorable hydrogeochemical conditions, the borate deposits finally formed in different zones of Da Qaidam Salt Lake.

| Location               | Type    | $^{11}\text{B}/^{10}\text{B}$ (SD) | $\delta^{11}\text{B}$ (%) |
|------------------------|---------|---------------------------------|---------------------------|
| Da Qaidam Salt Lake    | Pinnoite| 3.9962                          | -13.30                    |
| Da Qaidam Salt Lake    | Ulexite | 4.0121                          | -7.80                     |
| Da Qaidam Salt Lake    | Borate earth | 4.0251          | -4.60                     |
| Da Qaidam Salt Lake    | Hydroboracite | 4.0063              | -9.23                     |

5. Conclusions

The ore-forming mechanism of borate deposits as follows: the boron-bearing brine are formed in saline lake, with the characteristic of $\text{B}_2\text{O}_7^{2-}$ under the evaporation and concentration effect; then it transformed into $\text{BO}_4^2-$ under the dilution and depolymerization effect; the borate deposits are finally formed under the adulteration effect and diagenetic compression. Therefore, the borate formation was controlled by a coupling mechanism, i.e., the inherent geochemical characteristics and the external conditions.

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