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# Pinnoite Deposit in DaQaidam Saline Lake, Qaidam Basin, China: Hydroclimatic, Sedimentologic, and Geochemical Constraints

JunQing Yu <sup>1,2,\*</sup> , Rongchang Hong <sup>1,2,3</sup>, Chunliang Gao <sup>1,2</sup>, Aiyong Cheng <sup>1,2</sup> and Lisa Zhang <sup>1,2</sup>

- <sup>1</sup> Key Laboratory of Comprehensive and Highly Efficient Utilization of Salt Lake Resources, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China; hongrongchang13@mails.ucas.edu.cn (R.H.); chunlianggao@isl.ac.cn (C.G.); chengaiying1119@126.com (A.C.); lisazhang@isl.ac.cn (L.Z.)
  - <sup>2</sup> Qinghai Provincial Key Laboratory of Geology and Environment of Salt Lakes, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China
  - <sup>3</sup> University of Chinese Academy of Sciences, Beijing 100049, China
- \* Correspondence: junqyu@isl.ac.cn; Tel.: +86-971-630-7153

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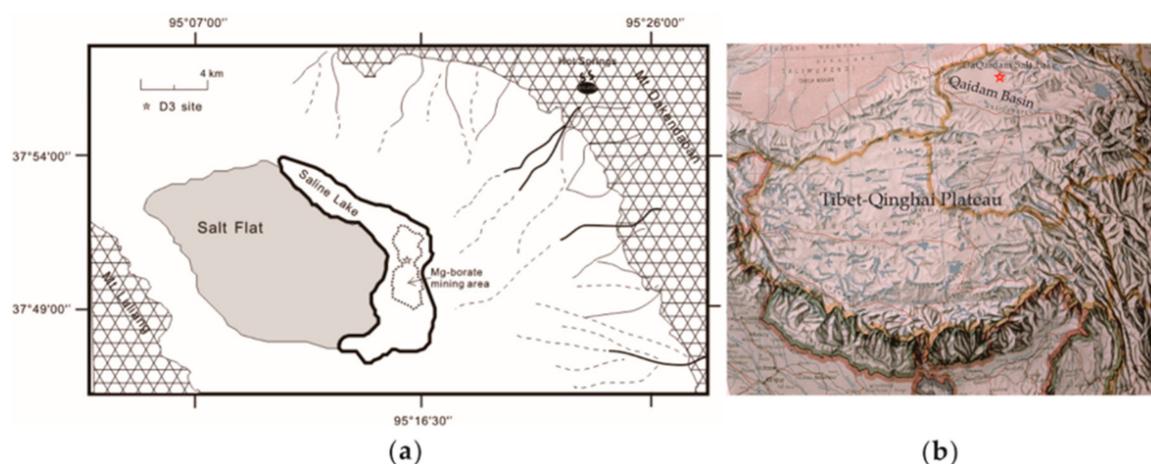
**Abstract:** Mg-borates were traditionally thought to be diagenetic products of other primary borate minerals. Here we report results from the study of pinnoite deposit from DaQaidam saline lake, indicating that pinnoite minerals are primary in origin. Within the detecting limit of X-ray powder diffraction analysis (XRD) analysis, no other borate minerals than pinnoite are detected from the Mg-borate deposit. The cemented pinnoite orebody shows the sedimentary structure of light-dark lamination couplets, which signal marked seasonal variations in brine chemistry. The scanning electronic microscopy coupled with an energy dispersive X-ray spectrometer (SEM-EDX) examination reveals that all pinnoite minerals displayed euhedral, giving no indication of diagenetic origin. A marked shift in lithology from clastic sediment to evaporitic deposit reflects a critical change in sedimentation regime associated with abrupt changes in hydroclimatic conditions. The deposition of the pinnoite ore-layer containing abundant hydromagnesite marked the beginning of the evaporite formation and the end of the clastic deposition. This suggests that aridification occurred abruptly and the saline lake was much more alkaline than today in the early-stage of the evaporite deposition. The intensified summer evaporation and seasonal variations in water chemistry brought about a shallow to nearly desiccated paleo-lake with pH exceeding 9.3, Mg/Ca ratio >39, and boron concentration >600 mg/L, which favored pinnoite precipitation and the formation of pinnoite deposit in the central DaQaidam saline lake.

**Keywords:** boron deposit; DaQaidam saline lake; evaporitic sequence; primary pinnoite; brine chemistry; hydroclimatic conditions

## 1. Introduction

Pinnoite ( $\text{MgB}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ) is one of the ~20 naturally occurring Mg-borate minerals identified as of 1996, and it is one of the borates important in commercial deposits under the circumstance that only a comparative few of the 230 borates are that important [1]. Notably, a pinnoite ore-layer found from the subbottom sedimentary sequence with a spatial distribution over ~10 km<sup>2</sup> in the central DaQaidam saline lake [2,3] is of great significance in gaining information for better understanding of the pinnoite-precipitating brine chemistry and constraints on pinnoite deposit formation.

DaQaidam Salt Lake is one of the three salt lakes containing solid-phase boron deposit among 25 salt lakes in Qaidam Basin, northwestern China. The borate ore bodies distributed in the eastern shore of the lake began to be used as a commercial product probably as early as in 970 AD [4]. Geological and mineralogical study of the onshore borate deposit found that ulexite ( $\text{NaCaB}_5\text{O}_8 \cdot 8\text{H}_2\text{O}$ ) and hydroboracite ( $\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$ ) are the dominant borate minerals, and that the input of boron-bearing water from hot springs from Mt. Dakendaban has been of great importance for the formation of Na–Ca- and Ca–Mg-borate deposits [5,6]. According to Qu et al. (1981), hydroboracite occurs as 0.5–2 mm spherical grains in the ore layers within gypsiferous deposits, and the borate ooids comprise ~70% hydroboracite in addition to dolomite or hydromagnesite and clay. Both primary and secondary ulexite minerals were identified from the onshore borate deposit. The former was primarily formed in the NaCl supersaturated brine with lower  $\text{SO}_4^{2-}$  and  $\text{Mg}^{2+}$ , but richer in  $\text{Ca}^{2+}$ . The latter occurred in the form of ulexite nodules capping on top of the hydroboracite layers, which were converted from hydroboracite [5]. Subordinate borate minerals identified from the onshore deposit include kurnakovite ( $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ ), pinnoite, inderite ( $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$ ), hungchaoite ( $\text{MgB}_4\text{O}_5(\text{OH})_4 \cdot 7\text{H}_2\text{O}$ ), and carboborite ( $\text{Ca}_2\text{Mg}(\text{CO}_3)_2\text{B}_2(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ ). Experimental result indicates that hungchaoite is stable in the  $\text{H}_3\text{BO}_3$  solution rich in  $\text{Mg}^{2+}$ , and it is transformed into inderite or kurnakovite when the solution is diluted or supplemented with borax. The onshore borate deposit is overall characterized by the site-to-site different occurrence of the borate minerals, indicating a complex deposition system in which geochemical conditions at one site differed from another in a very short distance [5]. Interestingly, borate deposit found from the offshore evaporitic sequence (Figure 1, dotted area in the saline lake) contains only pinnoite, which was formed on the paleo-lake bottom earlier than the onshore borate formation [2,3,5,7]. In order to better understand the sedimentary process and chemistry of the ore-forming brine associated with the genesis of the Mg-borate deposit, we have performed field investigations to examine the mode of occurrence of the pinnoite ore-layer in the subbottom evaporitic sequence and an integrated lithologic and mineralogical study of a type section, D3, selected from the center of the offshore borate deposit (Figure 1). Based on the results from our field and laboratory investigations, we discuss hydroclimatic, geochemical and sedimentologic constraints on the pinnoite deposit formation in DaQaidam saline lake.



**Figure 1.** DaQaidam Salt Lake (a) is a closed-basin lake, located in the northern Qaidam Basin of the Tibet-Qinghai Plateau (b). It includes both perennial saline lake and salt flat with a total area of ~235 km<sup>2</sup>. The boron deposit found in the subbottom evaporitic sequence is of Mg-borate type, distributed in the dotted area of the saline lake. The empty star indicates the location of the D3 section of the evaporitic sequence.

### Study Area

DaQaidam Salt Lake comprises both saline lake and salt flat with a total area of about 235 km<sup>2</sup> (Figure 1). It lies in a closed-drainage subbasin of the northern Qaidam Basin with a large catchment area of more than 2000 km<sup>2</sup>. Geologically, the catchment area is situated in the tectonic belt between Qilian Block and Qaidam Block. Mt. Luliang to the southwest of the lake (Figure 1) is an eclogite-bearing terrane, the part of the North Qaidam ultra-high pressure metamorphic (UHPM) belt [8]. Mt. Dakendaban to the northeast contains probably the largest granite terrane in western China with an area of ~2200 km<sup>2</sup>, which intruded into country rocks including medium- and high-grade Proterozoic metamorphic rocks, Paleozoic sedimentary, and intermediate-mafic volcanic rocks [9]. According to Li [10], the calculated boron Clarke value of the region is about nine times higher than the global mean value. Nevertheless, the inflow of hot spring waters from Mt. Dakendaban (Figure 1; Table 1 [6]) played a key role in providing sufficient amounts of boron-bearing water for evaporative formation of borate deposits in DaQaidam Salt Lake.

**Table 1.** Chemical composition of the hot spring water in mg/L [6] (Refer to Figure 1 for the location).

Types of Water	TDS <sup>1</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	B <sub>2</sub> O <sub>3</sub>
Hot spring water	1235	19.1	348.0	28.6	0.7	361.2	195.0	197.1	137.5
Baligou River <sup>2</sup>	-	3.2	78.1	65.2	13.6	72.3	25.6	-	26.8

<sup>1</sup> TDS: Total Dissolved Solid; <sup>2</sup> Data after [11].

DaQaidam saline lake shows Mg<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup> type of hypersaline brine with total dissolved solid up to 375 g/L. Table 2 [12] shows ion concentrations and other parameters of the brine measured before mining the subbottom pinnoite deposit. The lake is fed by a number of streams originating mainly from the northeastern high altitude mountains. None of the streams are perennial. All ephemeral streams maximize their river-runoff in summer months when precipitation in the mountain catchment is enhanced. The enlargement of the saline lake occurs in summer months, inundating part of the salt flat. Some streams seep into underground in the piedmont of Mt. Dakendaban, continue their subsurface drainage within alluvial fans towards the terminal saline lake.

**Table 2.** Chemical parameters of DaQaidam saline lake brine<sup>†</sup>.

Ions	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	B <sup>3+</sup>	Li <sup>-</sup>
mg/L	88,386	3222	9697	453.5	155,892	16,567	105.1	181.1	469.8	84.9
Date of Sampling	TDS* (g/L)		pH		Relative Density		Hydrochemical Type			
1980.04	274.4		7.95		1.174		Mg <sup>2+</sup> -SO <sub>4</sub> <sup>2-</sup>			

<sup>†</sup> Data after Zhang [12]; \* TDS: total dissolved solid.

According to a monthly record from 1961 to 1962, the annual precipitation and evaporation at DaQaidam Salt Lake is respectively 33.3 mm and 2316.2 mm, and E/P ≈ 70. Under such an arid condition maintaining DaQaidam saline lake perennial requires inflow water supply from large amounts of precipitation-related stream runoff from mountain catchment. Changes in lake level and water chemistry could result from the changes of hydroclimatic conditions, which can be documented in the sediment record. In other words, a prominent shift in lithology may result from a marked change of the sedimentation regime associated with an abrupt hydroclimatic change [13], and variations in the mineralogical composition of the evaporitic sediment are the consequence of chemical changes of the saline lake, linked with changes in inflow/evaporation. About 85% of the annual evaporation occurs in May–October [14]. The contrasting rates of evaporation between summer and winter exert an important control on the chemical sedimentation of the saline lake. The contrasting rates could be amplified in the past warmer period, resulting in more intensified summer evaporation, which will be discussed later in the paper.

## 2. Materials and Methods

Information available from previous investigation about the subbottom sedimentary history of the DaQaidam saline lake was limited partly because the evaporitic sediment was often poorly recovered with disturbance by drilling operation. Our work took advantage of the mining field and excavated an intact sedimentary sequence, the D3 section, with detailed sampling for mineralogical and sedimentological study. This work focused on the study of the lower section from 350 cm to 480 cm of the D3 sedimentary profile, which is located at the center of the mining area of the pinnoite deposit (N 37°50'26", E 95°15'48"). Lithologic logging was done in the field and sampling resolution is about one centimeter. X-ray powder diffraction analysis (XRD) was applied to the determination of mineralogical composition of the evaporitic sediment, including the borate deposit. Pinnoite mineralogy was identified using a scanning electronic microscopy coupled with an energy dispersive X-ray spectrometer (SEM-EDX). Application of above-mentioned methods helped to establish a mineral assemblage record accompanying lithologic shifts for the evaporitic sequence.

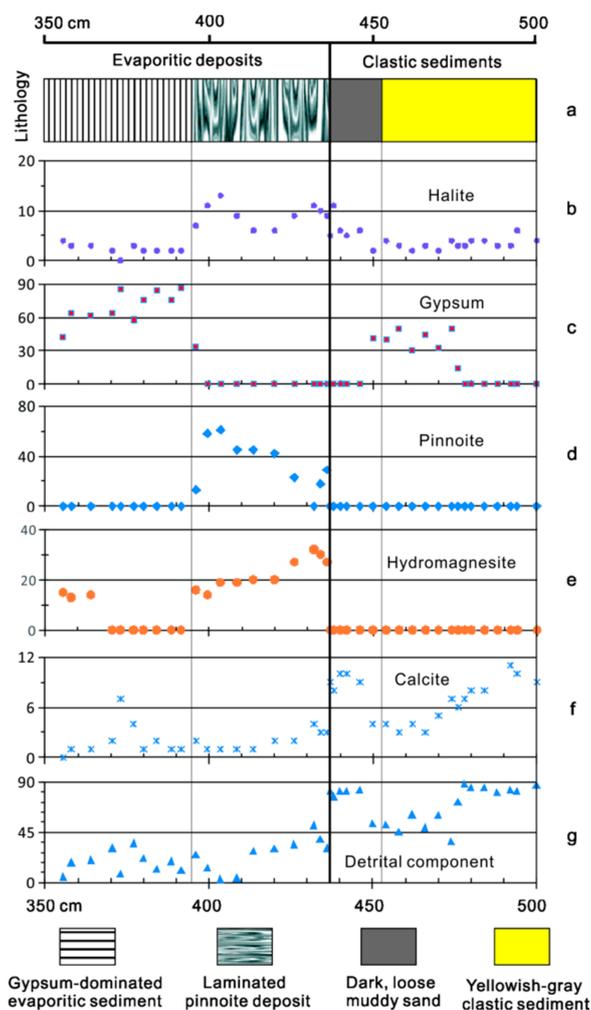
## 3. Results

### 3.1. Lithology

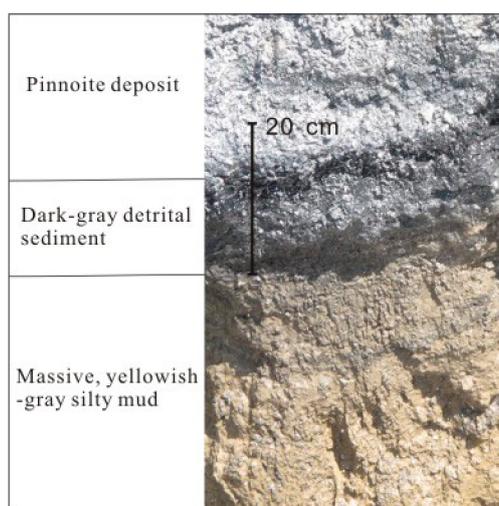
A lithologic boundary occurred at the depth of 437 cm of D3 section, above which is the 437-cm-thick evaporitic sequence (Figure 2a–e), and below which is the clastic sediment (Figure 2a,f,g). According to the mining record, the yellowish-gray silty mud, as also shown in Figure 3, occurs ubiquitously over the mining area (Figure 1a), functions as the aquifuge confining the interstitial brines in the overlying evaporitic deposit. The basal yellowish-gray silty mud (Figure 2a) comprises over 90% detrital component (Figure 2g), mainly quartz, muscovite, albite, and calcite. Gypsum began to occur from the depth of 477 cm up to the top of the yellowish sediment (Figure 2c) ranging from 14% to 50%, alongside with a decrease in detrital component (Figure 2g). This mineralogical change appears noticeable, even though sediment color and massive structure remained unchanged. In consideration that the top 24-cm yellowish sediment is dominantly composed of clastic components with higher water content, the increased gypsum resulted most likely from porewater dry-ups of the clastic sediment. We therefore attribute the increase of gypsum in the top 24-cm thick yellowish clastic sediment to be the signal of the increase of the paleo-lake salinity, namely, the paleo-lake water richer in  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  was incorporated into the porewater of the clastic sediment.

A marked lithologic change is indicated by the deposition of a 16-cm dark-gray layer overlying on the yellowish sediment (Figures 2 and 3). The darker layer, containing little organic matter, is composed of loose and coarser detrital sediment with the characteristics of flush flood deposition. In addition, halite content increased for about 3.6% in the darker layer in comparison with that in the underlying yellowish sediment. Above the darker detrital layer is the pinnoite ore-layer as the base of the evaporitic sequence of DaQaidam saline lake, which marked the beginning of the evaporitic deposition (Figure 2a,d).

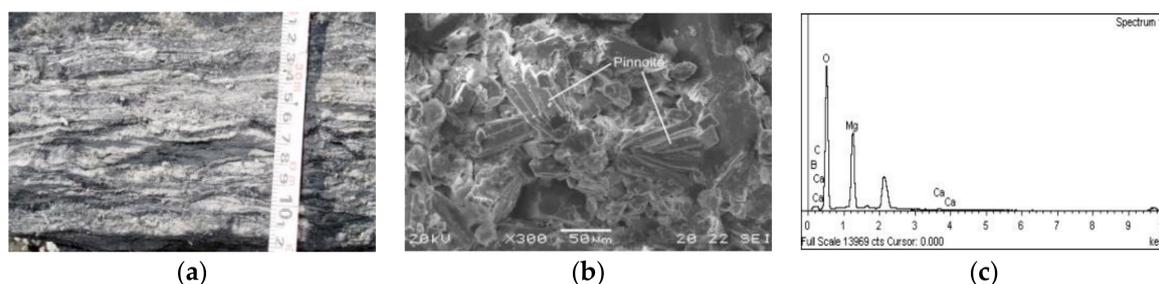
The pinnoite ore-layer (Figure 4a) sitting on the 16-cm-thick dark-gray detrital sediment (Figure 2a) exhibits well-laminated sedimentary structure. Many of the laminations occur as light and dark couplets. The sedimentary structures are of typical lacustrine deposition with the characteristics of annual/seasonal precipitation, indicating strong seasonality during the formation of pinnoite deposit. The laminated pinnoite-ore body occurs as cemented evaporite stratum rich in hydromagnesite, implying that the saline lake level went down seasonally to near desiccation conditions due to intense summer evaporation.



**Figure 2.** Lithology (a) and a mineral assemblage record (b–g) for the lower part (350–500 cm) of the D3 sediment section excavated from the middle of DaQaidam saline lake.



**Figure 3.** The basal clastic sediment of D3 section is composed of yellowish-gray lacustrine silty mud, functions as the aquifuge confining the interstitial brine in the overlying evaporitic deposit. It is overlaid by a 16-cm dark-gray layer characterized by loose and coarser detrital sediment which is then covered by pinnoite ore-layer.



**Figure 4.** (a) Cemented pinnoite orebody with the sedimentary structure of light-dark lamination couplets; (b) Scanning electronic microscopy (SEM) microphotograph of pinnoite crystals in the orebody; (c) An energy dispersive X-ray (EDX) spectrometer spectrum of all elements of the pinnoite crystal on the right (b).

A 40-cm-thick layer above the pinnoite ore-layer is overall rich in gypsum (58–87%), along with halite (~3%) and detrital component (11–35%). It is also characterized basically by gypsum-detritus lamination couplets though not regularly present in the entire layer. The change to gypsum-dominated evaporite deposition from preceding pinnoite and hydromagnesite deposition reflects a threshold of chemical composition variations of the ore-forming brine, at which pinnoite nucleation ceased and turned in favor of gypsum deposition.

### 3.2. XRD and SEM-EDX Analysis

Determined by XRD analysis, the mineral contents against depth of the sedimentary section studied are shown in Figure 2b–g. The detrital component includes quartz, feldspar, muscovite, and clinocllore. Calcite content is higher in the lower clastic sediments and shows a variation trend consistent with the trend of detrital component (Figure 2f,g), suggesting that the main portion of calcite in the lower detritus-dominated sediments corresponds to carbonate detritals.

Within the detecting limit of XRD analysis, pinnoite is the only borate mineral detected from the sediments of D3 section. The borate ore-layer contains 13–61% pinnoite, based on the XRD analyses of nine samples selected from the ore-layer (Figure 2a,d). Identified by SEM-EDX microanalysis, the pinnoite crystals are 50–100  $\mu\text{m}$  in length with orthorhombic structure (Figure 4b). They present in a single crystal or appear as arrowhead-shaped aggregates. The pinnoite crystal on the right, as pointed in Figure 4b, is selected for EDX analysis and a spectrum of all elements is shown in Figure 4c. The analytical data shows that the pinnoite crystal contains 18.36% B, 13.56% Mg, and 62.41% O in weight percentage. Mineralogical results from both XRD and SEM-EDX analysis indicate that the well-formed euhedral crystals neither are the diagenetic products of other borate minerals nor have diagenetic association with other minerals. In addition, it is unlikely that the pinnoite crystals were formed in the way of interstitial growing after the deposition of the ore-layer because whether or not to have pinnoite precipitates depends on the chemistry of the paleo-lake, as clearly indicated by the mineral assemblage record showing in the following Section 3.3. (Also refer to the last paragraph of Section 4). They must have primarily formed either directly from the surface brine or nucleated in the water and sediment interface.

### 3.3. Mineral Assemblage and Brine Chemistry

The paleo-lake was basically in freshwater conditions during the deposition of the yellowish-gray sediment below 477 cm, as suggested by the predominance of clastic component (>90%) with average 2.6% halite. The increase in salinity of the paleo-lake near the end of the clastic deposition is implied by the increase of gypsum from 14% to 50% in the top 24-cm-thick yellowish-gray sediment (Figure 2c,g). The mineralogical record suggests that the paleo-lake has changed from fresh to brackish before the onset of the saline lake conditions, and that the brackish waterbody at that time was relatively rich in

$\text{Ca}^{2+}$ , determined primarily by the geochemical composition of the water inflow from the mountain catchment (Table 1).

The 16-cm-thick dark-gray layer composed mainly of detrital sediment (Figure 2a,f,g) signals an event of enhanced catchment inflow (refer to Section 3.1), which may have resulted in a dilution of the lake water, as suggested by the disappearance of gypsum that occurred in the underlying sediment. However, the fact that a slight increase in both halite and calcite in the loose and coarser darker sediment implies the seasonal variations between fresh and brackish of the paleo-lake, due possibly to the enhanced summer evaporation.

The pinnoite ore-layer is composed of, on average, 37.1% pinnoite, 22.4% hydromagnesite, 9.1% halite, 2.4% calcite, and 29% detrital component (Figure 2). The pinnoite deposit formation marked the beginning of the evaporitic deposition, as well as the commencement of the permanent saline lake conditions. The dominant evaporite minerals of the ore-layer are Mg-carbonate and Mg-borate, together accounting for nearly 60%. This indicates highly alkaline conditions of the paleo-lake following the onset of evaporite deposition of DaQaidam saline lake. The pH value of the paleo-lake is estimated between 9 and 9.3, which is much higher than the present-day pH value 7.9. The estimation is based on: (1) much more  $\text{HCO}_3^-$  is required for precipitating larger amounts of  $\text{MgCO}_3$  from the saline lake and (2) an alkaline brine was crucial in creating chemical conditions favorable for precipitating pinnoite from the brine because the charged species of boron anion,  $\text{B}(\text{OH})_4^-$ , could not be predominant only if pH is above 9.24 [15].

The cessation of pinnoite precipitation may result from a substantial decrease in boron concentration of the brine. In other words, boron became insufficient in the surface brine, following pinnoite deposit formation. In addition, the decrease of magnesium concentration in the brine as the consequence of Mg-borate and hydromagnesite deposition may also play a role in conjunction with an accumulative increase in calcium concentration in the paleo-lake. As a result, the brine turned to be in favor of gypsum precipitation (Figure 2c).

#### 4. Discussion

One of the important facts revealed by this study is the ubiquitous distribution of the yellowish-gray clastic sediment, which functions as the major aquifuge confining the interstitial brine in the overlying evaporitic sequence (Figures 1–3). According to mining record, the pinnoite ore-layer as a basal evaporitic deposit occurred always on top of the yellowish clastic sediment. The pinnoite ore-layer may not occur everywhere over the mining area of the saline lake and the occurring depth and thickness of the pinnoite ore-layer may vary from site to site. This is attributable to the paleo-topography of the saline lake bottom before the evaporitic deposition. Field observation found that the visible sediment character, such as sedimentary structure, of the evaporitic deposit above the pinnoite ore-layer show differences among excavated sediment sections. For such a shallow saline lake, the past changes of lake level and water chemistry on seasonal/decadal/centennial time scales may have resulted in the lateral differences.

The pinnoite deposit was previously anticipated to be formed in the stage following carbonate deposition [5]. We have however found solid evidence that the pinnoite ore-layer overlies right on clastic sediments (Figure 2), and that the Mg-boron deposit marked the onset of the evaporitic deposition in the central area of the DaQaidam saline lake. The lithostratigraphic evidence clearly indicates a transition from clastic to Mg-borate deposition in the lacustrine environment. In fact, the sequential pattern from clastic directly to evaporitic deposition with no carbonate facies in between is not of surprise as it has occurred in other saline lakes in the arid Qaidam Basin as the consequence of abrupt hydroclimatic change [16,17]. Our investigation found that the hydrological response to climate warming in high altitude mountain catchments contrasts strikingly to that in the hyperarid Qaidam Basin: (1) precipitation is enhanced in high-altitude mountain catchments because warmer surface trigger condensation in mountainous topography by increased vertical airflows [16], which increases catchment runoff draining into the terminal saline lakes in the basin

where annual precipitation is around 30 mm and (2) aridification is intensified in the Qaidam Basin as the consequence of warming-induced enhancement of evaporation under the circumstance of a little increase of precipitation in the basin. As a result, the inflow water maximized in summer months is quickly enriched by the intensified evaporation, resulting in evaporite deposition. The sudden shift to evaporite formation induced by abrupt hydroclimatic change also explains why there occurred no carbonate sedimentation between clastic and evaporite deposition. A carbonate facies, if it occurred, would represent the gradual enrichment process of a deeper freshwater lake. In the case of DaQaidam saline lake, sediment evidence suggests a rather shallow lake environment during the deposition of the basal clastic sediment due to the limitation in both catchment inflow and summer evaporation under a cold glacial climate. Moreover, what is also important in regard to the deposition of the pinnoite ore-layer is the increased input of boron-bearing water supply from hot springs. The boron ion concentration of the hot spring water ranges between 39.8 and 49.5 mg/L, according to our recent measurements. The fact that the outflow of the hot springs peaks during the summer months confirms that the circulation of the underground hot water links with the seepage of the atmospheric precipitation. The increased inflow of boron-bearing water at the beginning of the evaporite deposition was associated with warming-induced enhancement of mountainous precipitation that brought about increased outflow from hot springs. Therefore, the differential effect of climate warming between high mountain catchment and the arid basin is crucial for the formation of evaporitic sequence and associated boron deposits in DaQaidam saline lake. Questions may arise as to why there is no pinnoite deposition today on the lake bottom of DaQaidam saline lake, where an eight-year average value of boron ion concentration was as high as 532 mg/L [10].

Results suggest that geochemical and sedimentologic conditions most favorable for pinnoite deposit formation include: (1) more alkaline conditions than today with pH between 9 and 9.3, as evidenced by the co-deposition of large amounts of hydromagnesite; (2) sufficient amounts of  $Mg^{2+}$  and boron ions in the ore-forming brine; and (3) a shallower to nearly desiccated paleo-lake, as implied by the cementation of the Mg-borate layer and by much smaller paleo-lake size as confined by the mining area (Figure 1) of the pinnoite deposit. In addition, the Mg/Ca ratio is most likely an important factor affecting whether the brine favors pinnoite precipitation. In some modern lacustrine environment, hydromagnesite precipitation is associated with an extremely high Mg/Ca molar ratio  $>39$  [18]. By comparison, DaQaidam saline lake today has a pH 7.9, a Mg/Ca molar ratio 35.6, boron concentration of 532 mg/L, and a much enlarged lake size. As such, it is not surprising that pinnoite precipitation has ceased today in the offshore area of the saline lake, which is also confirmed by the data of XRD analysis for sediment trap collections. Neither have any borate minerals been detected, including pinnoite, from the evaporitic sediment deposited approximately in the last 1000 years in the middle of the DaQaidam saline lake [19], simply because the geochemical and sedimentologic conditions since then became unfavorable for pinnoite precipitation.

The Miocene Kirka borate deposit, the world's most important  $B_2O_3$  producer, is one of the borate districts of the Neogene Basins in western Turkey. A horizon of Mg-borates discontinuously overlies the main orebody of borax in the central lacustrine basin, and the Mg-borates were attributed to be the ultimate evaporitic precipitates from the fractionation of the initial boratiferous brine, instead of previous interpretation as the products of reaction between preexisting borates and groundwater [20]. The study of the borate deposit at Eagle Borax spring, Death Valley, California has recognized that magnesium is a significant component of borate-precipitating waters, from which the precipitation of borates and associated minerals at different concentration stages can be shown by a modified chemical divides diagram [21]. According to Crowley [21], depending on the initial  $Ca + Mg/HCO_3 + BO_3$  ratio, waters evolve toward compositions either enriched in bicarbonate + borate and depleted in Ca + Mg or vice versa. In the study of the pinnoite deposit at DaQaidam, we found that a suitable alkalinity of the initial brine is indeed crucial for the formation of the Mg-borate deposit, in addition to the presence of sufficient amounts of B and Mg or, precisely, a very high Mg/Ca ratio, as discussed above in the paper. When the paleo-lake water maintained sufficient  $Mg^{2+}$  with a pH buffered around 9.3,

seasonal variations in lake-level and water chemistry, as a function of inflow/evaporation budget, determined which mineral(s) precipitate including pinnoite, hydromagnesite and halite at different time of a year. It is proposed that the fine pinnoite crystals in the subbottom ore-layer (Figure 4a) precipitate during the summer months when evaporation has substantially enhanced following the enlargement of the saline lake by water inflows from the precipitation-induced runoff of the mountain catchment. We also propose a co-precipitation mode of both pinnoite and hydromagnesite basically formed as the consequence of evaporitic enrichment of the lake waters. It is however possible that the primary precipitation of pinnoite was ahead of hydromagnesite on seasonal scale of a year because of kinetic factors [22], as noted by Crowley [21].

The deposition of the pinnoite ore-layer ceased abruptly following the Mg-borate deposition for a century (estimated based on lamination counting), which gave way to the dominant precipitation of gypsum (Figure 2a,c,d). Hydromagnesite, which was abundant and inversely covarying with pinnoite in the ore-layer, became absent in the overlaying gypsum layer (Figure 2e). This changeover is attributed to: (1) decreased boron concentration of the water as a result of pinnoite precipitation and (2) decreased Mg and accumulatively increased Ca of the water due to hydromagnesite precipitation during the deposition of the ore-layer. Most likely, it reflects a dynamic shift of the water composition type from  $Mg > Ca / (HCO_3 + BO_3) > SO_4$  to  $Mg < Ca / (HCO_3 + BO_3) < SO_4$  on decadal to centennial scale in the depositional system of DaQaidam saline lake. Further investigation is required on the evaporite sequence and pinnoite ore-bodies of DaQaidam saline lake in order to add new information for the calculation of phase relations for Mg-borates and other evaporites.

## 5. Concluding Remarks

Sediment evidence suggests that the factors of summer evaporation intensity, inflow/evaporation budget, and seasonal variation pattern in lake level and brine chemistry varied in response to the hydroclimatic change of the time. The most remarkable hydroclimatic change documented in the saline lake sedimentary sequence is the commencement of the evaporitic deposition following the sudden cessation of clastic sedimentation. The pinnoite deposit formation in the early stage of the evaporitic deposition represents the initiation of a new hydroclimate regime with intensified summer evaporation and seasonality. The hydroclimatic change played an important role in: (1) initiating the recent pattern of hydrothermal circulation with remarkably enhanced discharge of boron-rich water from hot springs into the saline lake due to the critical participation of strengthened mountainous meteoric waters through infiltration and (2) establishing favorable sedimentologic and geochemical conditions for the deposition of the pinnoite ore-layer, specifically, a shallower saline lake (than today) with boron concentration  $>600$  mg/L, Mg/Ca molar ratio  $>39$  and pH above 9.3. The light-dark lamination couplets of the pinnoite ore-layer evidenced the consequence of enhanced seasonal variations in lake level and brine chemistry. Pinnoite as the sole Mg-borate mineral in the laminated evaporitic deposit resulted from chemical precipitation in the saline lake, rather than interstitial production, as indicated by the mineral assemblage record. Moreover, SEM-EDX examination for the borate ore-layer found no mineralogical indication of the euhedral pinnoite crystals for being associated with other minerals. It is therefore conclusive that pinnoite minerals in the Mg-borate deposit of DaQaidam saline lake are primary in origin.

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## References

- Garrett, D.E. *BORATES Handbook of Deposits, Processing, Properties, and Use*; Academic Press: San Diego, CA, USA, 1998; pp. 1–483.
- Gao, C.L. Sedimentary Evolution of DaQaidam and Taijinaier Salt Lakes and a Case Study on the Genesis of Borate Ore and Lithium Brine Deposits. Ph.D. Thesis, Graduate University of Chinese Academy of Sciences, Beijing, China, 2012. (In Chinese)
- He, X.; Yu, J.; Zhang, L.; Gao, C.; Cheng, A. A Mineralogical Record from the Sediment Section DCD03 of Da Qaidam Salt Lake: Implications for Environmental Change. *J. Salt Lake Res.* **2013**, *21*, 10–15. (In Chinese)
- Gao, S.; Song, P.; Xia, S.; Zheng, M. *Chemistry of Salt Lakes with Boron and Lithium Deposit*; Science Press: Beijing, China, 2007; p. 522. (In Chinese)
- Qu, Y.; Han, W. On the study of the formational environment of borate minerals from DaQaidam Salt Lake. *J. Miner. Petrol.* **1981**, *Z1*, 86–93. (In Chinese)
- Yang, Q. Geological overview of the boron deposits of DaQaidam and XiaoQaidam salt lakes, Qaidam Basin, Qinghai Province. *Manag. Strategy Qinghai Land Resour.* **1983**, *3*, 38–63. (In Chinese)
- Liu, D.; Gao, S. Discovery of Pinnoite from the Deposit of Dachaidam Salt Lake. *J. Salt Lake Res.* **1995**, *3*, 1–9. (In Chinese)
- Wang, M.; Song, S.; Niu, Y.; Su, L. Post-collisional magmatism: Consequences of UHPM terrane exhumation and orogen collapse, N. Qaidam UHPM belt, NW China. *Lithos* **2014**, *210–211*, 181–198. [[CrossRef](#)]
- Wu, C.; Wooden, J.L.; Yang, J.; Robinson, P.T.; Zheng, L.; Shi, R.; Chen, S. Granitic Magmatism in the North Qaidam Early Paleozoic Ultrahigh-Pressure Metamorphic Belt, Northwest China. *Int. Geol. Rev.* **2006**, *48*, 223–240.
- Li, J. Distributive regularity of boron and lithium in Da-Qaidam Salt Lake. *J. Salt Lake Res.* **1994**, *2*, 18–24. (In Chinese)
- Li, J.; Dong, H.; Jiang, Y.; Nie, Y.; Zhu, G.; Li, L. Geochemical genesis of the springs in Wenquan Ditch of Da Qaidam area. *J. Salt Lake Res.* **2017**, *2*, 55–59. (In Chinese)
- Zhang, P. *Salt Lakes in Qaidam Basin*; Science Press: Beijing, China, 1987; pp. 1–235. (In Chinese)
- Yu, J.; Kelts, K. Abrupt changes in climatic conditions across the late-glacial/Holocene transition on the N.E. Tibet-Qinghai Plateau: Evidence from Lake Qinghai, China. *J. Paleolimnol.* **2002**, *26*, 195–206. [[CrossRef](#)]
- Li, G.; Gao, S.; Xue, S.; Zhu, L.; Ding, J. Annual variations in lake level and brine chemistry of DaQaidam Salt Lake. *J. Salt Lake Res.* **1991**, *2*, 1–6. (In Chinese)
- Parks, J.L.; Edwards, M. Boron in the Environment. *Crit. Rev. Environ. Sci. Technol.* **2005**, *35*, 81–114. [[CrossRef](#)]
- Yu, J.; Gao, C.; Cheng, A.; Liu, Y.; Zhang, L.; He, X. Geomorphic, hydroclimatic and hydrothermal controls on the formation of lithium brine deposits in the Qaidam Basin, northern Tibetan Plateau, China. *Ore Geol. Rev.* **2013**, *50*, 171–183. [[CrossRef](#)]
- Zhan, D.; Yu, J.; Gao, C.; Zhang, L.; Cheng, A. Hydrogeochemical conditions and lithium brine formation in the four salt lakes of Qaidam Basin. *J. Lake Sci.* **2010**, *22*, 783–792. (In Chinese)
- Chagas, A.A.P.; Webb, G.E.; Burne, R.V.; Southam, G. Modern lacustrine microbialites: Towards a synthesis of aqueous and carbonate geochemistry and mineralogy. *Earth Sci. Rev.* **2016**, *162*, 338–363. [[CrossRef](#)]
- Gao, C.; Zhang, L.; Yu, J.; Cheng, A.; Liu, Y. A mineralogical record of brine evolution and environmental change from Da Qaidam Salt Lake in the northern Qaidam Basin. *Geochimica* **2011**, *40*, 156–162. (In Chinese)
- Helvacı, C.; Orti, F. Zoning in the Kirka borate deposit, western Turkey: Primary evaporitic fractionation or diagenetic modifications? *Can. Mineral.* **2004**, *42*, 1179–1204. [[CrossRef](#)]
- Crowley, J.K. Mg- and K-bearing borates and associated evaporites at Eagle Borax Spring, Death Valley, California: A spectroscopic exploration. *Econ. Geol.* **1996**, *91*, 622–635. [[CrossRef](#)]
- Felmy, A.R.; Weary, J.H. The prediction of borate mineral equilibria in natural waters: Application to Searles Lake, California. *Geochim. Cosmochim. Acta* **1986**, *50*, 2771–2783. [[CrossRef](#)]

