

Borate Minerals in Salt Lake Deposits at Chaidamu Basin, China

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ABSTRACT

There are many inland rich boron salt lakes in the north margin of Chaidamu Basin, such as Dachaidan, Xiachaidan and Mahai Lakes, which formed in later Pleistocene. The main sources of boron materials are from the hot springs and mud volcanoes. Surface brines and intercrystalline brines in the salt lakes are $MgSO_4$ -subtype. B_2O_3 content averages about 2000 mg/l, up to 5200 mg/l maximum. Borate ore bodies of the lake bottom and the lake shore occur in different deposited layers of salts. The main borate minerals are pinnoite and ulexite, the others are hydroboracite, Kurnakovite, inderite, carborite, macallisterite, hungchaoite and minor borax, which occur in the lake

shore only. Borate minerals are associated with different salts such as calcite, aragonite, gypsum, halite, mirabilite, thenardite, glauberite, hydroglauberite, bloedite, epsomite, schoenite and uklonskovite.

According to the studies of morphology and occurrence of the borate ore bodies and paragenesis relationship of minerals, it was found that borate minerals of salt lake are not common evaporitic minerals. The results of observation and experiment show that rich boron brines during the desalination are often associated with the precipitation of borate.

INTRODUCTION

Many researchers for a long time have noticed that borate minerals can be associated with other salt minerals of different solubilities, occurring in different stages of salt separation. Van't Hoff and Nikulaev *et al.* found, during the experiment on brine evaporation, that the boron content of the brine was constantly increasing as evaporation went on, but no borate separated out even at the eutectic point. As early as 1940, Nikulaev and Kurnakov made the eutectic brine further concentrated by means of isothermal evaporation, but still no borate minerals appeared even when the B_2O_3 content reached 4%. Later, Valyashko (1962) held a eutectic brine with B_2O_3 content of 1.2% in a quiet state for four years, at which point he found some white borate magnesium had precipitated and which was called 'eutectic borate.' The facts show that borate minerals, different from other ordinary salt minerals, are not simple evapor-deposited minerals.

Based on study of the borate minerals in Qinghai saline lakes, the authors believe that the formation of borate is closely related to the desalination of boron bearing brine. In this paper, the important function of hydrolyzation to the borate sedimentation is going to be discussed; we

hope it will be helpful to understanding the origin of borate minerals in certain ancient salt deposits.

GENERAL STATEMENT

Quaternary saline lakes in Chaidamu Basin Qinghai Province are widely distributed. But lakes rich in boron with borate sediment are confined to the northern margin of the basin, such as Dachaidan Lake, Xiaochaidan Lake and Mahai Lake, among which the former two are the most typical (Figure 1).

These boron-rich saline lakes were formed in Late Pleistocene. The main resources of boron-bearing materials are closely related to the hot springs and mud volcanoes which are still active. Water of the lakes and intercrystalline brine belong to the $MgSO_4$ sub-type, salinity generally being 320 to 350 g/l and B_2O_3 content in brine between 2000 and 5200 mg/l. Besides a high boron content, these lakes also contain many other useful elements such as K, Mg, Li, (Table 1).

Sedimentary borate bodies in saline lakes occur both at the bottom and within the shore salt sediments. The bottom borate bodies lie in the sequences of salt-mud-bearing gypsum, mirabilite and halite. The main ore bed of

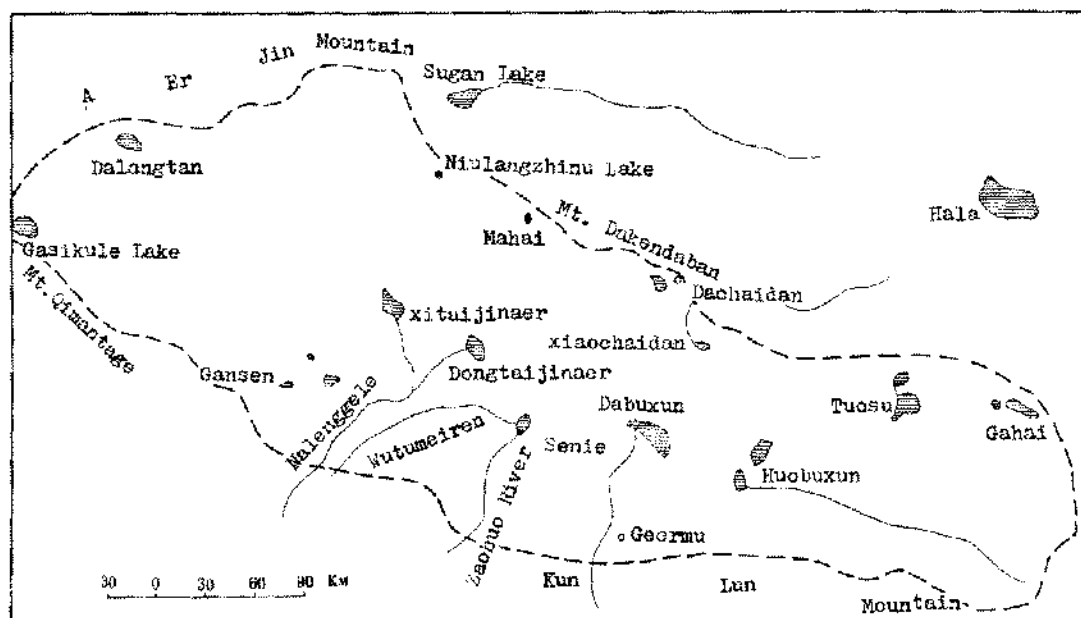


Figure 1. Distribution of Saline Lakes in Chaidamu Basin, Qinghai

TABLE I
Chemical Composition of Boron-rich Saline Lake of Chaidamu Basin

Composition (G/L)	Na	Mg	K	Ca	Cl	SO ₄	HCO ₃	CO ₂	Salinity	B ₂ O ₃	LiCl	Br	Sampling Dates
										(Mg/L)			
Dachaidan: surface	100.25	17.28	5.62	0.31	186.32	30.62	—	—	340.4	5202.5	1776.1	140.0	7.1971
brine	106.39	12.28	4.02	0.42	186.57	22.47	—	—	332.5	2649.1	1083.6	70.0	8-9.1971
inter- crystalline	83.59	23.12	5.85	0.21	197.53	32.86	0.65	0.13	343.94	2384.6	2503.9	107.2	4-8.1963
brine	63.43	30.47	5.61	0.24	152.62	56.17	0.84	0.44	309.82	2763.5	2326.4	43.4	" "
Xiao- chaidan:													
surface	108.20	13.50	3.26	—	186.57	22.47	—	—	334.00	3729.3	—	46.0	5.1959
brine	41.50	5.57	1.40	—	180.80	37.44	—	—	266.71	3600.0	280.7	20.8	7.1959
Mahai: inter- crystalline	102.10	12.16	1.18	0.94	137.07	29.46	—	—	282.91	549.0	390.8	—	5.1958
brine													

the shore borate deposit is exposed, being the most recent boron-bearing bed. Although the distribution range of the latter is limited its grade is higher and easy to mine.

GENERAL CHARACTERISTICS OF THE BORATE MINERALS

The principal features of borate minerals in boron-rich saline lakes north of Chaidamu Basin are listed in Table 2 (mineral crystallography can be seen in Figure 1 to 7). These minerals are mainly composed of borates of Mg, Ca/Mg and Na/Ca. Up to now no borate containing only

Ca has been found. All of them, without exception, are hydrated borates. Except for carboborite, having CO_3^{2-} , the above mentioned borate minerals have no additional anion. Based on their structure chemistry, the borate minerals are nothing but all poly-borates in a hydrated state. The basic structural unit of boron is B-O triangle and B-O tetrahedron, one being linked with the others through H-bond to form complicated borate polyanions. According to the structure analysis, we can see that pinnoite is two-B borate, kurnakovite, inderite and hydroboracite are three-B borate, hungchaoite and borax are

TABLE 2
Chemical and Physical Characters of the Borate Minerals in Qinghai Saline Lakes

Minerals	Crystal-chemical for.	Cryst. system & cell parameter	Colour & luster	Morpho.	H & S.G.	Cleav.	Optic char.	X-diffr. strong lines
pinnoite (photo a)	$\text{Mg}(\text{P}_2\text{O}_7(\text{OH})_6)$	tetragonal $\text{C}4^3\text{-P}4_2$ or $\text{P}4_2/\text{M}$; a 7.62 Å, c 8.19 Å; $Z=4$	noncolour, white or gray; glassy	columnar elongated along C- axis	3.5(H) 2.27(S.G.)	—	uniaxial (+) Ng 1.576 No. 1.565	7.63(6) 5.39(10) 3.15(9) 2.314(9)
hungchaoite (photo b)	$\text{Mg}(\text{B}_4\text{O}_5(\text{OH})_4) \cdot 8\text{H}_2\text{O}$	triclinic P1 or P1 a 10.650, b 8.805, c 7.889; α 108° .59 β 103° .40, γ 97° .11	white, gray; earthy	fine- grained aggregate	2 1.70-1.73 (S.G.)	—	biaxial Ng 1.4899 Nm 1.4851 Np. 1.4415 2V 36°	4.07(10) 3.34(9) 2.902(10) 2.734(9)
macalisterite (photo b)	$\text{Mg}_2(\text{B}_6\text{O}_7(\text{OH})_6)_2 \cdot 9\text{H}_2\text{O}$	trigonal a 11.546 c 35.562; $Z=6$	same as the above	same as the above	2.5(H) 1.85(S.G.)	—	uniaxial No 1.504 Ne 1.459	8.80(10) 4.08(10) 3.36(10) 3.27(10)
inderite (photo c)	$\text{Mg}(\text{B}_3\text{O}_3(\text{OH})_5) \cdot 5\text{H}_2\text{O}$	monoclinic $\text{C}2_2^2\text{-P}2_1/\text{A}$ a 12.12, b 13.18, c 6.83; β 104° 49', $Z=2$	non-colour or white; glassy	needle or columnar elongated C-axis	2.5(H) 1.78- 1.79 (S.G.)	perfect clear (110) (001)	biaxial Ng 1.5055 Nm 1.4920 Np 1.4387 2V 37° 52'	5.69(10) 5.02(9) 3.36(10) 2.944(8)
kurnakovite (photo d)	$\text{Mg}(\text{B}_3\text{O}_3(\text{OH})_5) \cdot 5\text{H}_2\text{O}$	triclinic $\text{C}1^1\text{-P}1$; a 6.44 b 10.68, c 8.36; $Z=1$ α 106° .04, β 108° .32 γ 98° 10'	noncolour lightyellow; glassy	thick tabular	3(H) 1.847 (S.G.)	median (011) poor (010)	biaxial Ng 1.5245 Nm 1.5100 Np 1.4908 2V 80°	7.12(10) 5.30(8) 4.94(10) 3.16(9)
borax	$\text{Na}_2(\text{B}_4\text{O}_5(\text{OH})_4) \cdot 8\text{H}_2\text{O}$	monoclinic $\text{C}2^2\text{-C}2/\text{C}$; a 11.84, b 10.63 c 12.32, β 106° 35' $Z=4$	noncolour; glassy	short columnar	2-2.5(H) 1.715 (S.G.)	perfect (100) median (110)	biaxial Ng 1.4709 Nm 1.4458 Np 1.4664 2V 39° 58'	4.92(7) 3.955(6) 2.825(9) 2.559(10)
ulexite (photo e)	$\text{NaCa}(\text{B}_3\text{O}_7(\text{OH})) \cdot 3\text{H}_2\text{O}$	triclinic $\text{C}1^1\text{-P}1$ a 8.81, b 12.86, c 6.68 α 90° 15' β 109° 10' γ 105° 05' $Z=2$	non-colour white; silky	needle & fabric elongated C-axis	2.5(H) 1.955 (S.G.)	perfect (010) Median (110) poor (110)	biaxial Ng 1.5184 Nm 1.5054 Np 1.4790 2V 78°	12.31(10) 7.81(8) 5.90(6) 4.12(6)
Hydroboracite (photo f)	$\text{CaMg}(\text{B}_3\text{O}_4(\text{OH})_3)_2 \cdot 3\text{H}_2\text{O}$	monoclinic $\text{C}2_2^2\text{-P}2/\text{C}$ a 11.54, b 6.56, c 8.18 β 102° 50' $Z=2$	earth yellow; earthy	radial pelletoid aggregate	2(H) 2.167 (S.G.)	perfect (010) median (100)	biaxial Ng 1.572 Nm 1.536 Np 1.521 2V 60°-40°	6.71(8) 5.72(8) 2.449(10) 2.210(9)
carbaborite (photo g)	$\text{MgCa}(\text{CO}_3)_2(\text{B}(\text{OH})_4)_2 \cdot 4\text{H}_2\text{O}$	monoclinic $\text{C}2_2^2\text{-P}2_1/\text{N}$, a 11.05, b 6.68 c 10.69, β 116° 48' $Z=2$	noncolour, light brown; glassy	wedge-like aggregate	2(H) 2.105 (S.G.)	perfect (101) clear (110) poor (101)	biaxial Ng 1.5693 Nm 1.5459 Np 1.5069 2V 75°	5.63(10) 4.315(10) 3.136(8) 2.160(8)

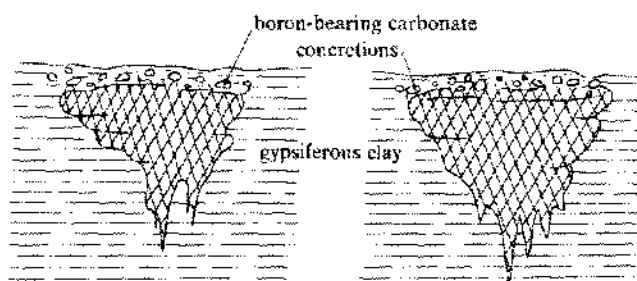


Figure 2. Cross-section of the Borate Ore Body in Xiaochaidan Saline Lake (schematic)

four-B borate, ulexite is five-B borate, and macallisterite is six-B borate (Table 2).

Most of the borate minerals, according to their occurrences, are primary sediments from saline water. Carbo-borite is a mineral of secondary transformation. Borax results from the evaporation of shore B-bearing underwater which moves upward to the surface by capillarity. The boron ore body in the lake bottom is mainly composed of pinnoite and ulexite, while the shore boron ore body is of hydroboracite and ulexite. Some other borate minerals are found only onshore and are limited in distribution. Minerals associated with borate are commonly carbonate, gypsum, halite, mirabilite, schoenite and bloedite; besides these, there are also glauberite, hydro-glauberite, epsomite, thenardite, uklonshovite and so on. Obviously these minerals were formed at various stages of salt separation (See Figures 4a-g).

RELATIONSHIP BETWEEN FORMATION OF BORATE MINERALS AND ACTIVITY OF FRESH WATER

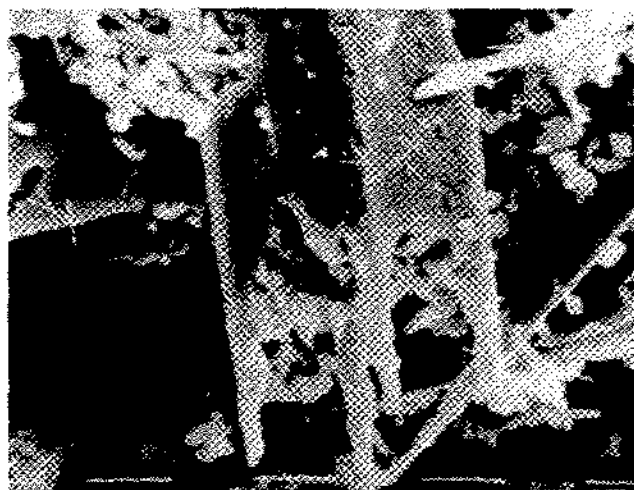
At present, the Qinghai saline lakes are still evolving and developing, and sedimentation and inversion of some borate minerals is still going on. Some noticeable phenomena noticed during our work are important in the understanding of borate deposition.

In exploration, pinnoite-ulexite ore bodies at the bottoms of both Dachaidan and Xiaochaidan were considered as stratoid bodies or large lenses. However, mining of the Xiaochaidan bottom deposit showed that although these so-called stratoid ore bodies had certain depositional horizons, actually they were isolated ore bodies in the shape of pails, pans, and nests. Morphologically, many bodies were similar to karst caps, and at the lower part of the bodies one or several 'roots,' big or small, usually could be seen; these might be the channels of upward-moving springs (Figure 2). Wall rock of the mineral bodies are formed by horizontally-bedded gypsiferous clays. This phenomenon shows that the formation of borate bodies is related to the upwelling activity of the underground fresh water.

Relation between the distribution of borate minerals and artesian spring activity is more conspicuous at the shore borate area, on the eastern part of Dachaidan Lake. This area is located at a spring-overflow zone along the piedmont of Dakendaban Mountain. There are still plenty of artesian springs at present in the area and its adjacent surroundings. The diffusion range of the up-

Figure 3. Boric Polyanions and Corresponding Borate Minerals

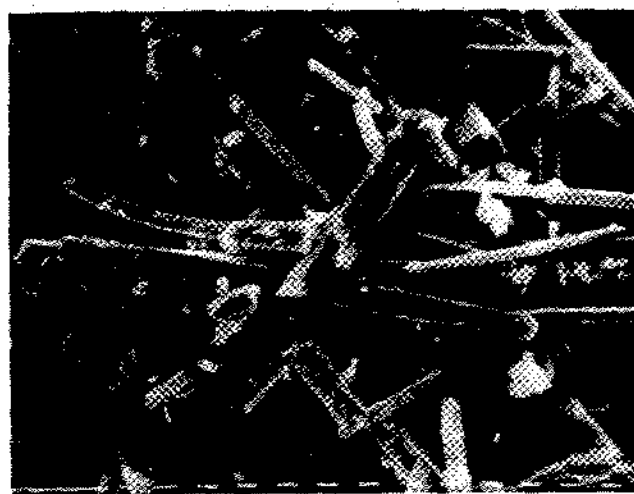
Polyanion	Structural Type	Corresponding Mineral
$(B_5O_4(OH)_4)^{-1}$ $4\Delta + T$		Sborgite $Na(B_5O_6(OH)_4) \cdot 3H_2O$ santite $K(B_5O_6(OH)_4) \cdot 2H_2O$
$(B_3O_3(OH)_4)^{-1}$ $2\Delta + T$		arneghinite $Na(B_3O_3(OH)_4)$
$(B_4O_5(OH)_4)^{-2}$ $2\Delta + 2T$		borax $Na(B_4O_5(OH)_4) \cdot 8H_2O$ hungchaoite $Mg(B_4O_5(OH)_4) \cdot 7H_2O$ tincalconite $Na(B_4O_5(OH)_4) \cdot 3H_2O$
$(B_3O_3(OH)_5)^{-2}$ $\Delta + 2T$		inderite $Mg(B_3O_3(OH)_5) \cdot 5H_2O$ kurnakovite $Mg(B_3O_3(OH)_5) \cdot 5H_2O$ inyoite $Ca(B_3O_3(OH)_5)_2 \cdot 4H_2O$ inderborite $CaMg(B_3O_3(OH)_5)_2 \cdot 6H_2O$



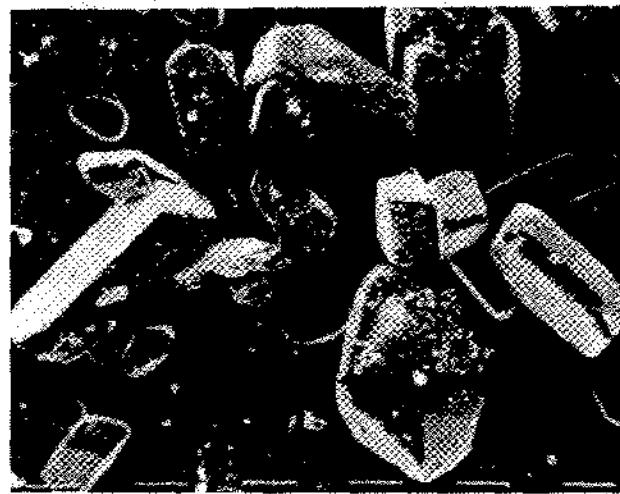
a. Punoite Crystal $\times 1250$



b. Hungchaoite and Macallisterite Crystals $\times 1250$



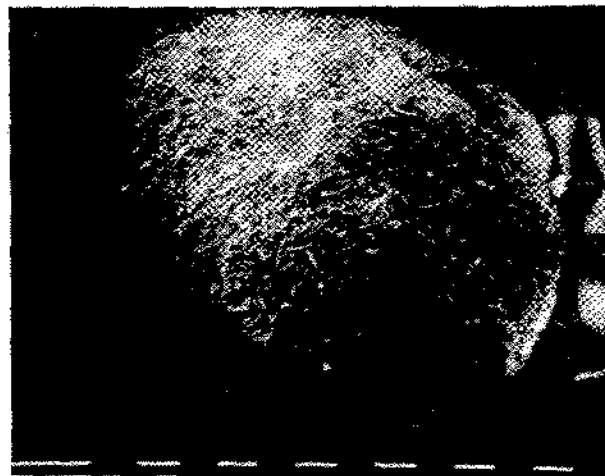
c. Inderite Crystal $\times 480$



d. Kurnakovite Crystal $\times 80$



e. Ulexite Crystal $\times 640$



f. Hydroboracite Crystal $\times 640$

Figure 4. SEM Photographs of the various minerals discussed in the text.

g. Carboborite Crystal $\times 224$

Figure 4. (continued)



Figure 5. Appearance of an Upwelling Spring, White—Borate Minerals, Dark—Salt Incrustation

ward-moving springs differs from place to place from several hundred square meters to several square meters. Within the area we can find white sinters composed of hungchaoite and macallisterite around the upwelling spring and its bottom (Figure 5). The general spring water salinity is 12.156 g/l, which is much lower than the 340.19 g/l of the comparable lake surface saline water.

Cation Ca content of the spring is typically higher than that of the lake surface saline water, but B_2O_3 content of the two is close (Table 3). Hungchaoite lies directly above the gypsum-hydroboracite unit. Its thickness is from 0.5 cm to 1 cm. Just above the hungchaoite is about 0.4 cm to 0.8 cm of macallisterite. Within the shore gypsum-hydroboracite unit, there is intercrystalline saline water the composition of which is close to that of the lake-surface saline water. The accumulation of hungchaoite and macallisterite is clearly the result of the lower mineralized spring water acting on intercrystalline brine water than that of the brine evaporation and concentration. So, the process of desalination of B-bearing brine is of considerable importance to the formation of natural borate minerals.

RELATIONSHIP BETWEEN EXISTING STATE OF BORON IN SOLUTION AND STRUCTURAL CHARACTERS OF HYDRO-BORATE MINERALS

In hydro-borate, B-O triangle and B-O tetrahedron are joined together by H-bond into complicated polyanions.

TABLE 3

Chemical Composition of Upwelling Spring Water of East Onshore Ore Area and Lake Water of Dachaidan Saline Lake

Composition (Mg/L)	K	Na	Mg	Ca	Cl	SO ₄	HCO ₃	CO ₂	B ₂ O ₃	S.G.	Salinity (G/L)
upwelling spring water	47.76	1400.45	821.71	706.52	1316.08	4618.15	384.41	684.11	2177.5	1.0001	12.156
surface saline water	4614.93	100179.04	16489.2	452.90	185847.32	27256.15	2770.22	—	2566.7	1.2136	340.19

Because the joining of H with $(\text{BO}_3)^{3-}$ and $(\text{BO}_4)^{5-}$ is so stable that common metallic cations can not exist by replacing H in boric acid molecule, therefore, they act upon each other to form complicated minerals with different composition. The existence of borate polyanions in hydrated form decides the basic character of the resulting hydro-borate. The formation of these anions is dependent on the chemical nature of boron and its behavior in solution (1982, Gao and Li).

In a water solution, boric acid is a Lewis-type acid, accepting electrons but not providing protons, so it is easily hydrolyzed. The hydrated materials that formed are polymerized and become complicated polyanions. Boron is changed into a state of coordination number surplus by the hydrolyzation, and this is favourable to the formation of borate minerals. In solution, the greater the quantity of boric acid and water, the faster the hydrolyzation will take place.

The degree of complexing and mode of boron precipitation is closely related to the pH of solution. Experiment (Ingri, 1962) shows that boron is in the form of H_3BO_3 in an acid solution with a pH lower than 5, but it is in the form of $(\text{B}(\text{OH})_4)^{-}$ when the pH is greater than 12.5. The existence mode of boron changes in accordance with the concentrations of boron when the solution pH is between 5 and 12.5. When the concentration of solution is below 0.025M, boron is in the forms of H_3BO_3 and $(\text{B}(\text{OH})_4)^{-}$, but when concentration is greater than 0.025M various multi-boron polyanions occur, such as $(\text{B}_3\text{O}_3(\text{OH})_4)^{1-}$, $(\text{B}_3\text{O}_3(\text{OH})_5)^{2-}$, $(\text{B}_4\text{O}_5(\text{OH})_4)^{2-}$ and $(\text{B}_5\text{O}_6(\text{OH})_4)^{1-}$. Studies have revealed that all these polyanions have been found in the crystalline structures of the related borate minerals (Figure 3; also see Christ and Clark, 1977). These experiments, however, are basically made in a low-salinity solution, without consideration of the fact that polymerization would intensify in a high-salinity solution. For instance, the existence of much neutral-salt can increase the dissociation of boric acid and form more complicated borate polyanions.

The pH value of the brine in the Qinghai boron-rich saline lakes is about 7 to 9. In the process of evaporation and salt separation, the MgCl_2 content increases constantly and hydrolyzation is intense, forming $\text{Mg}(\text{OH})\text{Cl}$ and saline water with a gradual increase in acidity. The pH value of eutectic saline water may decrease to about 5. There no natural co-saturated saline water existing in the salt lakes. The salt lake saline waters are weakly alkaline, different from the high alkalinity and B-rich carbonate saline lakes in Xizang, and according to Table 1 the molar concentration of boron in saline water are all higher than 0.025 M, respectively being 0.031 and 0.037M. The experimental information mentioned above shows that boron in saline water should be of hydrated multi-nucleus polyanions. This is why nearly all salt lake borate minerals of Chaidamu Basin are poly-hydrated borates.

SEDIMENTARY CONDITIONS OF BORATE MINERALS IN SALT LAKE

In natural waters boron tends to be divergent. Evaporation of water body is the necessary condition for boron concentration in large quantity, but evaporation itself cannot directly lead boron to precipitate from solution. Polymerization of hydrated boric acid polyanions in saline waters are constantly accelerated with the evaporation and concentration. Even if there are co-precipitated metallic cations, no precipitation will occur to this super-saturated complicated polyanions. Facts show that the addition of fresh water or low-salinity water may force the formation of borate minerals, for natural saline water is desalinated by the addition of fresh waters. This desalination process can increase the speed of boric acid hydrolyzation, decrease the concentration of hydrolysate and slow down the reaction speed toward opposite direction and equilibrium becomes favourable to the direction of separation of borate. Because desalination of saline water can take place at any stage of salt separation, borate can usually be associated with other salt minerals of quite different solubility.

Borate minerals are formed in the process of desalination of boron-bearing saline water, which has been confirmed by geological occurrence of borate minerals in certain potash deposits in the world. For instance, in the Salt Springs potash deposit, New Brunswick, Canada (Anderle *et al.*, 1979), laminated and nodular borate minerals occur in the Cossidy Lake formation within a halite member which is above the potash member. The minerals are usually accompanied by green mudstone and grey anhydrite which reflect the environment of desalination. There are some similar characters in the Khorat potash deposit in Thailand as well.

The fact that desalination speeds the deposition of borate minerals is important for studying borate formation conditions, but it is not the only factor. Low-temperature refrigeration can also promote borate precipitation, which can be confirmed by association of borate minerals and cool-loving minerals such as mirabilite in Qinghai saline lakes. Boron-rich brine which remains quiet for a long period can also permit separation of borate minerals. The "quiet condition" can occur with boron-bearing intercrystalline brine, which can form disseminated borate minerals with a salt bed but this problem will not be discussed any further here.

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