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A Raman Investigation on the Boron form Occurring in Salt Lake Brine during Evaporation

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Abstract: Boron resources are abundant in the Da Qaidam Salt Lake of the Qaidamu basin in China, which has generated significant attention due to the presence of polyborate species in brine from this lake. In this study, Raman spectroscopy was used to investigate the existing form of boron in brine during evaporation. $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$, $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgCl}_2 - \text{H}_2\text{O}$, and $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgSO}_4 - \text{H}_2\text{O}$ solutions were also studied to determine the influence of boron concentration, pH, and electrolytes on the borate speciation from brine. The mononborates $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ were found to be the only forms present in natural salt lake brine. Brine evaporation promoted the formation of the polyborate anions $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ and also promoted the disappearance of the $\text{B}(\text{OH})_4^-$ ion from brine at boron concentrations of more than 11 g/L B_2O_3 . The pentaborate ion $\text{B}_5\text{O}_6(\text{OH})_4^-$ was sensitive to the solution pH and appeared only at pH values less than 8.0. Meanwhile, the hexaborate ion $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ was observed to be more dependent on the electrolyte magnesium chloride due to its special properties, such as promoting boron accumulation, lowering solution pH, and also its strong affinity for water molecules, which were all beneficial for the polymerization of borate ions in brine. Interaction mechanisms between polyborate anions during evaporation are also proposed herein. **ake; evaporation; polyborate species; interaction mechanism.**

Key words: Raman spectrum; Da Qaidam Salt Lake; evaporation; polyborate species; interaction mechanism

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1 Introduction

There are a large number of boron-containing salt lakes in the Qaidam basin in China, such as the Qarhan, Da Qaidam, Xiao Qaidam, Yiliping, and East and West Taijinar salt lakes^[1]. Among these, the Da Qaidam salt lake is famous for its characteristics of having large boron reserves and many Mg-borate species^[2-3]. For example, five Mg-borates of the nine borate-containing minerals have been discovered in the salt deposits of the Da Qaidam salt lake. To study Mg-borate formation and boron exploitation from brine, Gao *et al.*^[4-7] investigated the chemical behavior of borate in brine and found that borate had a high supersaturated solubility during evaporation based on comprehensive statistics, meaning it accumulated in bischofite-saturated brine in the form of tetraborate $\text{MgO} \cdot 2\text{B}_2\text{O}_3$. Here, the term “comprehensive statistics” meant that besides tetraborate, other borates may have existed in brine when $n (\text{MgO} \cdot n\text{B}_2\text{O}_3)$ was > 2 , but the apparent result was that $n = 2$. These results have demonstrated the various apparent forms of borate in brine. However, there is no information about polyborate anion species existing in concentrated brine. According to the literature^[8,9], the polyborate equilibrium in a neutral solution was previously studied in the 1960s, and it was found that $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ monomers were the main forms in solution when the total boron concentration was less than 0.025 3 mol/L. As the boron concentration increased from 0.025 3 to 0.4 mol/L, the polyborate ions $\text{B}_3\text{O}_3(\text{OH})_4^-$ and $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ were found to be the main forms in solution. Furthermore, when the boron concentration ranged from 0.4 to 0.6 mol/L, the main forms changed to be $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ ions. Recently, Zhou^[10] and Zhu^[11-12] calculated the polyborate distribution of $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ ions in alkali metal borate solutions using a Newton iteration

algorithm, and also proposed the interaction mechanisms between different polyborates. However, polyborates in alkaline-earth metal borate solutions have rarely been reported. Since borate can accumulate in concentrated brine in the form of magnesium tetraborate ($\text{MgO} \cdot 2\text{B}_2\text{O}_3$), we previously recorded the Raman spectra of polyborate anions in bischofite-saturated brine and show here that $\text{B}(\text{OH})_3$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ were found to be the main forms in concentrated brine, while $\text{B}(\text{OH})_4^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ were the minor forms^[13-14]. It has been shown that boron exists in the forms $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ in natural salt lake brine^[15-16]. This finding revealed that borate species in brine changed greatly during evaporation. Yet, to date, the speciation of boron in brine and its main controlling factors through the process of evaporation have not been reported. In this study, Raman spectroscopy was used to investigate the boron form in brine and the polyborate formation during evaporation upon changes in boron concentration, pH and ionic composition. Relevant interaction mechanisms between polyborate anions during evaporation have also been proposed based on experimental Raman spectra.

2 Experimental Sections

2.1 Brine evaporation

In this study, a brine of density $1.2101 \text{ g} \cdot \text{ml}^{-1}$ obtained from the Da Qaidam salt lake was selected for evaporation at ambient temperature ($25 \pm 3 \text{ }^\circ\text{C}$) with a 250 W bulb. During the evaporation process, samples were taken in sequence at different densities for chemical analysis and Raman spectroscopy. Density measurement was carried out using a portable density/specific gravity Meter (DA-130N, KEM). The pH of the brine was measured using a pH meter (PB-10, Sartorius).

Based on the compositions of brine samples, solutions of $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$, $\text{MgO} \cdot 2\text{B}_2\text{O}_3 -$

MgCl₂ - H₂O, and MgO · 2B₂O₃ - MgSO₄ - H₂O were prepared and further concentrated by evaporation to study controlling factors for the boron speciation in brine, including boron concentration, pH, and ionic compositions. The boron concentration used was 1.1 g/L B₂O₃, and the MgCl₂ and MgSO₄ concentrations were 10 g/L, respectively.

2.2 Raman Spectroscopy

The Raman spectra of brine with boron concentrations of 1 - 60 g/L B₂O₃ were collected using a Raman spectrometer (DXR, Thermo). The laser wavelength used was 532 nm, and 80 cumulative exposures of 40 seconds each were taken. Spectral measurement was carried out using a 10 × objective lens, and the spectral resolution was about 1 cm⁻¹. Usually, the vibration bands of polyborate anions in solution have been found to be fewer than 1 000 cm⁻¹, and the most favorable scanning range was 400 - 1 200 cm⁻¹ during Raman determination^[17,18]. However, brine is a complicated system composed of sodium, potassium, lithium, magnesium, boron, chloride and sulfate. Sulfate ions alone have four kinds of Raman vibration wavenumbers in solution^[19,20]. These include the symmetrical stretching vibration ν_1 at ~980 cm⁻¹, the bending vibration ν_2 at ~450 cm⁻¹, the deformation vibration ν_3

at ~1 100 cm⁻¹, and the bending vibration ν_4 at ~610 cm⁻¹. Of these, ν_1 was the most characteristic band and had an intensity that often covered the spectra band of polyborate anions in brine. Thus, the spectral scanning range used was 400 - 950 cm⁻¹.

3 Results and Discussion

3.1 Raman spectra of borate in Da Qaidam brine during evaporation

Table 1 shows the composition evolution of brine during evaporation. The original brine DL0 was saturated with halite. As the evaporation started, the DL1, DL2, and DL4 brines were in sequence saturated with epsomite, carnallite and bischofite, respectively. The DL4 brine was saturated with bischofite, and was further concentrated to obtain brine DL5. As shown in Table 1, the boron concentration was increased from 1.03 to 64.47 g/L in the form of B₂O₃ during evaporation, while the brine pH decreased from 7.52 to 4.23. The magnesium concentration gradually increased to 123.91 g/L and the sulfate first increased to 77.91 g/L and subsequently decreased to 33.10 g/L due to the epsomite crystallization.

Table 1 Composition of the brine during evaporation at ambient temperature

brine	density /(g · cm ⁻³)	pH	Na ⁺	K ⁺	Li ⁺	Mg ²⁺	Ca ²⁺	B ₂ O ₃	Cl ⁻	SO ₄ ²⁻
DL0	1.2101	7.52	115.18	2.19	0.0491	7.29	0.537	1.03	190.93	14.39
DL1	1.2586	6.81	77.24	10.24	0.254	34.13	0.343	4.93	180.29	63.76
DL2	1.2930	6.28	32.78	22.73	0.598	63.46	0.098	11.31	196.25	77.91
DL3	1.3200	5.45	16.47	16.03	1.367	86.62	0.099	25.70	254.19	44.04
DL4	1.3917	4.32	-0.61	1.32	2.526	123.91	0.102	46.20	318.97	43.80
DL5	1.3956	4.23	0.66	0.31	3.735	122.93	0.098	64.47	321.92	33.10

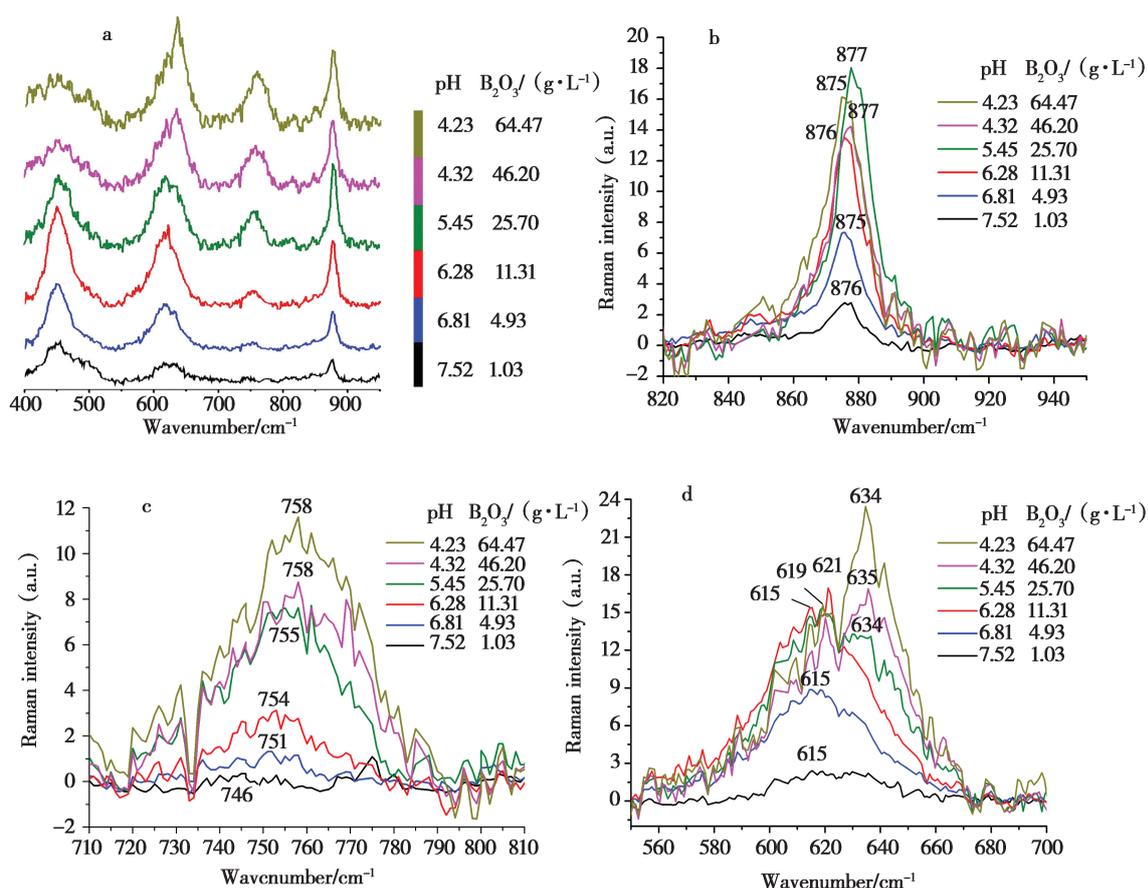


Fig. 1 Raman spectra of Da Qaidam brine during evaporation process

Table 2 Observed Raman wavenumbers of Da Qaidam brine during evaporation^a

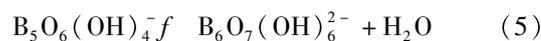
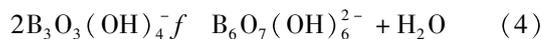
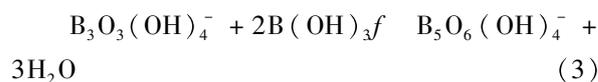
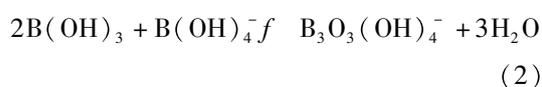
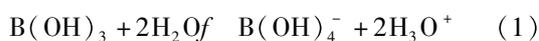
DL0	DL1	DL2	DL3	DL4	DL5	Assignment
pH = 7.52	pH = 6.18	pH = 6.28	pH = 5.45	pH = 4.32	pH = 4.23	
876 m	875 s	876 s	875 s	877 s	877 vs	$\nu_s(\text{B}_{(3)}-\text{O})$ B(OH) ₃
	751 w	754 w	755 m	758 s	758 s	$\nu_s(\text{B}_{(4)}-\text{O})$ [B ₅ O ₆ (OH) ₄] ⁻
744 w						$\nu_s(\text{B}_{(4)}-\text{O})$ [B(OH) ₄] ⁻
615 w	615 m	615s	615 s	615 s	615s	$\gamma(\text{S}-\text{O})/$ SO ₄ ²⁻ / $\nu_p[\text{B}_3\text{O}_3(\text{OH})_4]^-$ [B ₃ O ₃ (OH) ₄] ⁻
			619			
			621			
			634	635	634	$\nu_p[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$ [B ₆ O ₇ (OH) ₆] ²⁻
454 w	450 w	449 w	450w	451 m	450 m	$\gamma(\text{S}-\text{O})$ SO ₄ ²⁻

^ab - broad; s - strong; m - middle; w - weak; v - very. B₍₃₎, B₍₄₎ mean three and four coordinate boron, respectively.

Figure 1 shows the Raman spectra of the borates in concentrated brine. According to studies on polyborates^[14,18,21-24], the Raman spectra observed

were assigned and are listed in Table 2. As shown in Fig. 1 and Table 2, there were four bands present in the DL0 brine at 876, 744, 615, and 454 cm⁻¹,

respectively. The observed band at 876 cm^{-1} was $\text{B}(\text{OH})_3$, while the weak band at 744 cm^{-1} was characteristic of a $\text{B}(\text{OH})_4^-$ anion. Since the boron concentration was very low, the bands at 615 and 454 cm^{-1} were assigned to the bending vibrations ν_2 and ν_4 of SO_4^{2-} ions. These results revealed that the boron forms in the original brine from Da Qaidam were mainly $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$. However, as the boron concentration increased and the pH decreased with brine evaporation, the boron form changed greatly and polyborate formation occurred in the concentrated brine. First, the band at 744 cm^{-1} (Fig. 1c) gradually collapsed into the $754 - 758\text{ cm}^{-1}$ band of the symmetric stretching of $\text{B}_{(4)} - \text{O}$ in a $\text{B}_5\text{O}_6(\text{OH})_4^-$ ion, and the intensity increased with increasing boron concentration. Second, when the boron concentration was less than $11.31\text{ g/L B}_2\text{O}_3$, the bands (Fig. 1d) observed at $615 - 619\text{ cm}^{-1}$ were characteristic of a $\text{B}_3\text{O}_3(\text{OH})_4^-$ ion and the bending vibration ν_4 of a SO_4^{2-} ion. When the boron concentration was more than $11.31\text{ g/L B}_2\text{O}_3$, the polyborate formation of the $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ anion appeared in brine and a band was observed at $621 - 635\text{ cm}^{-1}$, as well as the shoulder bands of the $\text{B}_3\text{O}_3(\text{OH})_4^-$ and SO_4^{2-} ions. Additionally, the intensity of $\text{B}(\text{OH})_3$ at $\sim 876\text{ cm}^{-1}$ (Fig. 1a) first increased to a point and then decreased with increasing boron concentration, also indicating polyborate formation in the brine. According to the above observations, it can be concluded that the polyborate ions $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_5\text{O}_6(\text{OH})_4^-$ and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ were formed by polymerization throughout brine evaporation. Species such as $\text{B}(\text{OH})_4^-$ were determined to be minor contributors to boron concentration and gradually disappeared in concentrated brine. Therefore, the relevant interactions between polyborate anions in brine from the Da Qaidam salt lake during evaporation were delineated as follows,



Factors of the boron concentration, pH, and ionic compositions of the brine could be ascribed to this borate polymerization during evaporation. As shown in Table 1, the main composition of the brine DL4 or DL5 was $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgCl}_2 - \text{MgSO}_4 - \text{H}_2\text{O}$, and the influence of the magnesium chloride and magnesium sulfate on boron speciation was also investigated in this study.

3.2 Raman spectra of borate in aqueous solutions during evaporation

Figures 2 - 4 show the Raman spectra of borates in solutions of $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$, $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgCl}_2 - \text{H}_2\text{O}$, and $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgSO}_4 - \text{H}_2\text{O}$. The Raman bands ascribed to borates are given in Tables 3 - 5.

In the $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$ system, as shown in Fig. 2 and Table 3, the prepared solution with $1.14\text{ g/L B}_2\text{O}_3$ was weakly alkaline ($\text{pH} = 9.15$), and the boron forms present in solution contained the $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ anions. As the solution was concentrated by evaporation, the Mg-borate of $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 6\text{H}_2\text{O}$ crystallized out from the concentrated solution when the boron concentration was more than $27.66\text{ g/L B}_2\text{O}_3$. Since the crystallization rate was low, the solution was quickly concentrated to $78.30\text{ g/L B}_2\text{O}_3$ with few solids obtained. The Raman spectra of borate in solution (Figs. 2c, d) changed compared with that of Da Qaidam brine. There was no observed band of $\text{B}_5\text{O}_6(\text{OH})_4^-$ and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ anions in solution throughout evaporation. But the band for $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ at $567 - 572\text{ cm}^{-1}$ and band for the $\text{B}_3\text{O}_3(\text{OH})_4^-$ anion at $617 - 618\text{ cm}^{-1}$ appeared in the solution when the boron concentration was more than $13.35\text{ g/L B}_2\text{O}_3$, and its intensity increased with increasing boron concentration. Thus, the borates $\text{B}(\text{OH})_3$,

$B(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ were the main existing forms in the boron concentrated solution. This suggested a pH dependence on the boron speciation in solution. As can be seen from Fig. 1, the pH of the concentrated solution changed little after evaporation and it still remained weak alkaline (pH = 8.58), which was favorable for the distribution of the tetraborate anion $B_4O_5(OH)_4^{2-}$. Usually,

the polyborate anions $B_5O_6(OH)_4^-$ and $B_6O_7(OH)_6^{2-}$ tend to appear in a solution with a pH less than 8.0^[23]. Besides, the existing-form of $B_6O_7(OH)_6^{2-}$ ions also depended on the mole ratio of B_2O_3/MgO and the electrolytes, such as $MgCl_2$ and $MgSO_4$, present in the solution.

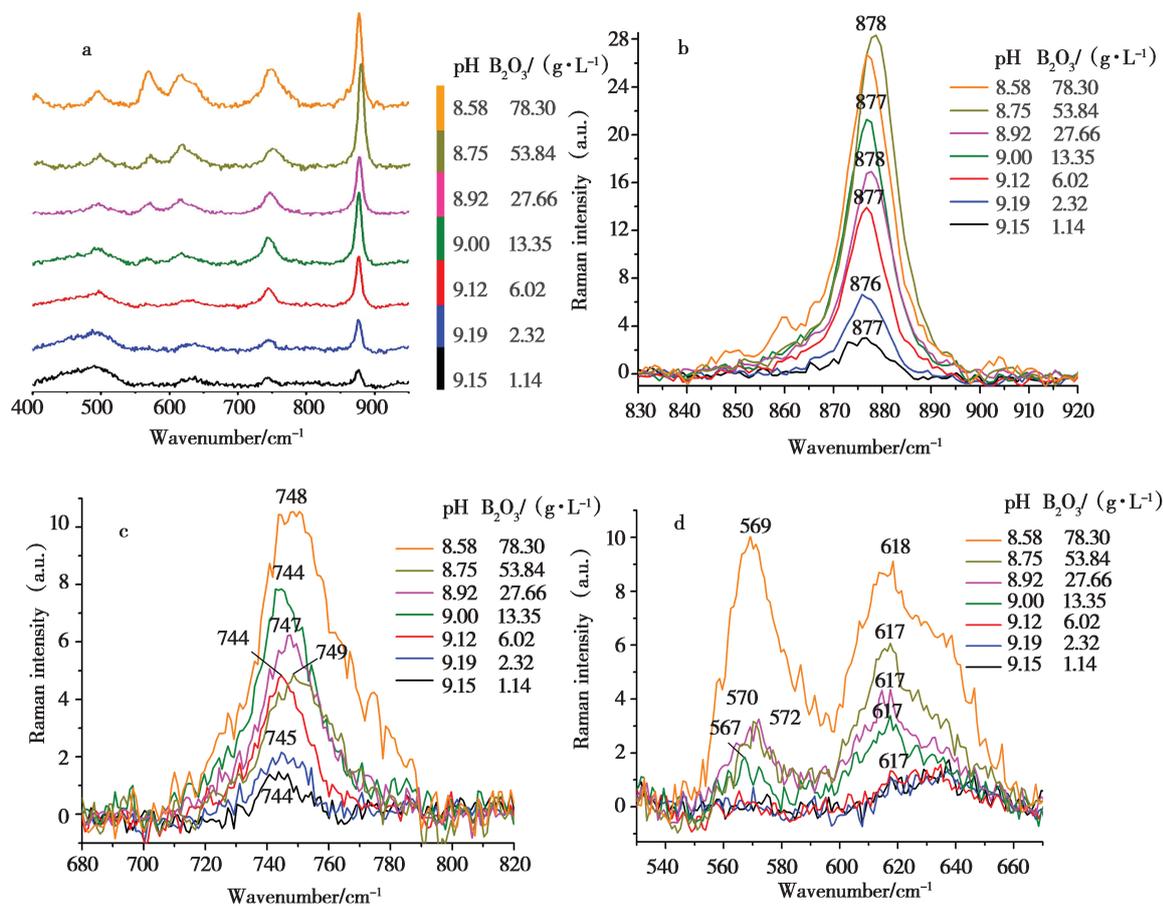


Fig. 2 Raman spectra of borate in $MgO \cdot 2B_2O_3 - H_2O$ solution during evaporation

However, in the $MgO \cdot 2B_2O_3 - MgCl_2 - H_2O$ system, as shown in Fig. 3 and Table 4, the solution pH decreased to 8.83 after the addition of magnesium chloride, and it dropped to 4.44 as the boron concentration increased to 74.16 g/L B_2O_3 after evaporation, which was similar to the pH value DL4 or DL5 brine. This was because both of them were saturated with bischofite, which has a pH of less than 4.5 in solution at 20 °C^[25]. Furthermore, borates were more stable in a magnesium chloride solu-

tion and did not drop out from the solution throughout the evaporation process. It is worth noting that the Raman spectra of borates in the magnesium chloride solution were also similar to the spectra of brine from the Da Qaidam salt lake. When the boron concentration was more than 13.98 g/L B_2O_3 , the polyborates $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$ and $B_6O_7(OH)_6^{2-}$ appeared in the solution. The band for $B_4O_5(OH)_4^{2-}$ at $\sim 570 \text{ cm}^{-1}$ disappeared in a magnesium chloride solution compared with the MgO

· $2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$ system. Thus, the main polyborate ions present in a bischofite saturated solution contained $\text{B}(\text{OH})_3$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_5\text{O}_6(\text{OH})_4^-$

and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ anions

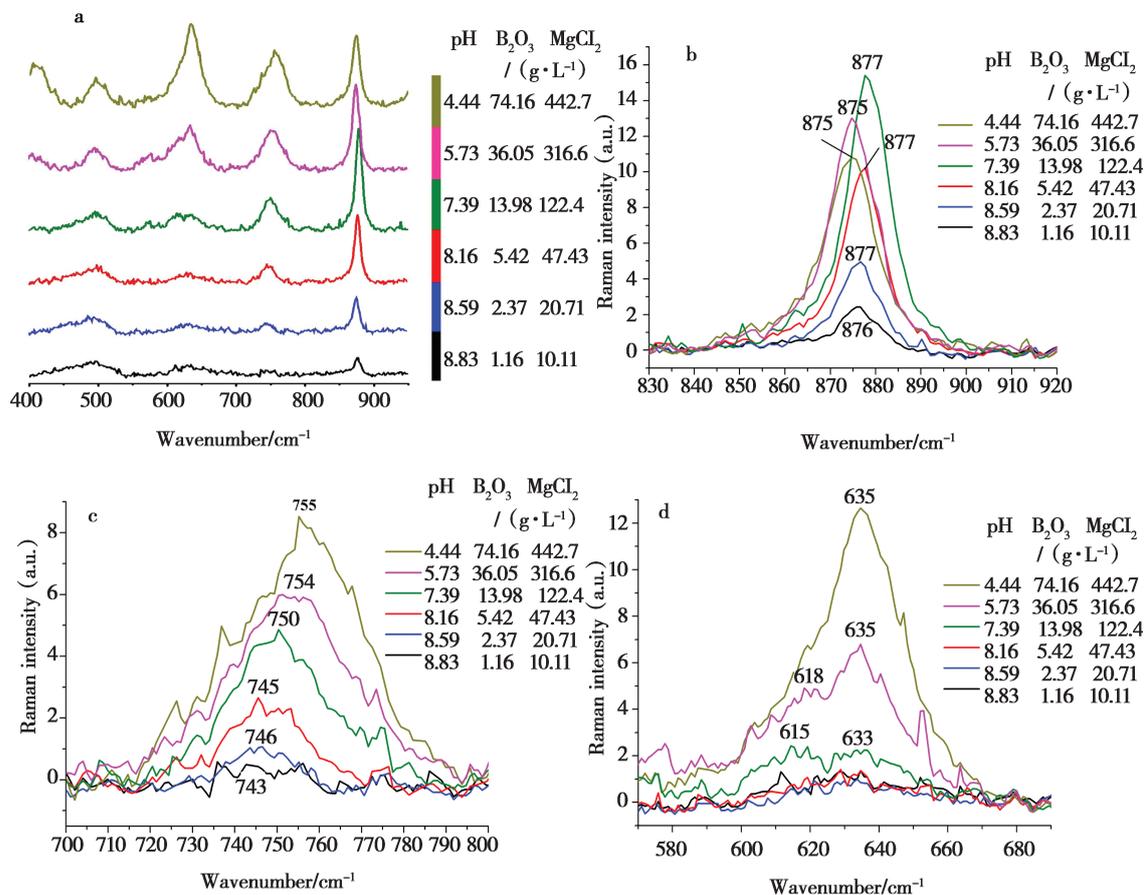


Fig. 3 Raman spectra of borate in $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgCl}_2 - \text{H}_2\text{O}$ solution during evaporation

Finally, in the $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgSO}_4 - \text{H}_2\text{O}$ system, as shown in Fig. 4 and Table 5, the addition of magnesium sulfate caused the prepared solution's pH to decrease to 9.03. The $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ anions, however, were still the only boron forms present in this solution. As the solution was concentrated to 14.11 g/L B_2O_3 , a shoulder band for the $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ anion appeared at $\sim 576 \text{ cm}^{-1}$ in the solution and its intensity increased with increasing boron concentration (Fig. 4d). Furthermore, it should be noted that the strong band at $\sim 617 \text{ cm}^{-1}$ was ascribed to the bending vibration ν_4 of SO_4^{2-} ions and was characteristic of a $\text{B}_3\text{O}_3(\text{OH})_4^-$ ion. It was not until the pH value was 7.13, close to neutral, that the $\text{B}_5\text{O}_6(\text{OH})_4^-$ anion appeared in the solution

at a boron concentration of 35.52 g/L B_2O_3 (Fig. 4c), also suggesting the pH dependence of the pentaborate ion presence in solution. When the solution was further evaporated to 72.73 g/L B_2O_3 , the pH increased to 7.20 due to epsomite crystallization. There was no obvious band for the $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ ion at $620 \sim 640 \text{ cm}^{-1}$ present in the epsomite-saturated solution. One possible reason was that the strong band for the SO_4^{2-} ion at $\sim 615 \text{ cm}^{-1}$ may have overlapped the band for the $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$ ion in this solution. Therefore, there were at least five polyborates present, $\text{B}(\text{OH})_3$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_5\text{O}_6(\text{OH})_4^-$, and $\text{B}_6\text{O}_7(\text{OH})_6^{2-}$, in the boron-concentrated magnesium sulfate solution.

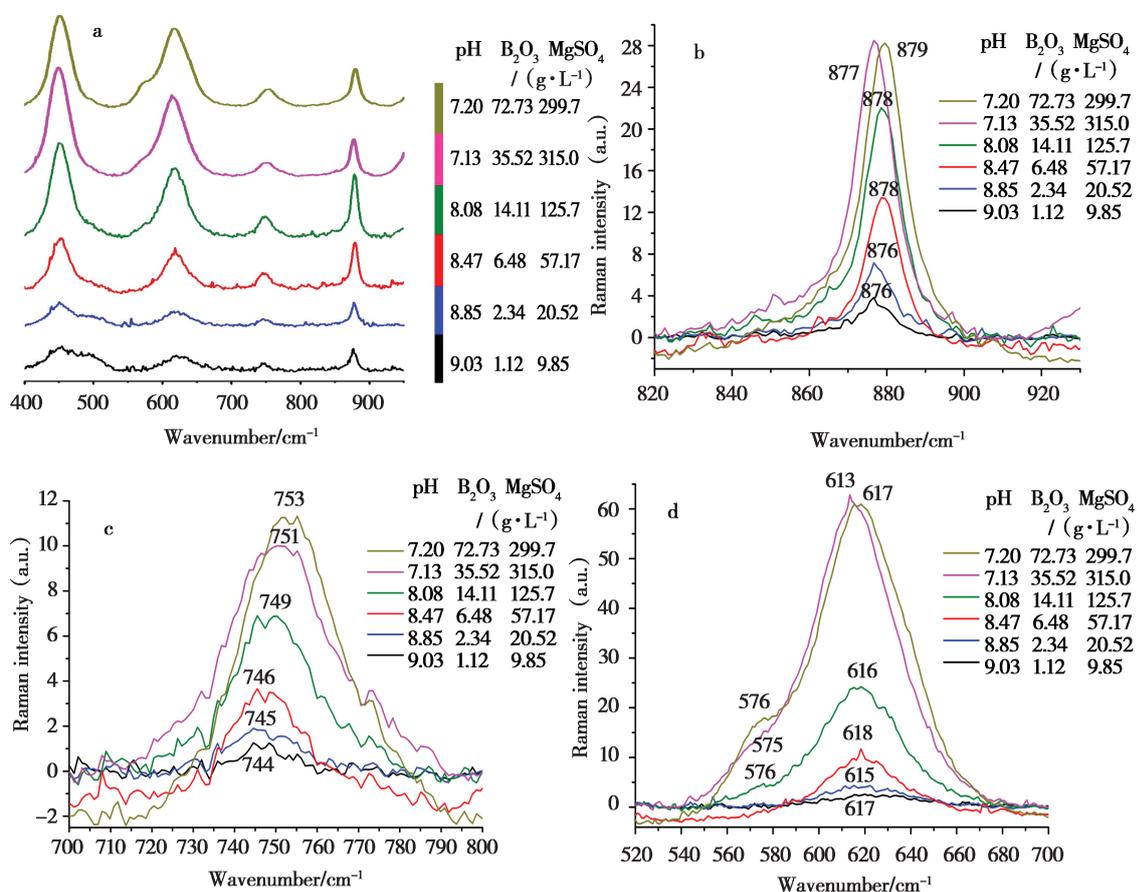


Fig. 4 Raman spectra of borate in $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgSO}_4 - \text{H}_2\text{O}$ solution during evaporation

Based on these above results, we propose that boron speciation was greatly affected by the boron concentration, pH and electrolytes present in a solution. When the boron concentration was less than

6 g/L B_2O_3 , only Raman spectra for the monoborates $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ were observed in a solution.

Table 3 Observed Raman wavenumbers of borate in $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{H}_2\text{O}$ solution during evaporation^a

1-L0	1-L1	1-L2	1-L3	1-L4	1-L5	1-L6	Assignment
pH = 9.15	pH = 9.19	pH = 9.12	pH = 9.00	pH = 8.92	pH = 8.75	pH = 8.58	
877 m	876 s	877 s	878 s	877 s	877 vs	878 vs	$\nu_s(\text{B}_{(3)} - \text{O})$ $\text{B}(\text{OH})_3$
744 w	745 w	744 m	744 s	747 s	749 m	748s	$\nu_s(\text{B}_{(4)} - \text{O})$ $[\text{B}(\text{OH})_4]^-$
-	-	-	617 w	617 w	617m	618m	$\nu_p[\text{B}_3\text{O}_3(\text{OH})_4]^-$ $[\text{B}_3\text{O}_3(\text{OH})_4]^-$
-	-	-	567 w	570 m	572 m	569 s	$\nu_p[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$
490 w	490 w	497 w	495w	496 m	495 m	496 m	$\delta_s(\text{B}_{(4)} - \text{O})$ $\text{B}(\text{OH})_3$

^ab - broad; s - strong; m - middle; w - weak; v - very. $\text{B}_{(3)}$, $\text{B}_{(4)}$ mean three and four coordinate boron, respectively.

Table 4 Observed Raman wavenumbers of borate in $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgCl}_2 - \text{H}_2\text{O}$ solution during evaporation ^a

2 - L0	2 - L1	2 - L2	2 - L3	2 - L4	2 - L5	Assignment	
pH = 8. 83	pH = 8. 59	pH = 8. 16	pH = 7. 39	pH = 5. 73	pH = 4. 44		
876 m	876 s	877 s	875 vs	876 s	875 s	$\nu_s(\text{B}_{(3)} - \text{O})$	$\text{B}(\text{OH})_3$
-	-	-	755 s	756 s	755 s	$\nu_s(\text{B}_{(4)} - \text{O})$	$[\text{B}_5\text{O}_6(\text{OH})_4]^-$
744 w	746w	745 m	-	-	-	$\nu_s(\text{B}_{(4)} - \text{O})$	$[\text{B}(\text{OH})_4]^-$
-	-	-	633 s	635 s	635 vs	$\nu_p[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$	$[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$
-	-	-	615	618	-	$\nu_p[\text{B}_3\text{O}_3(\text{OH})_4]^-$	$[\text{B}_3\text{O}_3(\text{OH})_4]^-$
494 w	494 w	494 w	495w	495w	495 s	$\delta_s(\text{B}_{(4)} - \text{O})$	$\text{B}(\text{OH})_3$

^ab - broad; s - strong; m - middle; w - weak; v - very. $\text{B}_{(3)}$, $\text{B}_{(4)}$ mean three and four coordinate boron, respectively.

Table 5 Observed Raman wavenumbers of borate in $\text{MgO} \cdot 2\text{B}_2\text{O}_3 - \text{MgSO}_4 - \text{H}_2\text{O}$ solution during evaporation ^a

3 - L0	3 - L1	3 - L2	3 - L3	3 - L4	3 - L5	Assignment	
pH = 9. 03	pH = 8. 85	pH = 8. 47	pH = 8. 08	pH = 7. 13	pH = 7. 20		
876 m	876 m	878 s	878 s	877 s	879 vs	$\nu_s(\text{B}_{(3)} - \text{O})$	$\text{B}(\text{OH})_3$
-	-	-	-	751m	753 s	$\nu_s(\text{B}_{(4)} - \text{O})$	$[\text{B}_5\text{O}_6(\text{OH})_4]^-$
744 w	745w	746 m	749 m	-	-	$\nu_s(\text{B}_{(4)} - \text{O})$	$[\text{B}(\text{OH})_4]^-$
617 w	615 w	618 m	616 s	613 vs	617 vs	$\gamma(\text{S} - \text{O}) /$ $\nu_p[\text{B}_3\text{O}_3(\text{OH})_4]^-$	$\text{SO}_4^{2-} /$ $[\text{B}_3\text{O}_3(\text{OH})_4]^-$
-	-	-	576 vw	575vw	576 m	$\nu_p[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$	$[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$
454 w	450w	452 s	450 vs	449 vs	451vs	$\gamma(\text{S} - \text{O})$	SO_4^{2-}

^ab - broad; s - strong; m - middle; w - weak; v - very. $\text{B}_{(3)}$, $\text{B}_{(4)}$ mean three and four coordinate boron, respectively.

When the boron concentration was less than 6 g/L B_2O_3 , only the Raman spectra for the monoborates $\text{B}(\text{OH})_3$ and $[\text{B}(\text{OH})_4]^-$ were observed in a solution. The pentaborate ion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ was sensitive to the solution pH and was often found present at pH values less than 8.0. In contrast the hexaborate ion $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$ was observed more often dependent on the electrolytes present in a solution, especially magnesium chloride. This was because the addition of magnesium chloride could promote the accumulation of borate in a solution. Furthermore, the saturation of magnesium chloride in solution also caused a lower pH, which was favorable for the formation of polyborate ions. Additionally, the magnesium ion is highly charged and has a strong affinity for water molecules. It exists in the form of $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ in an aqueous solution, causing a reduction of free water molecules, and this was benefi-

cial to the polymerization of borate ions.

4 Conclusions

Raman spectra of the boron-containing brine from the Da Qaidam salt lake were recorded during evaporation to investigate the boron forms present in brine and determine the interaction mechanisms between them. Factors governing boron form speciation in brine, including boron concentration, pH and the presence of electrolytes, were also studied. Our results showed that the monoborates $\text{B}(\text{OH})_3$ and $[\text{B}(\text{OH})_4]^-$ were found to be the only forms present in natural salt lake brine. As brine evaporation started, the $[\text{B}(\text{OH})_4]^-$ ion that was detected at $\sim 745 \text{ cm}^{-1}$ gradually disappeared, and the polyborate ions $[\text{B}_3\text{O}_3(\text{OH})_4]^-$, $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, and $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$ gradually appeared in the brine at boron concentra-

tions of more than 11 g/L B_2O_3 . When the brine was saturated with bischofite, the strong band of the $B_6O_7(OH)_6^{2-}$ at $\sim 635\text{ cm}^{-1}$ revealed that polymerization had occurred in brine. Thus, the polyborate ions $B(OH)_3$, $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^{-1}$, and $B_6O_7(OH)_6^{2-}$ were found to be the main forms in concentrated brine after evaporation. The electrolytes magnesium chloride and magnesium sulfate being present in brine greatly affected the boron speciation by promoting boron concentration and decreasing the solution pH. However, the properties of bischofite-saturated brine, such as the strong affinity of magnesium ions for water molecules, facilitated the polymerization of borate ions in brine.

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