



Investigations on Mg-borate kinetics and mechanisms during evaporation, dilution and crystallization by Raman spectroscopy

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ABSTRACT

Raman spectra of boron-concentrated, diluted, and corresponding mother solutions of brine were recorded at 298.15 K. The main polyborate anions present and their interactions in brine during evaporation and dilution were proposed according to the Raman spectra. The polyborate anions $B(OH)_3$, $B_3O_3(OH)_4^-$, $B_5O_6(OH)_4^-$, and $B_6O_7(OH)_6^{2-}$ were found to be the main forms in boron-concentrated brine with $B_3O_3(OH)_4^-$ ion being the principal form. Diluting brines with water accelerated depolymerization of $B_5O_6(OH)_4^-$ and $B_6O_7(OH)_6^{2-}$ anions into $B(OH)_3$ and $B_3O_3(OH)_4^-$ ions and generated OH^- ions, causing the pH of the solutions to increase from 4.2 to almost 8.0. Mg-borates precipitated from all diluted solutions could be classified as either hexaborates or triborates. A mechanism of solid phase transformation was also proposed and discussed based on Raman spectra analysis and solid species and solution pH data.

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1. Introduction

The Qinghai-Tibet Plateau of China contains hundreds of salt lakes that are abundant boron resources. Some of these salt lakes are depositing magnesium borates [1,2]. For example, Lake Da Qaidam, which is located at the foot of the Qilian Mountains, north of Qaidam Basin (95° 02' and 95° 22' E, 37° 46' and 37° 55' N), is a typical boron-rich $MgSO_4$ -subtype salt lake. To date, there have been nine borate-containing minerals discovered in the salt deposits of Da Qaidam salt lake, including the Mg-borates—pinnoite, inderite (kurnakovite), hungchaoite, and macallisterite, the Ca-Mg borates—hydroboracite and carboborite, the Ca-Na borate—ulexite, and the Na-borate—borax. To characterize the mechanisms of borate formation in the plateau, particularly of Mg-borates, Gao and his co-workers [3] studied the chemical behavior of borate during evaporation of salt lake brine and found borate has a high metastability due to the complexity of its polyborate ions in solution. Borate accumulates in the bischofite saturated brine and remains stable for a few months at room temperature in the form of tetraborate $MgO \cdot 2B_2O_3$ based on comprehensive statistics [4]. Here, the term “comprehensive statistics” means, besides

tetraborate, other borates may also exist in brine where $n (MgO \cdot nB_2O_3)$ is less or >2 , but must be satisfied with the apparent result $n = 2$. The supersolubility of borate in brine can reach up to 5.82% in the form of B_2O_3 [5] and Mg-borate does not precipitate from brine. However, when the boron-concentrated brine is diluted with water, different Mg-borate salts precipitate from diluted brine, where the types of salts vary depending on dilution ratio and working time (see Table 1) [6]. This phenomenon is referred to as “crystallization by dilution” and is a process distinct from “crystallization by evaporation.” Based on the composition of hot spring water supply of Da Qaidam salt lake and physico-chemical experiments on salt minerals [1,7,8], Gao concluded the new “crystallization by dilution” phenomenon is responsible for the formation of Mg-borates in the salt lake. The composition and concentration of other salts and temperature of the brine have an effect on the pH, which controls the precipitation of Mg-borate minerals.

Boron exists in the form of polyborate anions in aqueous solutions [9–13], that can transform into each other upon changes in boron concentration, pH, temperature, or ionic composition. A higher boron concentration and lower pH and temperature are favorable for polymerization of borate anions [10,12–14]. By contrast, ions tend to dissociate by hydrolysis to generate lower polyborate or monoborate species. Therefore, the mechanism of “crystallization by dilution” in bischofite-saturated brine could be dissociation of polyborate ions after dilution. However, the existing forms of polyborate anions in brine and interactions among them during evaporation and dilution remain unknown. The precipitation mechanisms of Mg-borates after

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Table 1
Borates species in diluted brine with different dilution ratios and working time^a.

No.	Volume dilution ratio (water/brine)	Compositions of initial liquid (wt%)				Solid phase after dilution for half a year	Solid phase after dilution for 5 years
		pH	MgCl ₂	MgSO ₄	MgB ₄ O ₇		
0	0:1	4.7	30.7	3.31	4.28	Hexaborate + chloropinnoite	Hexaborate + chloropinnoite
1	0.25: 1	5.5	26.0	2.80	3.62	Hexaborate + chloropinnoite	Hexaborate + chloropinnoite
2	0.5:1	6.0	22.5	2.43	3.10	Hexaborate + chloropinnoite	Inderite
3	1:1	7.0	17.8	1.92	2.48	Hungchaoite	Inderite
4	2:1	7.4	12.5	1.35	1.75	Inderite	Inderite
5	4:1	8.0	7.9	0.85	1.10	Inderite	Inderite
6	6:1	8.3	5.7	0.62	0.80	Inderite	Inderite
7	8:1	8.4	4.5	0.49	0.63	Inderite	Inderite
8	10:1	8.4	3.7	0.40	0.52	Mg(OH) ₂	Inderite
9	12:1	8.4	3.2	0.34	0.44	Mg(OH) ₂	Inderite

^a Hexaborate: MgO·3B₂O₃·7H₂O; Chloropinnoite: 2MgO·2B₂O₃·MgCl₂·14H₂O; Hungchaoite: MgO·2B₂O₃·9H₂O. Inderite: 2MgO·3B₂O₃·15H₂O.

Table 2
Compositions of the brine used in experiment (wt%).

Brine	Density (g/cm ³)	pH	Na ⁺	Mg ²⁺	K ⁺	B ₂ O ₃	Cl ⁻	SO ₄ ²⁻	Li ⁺
L0	1.3622	4.39	0.107	8.86	0.048	1.28	24.47	2.29	0.144
L2	1.3630	4.73	0.033	8.40	0.051	2.47	22.24	3.15	0.239
L3	1.3801	4.37	0.038	8.77	0.060	3.68	23.13	2.92	0.286
L4	1.3874	4.25	0.002	8.71	0.075	4.69	22.35	3.29	0.330

dilution are complex and understanding is limited. In the present study, Raman spectroscopy was used to identify polyborate ions in concentrated and diluted brine due to its advantages characterizing polyborate ions in solution [9,15]. Absorption peaks characteristic of polyborate anions in brine were assigned and the mechanisms underlying interaction among polyborate anions and precipitation of Mg-borates in diluted brine have been proposed based on experimental Raman spectra.

Table 3
Observed Raman wavenumbers of boron-concentrated brine during evaporation process^a.

L2	L3	L4	Assignment	
pH = 4.73	pH = 4.37	pH = 4.25		
–	1451w	1447 w	ν_{as} (B ₍₃₎ -O)	–
1100 bm	1104 bm	1107 bm	δ (B-O-H)	–
–	1055 m	1054 m	ν_{as} (B ₍₄₎ -O)	–
987 vs	985 vs	987 vs	ν_s (B ₍₃₎ -O)	[B ₃ O ₃ (OH) ₄] ⁻
876 m	875 s	876 s	ν_s (B ₍₃₎ -O)	B(OH) ₃
763 bm	758 bm	763 bs	ν_s (B ₍₄₎ -O)	[B ₃ O ₅ (OH) ₄] ²⁻
–	–	744 w	ν_s (B ₍₄₎ -O)	[B(OH) ₄] ⁻
628 m	641 s	634 s	ν_p [B ₆ O ₇ (OH) ₆] ²⁻	[B ₆ O ₇ (OH) ₆] ²⁻
614 m	–	–	ν_p [B ₃ O ₃ (OH) ₄] ⁻	[B ₃ O ₃ (OH) ₄] ⁻
–	–	562 w	ν_p [B ₄ O ₅ (OH) ₄] ²⁻	[B ₄ O ₅ (OH) ₄] ²⁻
479 w	440 w	480 w	δ_s (B ₍₄₎ -O)	[B ₃ O ₃ (OH) ₄] ⁻ /B(OH) ₃

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

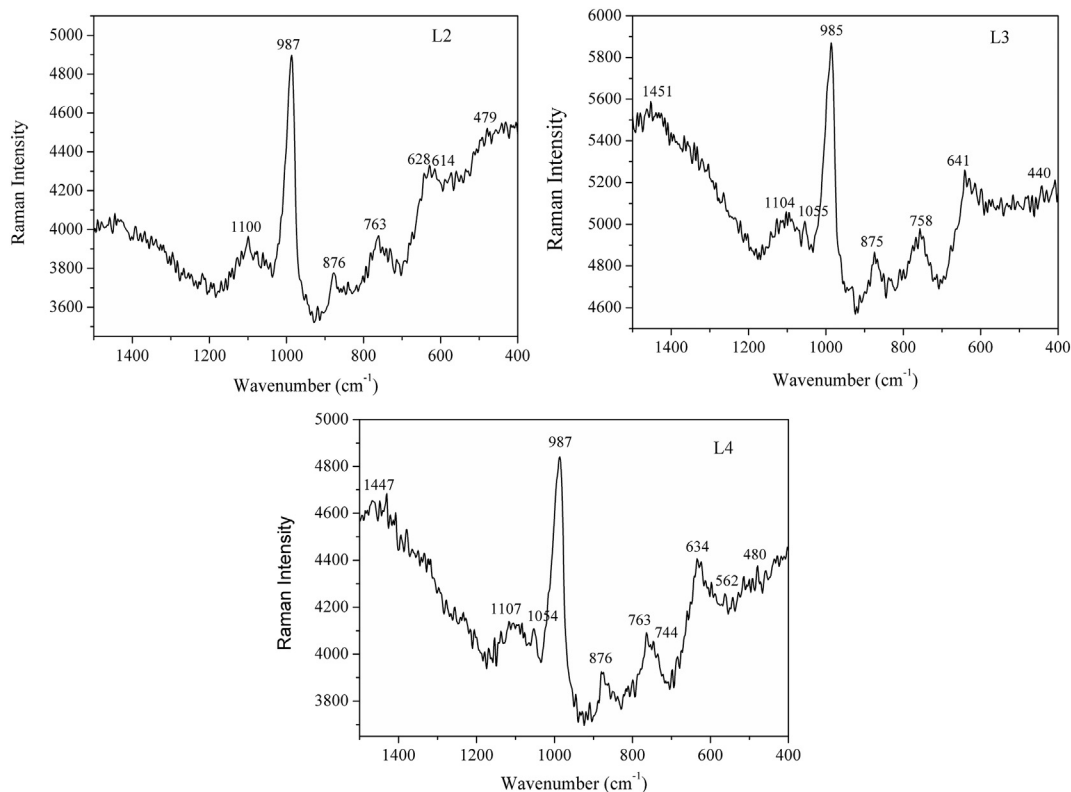


Fig. 1. Raman spectra of concentrated brines during evaporation process. Boron concentration (B₂O₃%): L2, 2.47; L3, 3.68; L4, 4.69.

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