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Experimental Determination of Solubilities of Sodium Tetraborate (Borax) in NaCl Solutions, and A Thermodynamic Model for the $Na–B(OH)_3–Cl–SO_4$ System to High Ionic Strengths at 25 °C, Revision 1 Corrections

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ABSTRACT

In this study, solubility experiments on sodium tetraborate (NaB_4O_7•$10H_2O$, borax) are conducted in NaCl solutions up to 5.0 m at room temperature (22.5 ± 1.5°C). In combination with solubility data of sodium tetraborate in Na_2SO_4 solutions from literature, the solubility constant (log K_{sp}) for sodium tetraborate for the following reaction,

$$Na_2B_4O_7•10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O\ (l) \quad (1)$$

is determined as –24.80 ± 0.10 based on the Pitzer model. In conjunction with the relevant Pitzer parameters, based on the above log K_{sp} for borax, and log β_1 (0.25 ± 0.01) evaluated from the literature for the following complex formation reaction,

$$Na^+ + B(OH)_4^- = NaB(OH)_4(aq) \quad (2)$$

a thermodynamic model with high precision is established for the Na^+–$B(OH)_3$–Cl^-–SO_4^{2-} system at high ionic strengths up to saturation of halite (NaCl), mirabilite (Na_2SO_4•$10H_2O$) and thenardite (Na_2SO_4). The model is validated by comparison of model predicted equilibrium compositions for the assemblages of borax alone, borax + halite, borax + mirabilite, borax + halite + thenardite, and borax + mirabilite + thenardite in the mixtures of NaCl + Na_2SO_4 to ionic strengths of 8.0 m, with independent experimental values from the literature. The differences in concentrations of major ions,

e.g., Na^+, Cl^-, and SO_4^{2-}, between model predicted and experimental values are generally less than 0.5%. The difference for total boron concentrations is less than 0.05 m with an error less than 25%.

The revised thermodynamic model is applied to the potential recovery of borax from boron-enriched brines via evaporation at 25°C, using the two brines from China as examples. The reaction path calculations suggest that the brine from the Zhabei Salt Lake in Xizang (Tibet) Autonomous Region, is suitable to recovery of borax via evaporation at 25°C, whereas the brine from the western Sichuan Province, although it is enriched in boron, is not suitable to extraction of boron as borax, but is suitable to extraction of potassium as sylvite, via evaporation at 25°C.

INTRODUCTION

Numerous actinide borates have been recently successfully synthesized (e.g., Wang et al., 2010, 2011, and references therein), including a Pu(III) borate, $Pu_2[B_{12}O_{18}(OH)_4Br_2(H_2O)_3]\bullet 0.5H_2O$. Furthermore, a recent experimental study has suggested that borate could potentially complex with Nd(III), an analog to Am(III) (Borkowski et al., 2010). Therefore, a comprehensive thermodynamic model involving interactions of borate with major ions in brines is needed to accurately describe the contributions of borate to the solubility of Am(III) in brines in salt formations, as they contain significant concentrations of borate. In brines associated with salt formations, they contain high concentrations of sodium along with significant concentrations of boron. For instance, at the Waste Isolation Pilot Plant (WIPP), a U.S. Department of Energy geological repository for the permanent disposal of defense-related transuranic

(TRU) waste (U.S. DOE, 1996), the Generic Weep Brine (GWB) and Energy Research and Development Administration Well 6 (ERDA-6), contain high concentrations of sodium and borate. Therefore, in geological repositories in salt formations, the interactions between sodium and borate will be important to the accurate description of the contributions of borate to the solubility of Am(III) in brines in salt formations.

A thermodynamic model for borate at high ionic strengths was developed more than two decades ago by Felmy and Weare (1986). In addition to the newly generated data at Sandia National Laboratories, there have also been numerous experimental data concerning borate in concentrated brines generated in China (e.g., Sang et al., 2011), since the discovery of enormous amounts of highly concentrated brines with high concentrations of B (up to 4994 mg/L) and Li (up to 90 mg/L), termed as "liquid ores", in Sichuan Province, China (e.g., Lin et al., 2000). Therefore, in light of new experimental data, the revision of the Felmy and Weare model is in order. There will be a series of upcoming publications in this area, and this paper is the first one in this series.

EXPERIMENTAL METHODS

In our solubility experiments, about 5 grams of the solubility controlling material—ACS reagent grade sodium tetraborate ($Na_2B_4O_7 \bullet 10H_2O$), i.e., borax, from Fisher Scientific was weighed out and placed into 150 mL plastic bottles. Then, 100 mL of supporting solutions were added into those bottles. Once filled, the lids of the bottles were sealed with parafilm. The supporting electrolytes are a series of NaCl solutions ranging from 0.010 m to 5.0 m. Undersaturation experiments are conducted at the laboratory room temperature ($22.5 \pm 1.5^{o}C$), and the duration of our experiments is

exceedingly long in comparison with the similar studies previously conducted (see RESULTS section). In the following, sodium tetraborate and borax will be interchangeably used.

The pH readings were measured with an Orion-Ross combination pH glass electrode, coupled with an Orion Research EA 940 pH meter that was calibrated with three pH buffers (pH 4, pH 7, and pH 10). In solutions with an ionic strength higher than 0.10 m, hydrogen-ion concentrations on molar scale (pcH) were determined from pH readings by using correction factors (Rai et al., 1995). Based on the equation in Xiong et al. (2010), pcHs are converted to hydrogen-ion concentrations on molal scale (pmH).

Solution samples were periodically withdrawn from experimental runs. Before solution samples were taken, pH readings of experimental runs were first measured. The sample size was usually 3 mL. After a solution sample was withdrawn from an experiment and filtered with a 0.2 μm syringe filter, the filtered solution was then weighed, acidified with 0.5 mL of concentrated TraceMetal® grade HNO_3 from Fisher Scientific, and finally diluted to a volume of 10 mL with DI water. If subsequent dilutions were needed, aliquots were taken from the first dilution samples for the second dilution, and aliquots of the second dilution were then taken for the further dilution.

Boron concentrations of solutions were analyzed with a Perkin Elmer dual-view inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Perkin Elmer DV 3300). Calibration blanks and standards were precisely matched with experimental matrices. The linear correlation coefficients of calibration curves in all

measurements were better than 0.9995. The analytical precision for ICP-AES is better than 1.00% in terms of the relative standard deviation (RSD) based on replicate analyses.

RESULTS

Experimental results are tabulated in Table 1. In Figure 1, solubilities of sodium tetraborate as a function of experimental time are displayed. From Figure 1, it is clear that steady-state concentrations are achieved in the first sampling, which was taken at 132 days (Table 1). It is assumed that steady-state concentrations represent equilibrium concentrations, as the duration of experiments, up to 567 days, is significantly longer than previous studies under similar conditions. For example, the equilibrium for the quaternary $Na_2B_4O_7$—Na_2SO_4—$K_2B_4O_7$—K_2SO_4—H_2O system at 15^{o}C was attained in 3-7 days (Sang et al., 2011).

In Figure 2, concentrations of boron as a function of molalities of NaCl are displayed. Figure 2 indicates that concentrations of boron in equilibrium with sodium tetraborate have a strong dependence on concentrations of NaCl, with substantial decrease in concentration of boron with increasing concentrations of NaCl. For instance, the solubilities of sodium tetraborate are ~0.50 m in terms of total boron concentrations in a 0.01 m NaCl solution, whereas the concentrations of boron decrease to ~0.15 m in a 5.0 m NaCl solution.

THERMODYNAMIC MODEL, DISCUSSIONS, AND APPLICATIONS

Felmy and Weare (1986) developed a thermodynamic model concerning borate in the system Na—K—Ca—Mg—H—Cl—SO_4—CO_2—$B(OH)_4$—H_2O, based on literature

data. This model will be abbreviated as the FW86 model hereafter. Their model is an extension of the Harvie et al. (1984) model to include borate species. In the FW86 model, the species, $NaB(OH)_4(aq)$, was not explicitly considered. However, numerous researchers have suggested the existence of this complex in solutions containing sodium (e.g., Reardon, 1976; Corti et al., 1980; Rowe et al., 1989; Pokrivski et al., 1995; Akinfiev et al., 2006). Therefore, this complex could be important in Na-rich solutions.

In the work of Reardon (1976), the formation constants for the reaction,

$$Na^+ + B(OH)_4^- = NaB(OH)_4(aq) \quad (1)$$

were determined in a NaCl medium with ionic strengths ranging from 0.165 m to 0.499 m at temperatures from 10 ^oC to 50 ^oC. To obtain the thermodynamic formation constants at infinite dilution, Reardon (1976) used the activity coefficients of HCO_3^- and $H_3BO_3(aq)$ to approximate those of $B(OH)_4^-$ and $NaB(OH)_4(aq)$, respectively. The thermodynamic formation constant at 25 ^oC for Reaction (1) obtained by Reardon (1976) was 0.22 ± 0.10.

In this study, conditional formation constants for Reaction (1) generated by Reardon (1976) are re-evaluated by using the SIT model, following the methodology of Grenthe et al. (1992). The log β_1 at 25 ^oC obtained is 0.25 ± 0.01 (Figure 3 and Table 2). Based on $\Delta\varepsilon = -0.04 \pm 0.02$, the log β_1 at 10 ^oC, 40 ^oC and 50 ^oC are also obtained (Table 2). These values are in agreement with those of Pokrowski et al. (1995).

147 With the above log β_1 for $NaB(OH)_4(aq)$, experimental solubility data of borax in
148 NaCl produced in this study, and solubility data of borax in Na_2SO_4 from
149 Sborgi et al. (1924), are utilized to model the Pitzer parameters and log K_{sp} for borax with
150 the aid of the computer code EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011).
151 The essence of the modeling is to minimize the difference between experimental and
152 model predicted values. The log K_{sp} for borax dissolution refers to the following
153 reaction,
154
155 $$Na_2B_4O_7{\bullet}10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O\ (l) \qquad (2)$$
156
157 In Figure 4, experimental data along with model predicted values are plotted. In
158 this plot, solubilities of $Na_2B_4O_7{\bullet}10H_2O$ in a Na_2SO_4 medium from Sborgi et al. (1924;
159 compiled in Linke, 1965, p. 826; and Silcock, 1979, Part 2, p. 582) are also included. It
160 should be mentioned that while the data of Sborgi et al. (1924) were tabulated in both of
161 the above compilations, Silcock (1979) cited an incorrect source. Notice that the values
162 predicted by the FW86 model are based on the parameters listed in Table 2. Similarly,
163 the values predicted by the model developed in this study are based on the parameters
164 tabulated in Table 3. It is clear from Figure 4 that the revised model developed in this
165 study performs very well in a wide range of ionic strength.
166 In Table 4, solution compositions of the assemblage of sodium tetraborate alone
167 or in equilibrium with other phases such as halite (NaCl), mirabilite ($Na_2SO_4{\bullet}10H_2O$),
168 and thenardite (Na_2SO_4), in mixtures of NaCl + Na_2SO_4 predicted by the revised model
169 and by the FW86 model are compared with independent experimental data from the

literature up to ionic strengths of 8.0 m, which are not used in model development in this study. The experimental data are from Van't Hoff and Blasdale (1905; compiled in Silcock, 1979) and Grushvitski and Flerinskava (1932; cited by Bukshtein et al., 1953-1954, and compiled in Silcock, 1979). The comparison demonstrates that while these two models have similar precisions in prediction of concentrations of major ions, i.e., Na^+, Cl^-, and SO_4^{2-} (Table 4), there is a significant improvement associated with the current model in predicting solubilities of sodium tetraborate. The validation test indicates that the differences between boron concentrations predicted by the current model and experimental solubilities are less than 0.05 m with an error less than 25% (Table 4 and Figure 5). In comparison, the differences between boron solubilities predicted by the FW86 model and experimental solubilities are generally higher than 0.05 m, and can be as high as 0.17 m with an error up to 146%.

The revised model indicates that sodium tetraborate has solubilities much lower in high ionic strength solutions in comparison with those predicted by the previous model. This would have a wide range of implications. As an example, in the following, we apply the current model to investigate the evolution of some boron-enriched brines in China as a function of evaporation at 25°C.

The mildly alkaline brine in the Zhabei Salt Lake in Xizang (Tibet) Autonomous Region, China, is enriched in boron (Gao et al., 2012) (Table 5). Similarly, as mentioned in Introduction, the brine from the gas field in the western Sichuan Province, China, is also enriched in boron (Table 6). Therefore, based on the thermodynamic model on sodium tetraborate developed in this study, using EQ3/6 Version 8.0a, we can quantitatively model by performing reaction path calculations the evolution of those

boron-enriched brines as a function of evaporation to provide insight into the potential recovery of boron as sodium tetraborate via evaporation. In the reaction path calculations, degrees of evaporation (DE) is defined as follows:

$$DE = (1-\frac{RMS}{OMS})\times 100\% = (1-\frac{RMS}{1000})\times 100\% \quad (3)$$

where *RMS* is residual mass of solvent in grams, *OMS* is original mass of solvent. In the reaction path calculations, *OMS* is scaled to 1000 grams of water.

In our reaction path calculations, the original aqueous solution masses for the Zhabei Salt Lake and western Sichuan gas field brines are 1146 and 1433 grams, respectively. As the original pH for the western Sichuan gas field brine was slightly acidic (pH = 6.18), and borax will not precipitate, its pH was adjusted to 9.0 before reaction path calculations. As the Zhabei Salt Lake brine is mildly alkaline, its pH was not adjusted for reaction path calculations.

In Figure 6, amounts of mineral precipitated in mole are displayed as a function of DE. From Figure 6, we can see that above DE 10, about 0.08 moles of borax will be precipitated. Hydromagnesite (5424) [$Mg_5(CO_3)_4(OH)_2{\bullet}4H_2O$] (Xiong and Lord, 2008; Xiong, 2011a) will also be precipitated. Trace amounts of calcite are also predicted to be precipitated (Figure 6). In the evaporation experiments with the Zhabei Salt Lake brine at 0^oC performed by Gao et al. (2012), the precipitation of borax and magnesium carbonate, possibly lansfordite ($MgCO_3{\bullet}5H_2O$), is also observed, based on phase identifications using a polarizing microscope. However, it is worth noting that their identification of lansfordite based on the optical method may not be exact. In fact, studies on the sediments in the similar lakes in Xizang (Tibet) Autonomous Region have

indicated the presence of hydromagnesite (5424) instead of lansfordite (Goto et al., 2003). Therefore, the magnesium carbonate identified by Gao et al. (2012) using the optical method could be hydromagnesite (5424). In their evaporation experiments at 0^{o}C, Gao et al. (2012) did not mention the presence of calcite. This may be due to the presence of calcite in trace amount, or the kinetics of calcite crystallization. In addition, because of lower solubilities for salts at lower temperatures, mirabilite (Na_2SO_4•$12H_2O$), halite (NaCl), and sylvite (KCl) are also precipitated as major minerals in evaporation experiments at 0^{o}C of Gao et al. (2012). In contrast, because of undersaturation in respect with mirabilite at 25^{o}C, sulfate concentrations remain high during the evaporation at 25^{o}C (Figure 7A).

Evaporation of the brine from the gas field in the western Sichuan Province does not precipitate borax and hydromagnesite (5424). Instead, halite, anhydrite ($CaSO_4$), brucite [$Mg(OH)_2$], magnesium chloride hydroxide hydrate (phase 5) [$Mg_3Cl(OH)_5$•$4H_2O$] (Xiong et al., 2010), and sylvite are precipitated (Figure 6). Notice that brucite is stable up to DE ~40. Above DE ~40, brucite is replaced by phase 5 (Figure 6). The absence of borax during evaporation of the brine from the western Sichuan Province is due to the fact that the brine has higher magnesium concentrations when the brine is chemically evolved (Figures 7A and 7B). In the evaporation experiments with the brines having significant concentrations of magnesium and boron performed by Gao and Li (1982) at temperatures from 16^{o}C to 27^{o}C, the precipitation of borax is not observed neither because of high concentrations of magnesium. In our own solubility experiments, we also observe that borax has much higher solubilities in magnesium chloride solutions, which will be published later. In other words, the absence

239 of borax in the brine from the western Sichuan Province is well explained by the fact that
240 borax has higher solubilities in solutions with significant concentrations of magnesium.
241 In terms of chemical evolution of the brines induced by evaporation, the brine
242 from the Zhabei Salt Lake is dominated by Na-SO_4-Cl-B_4O_7 (Figure 7A), whereas the
243 brine from the western Sichuan Province is dominated by Na-K-Mg-Cl (Figure 7B).
244 The above reaction path calculations indicate that the brine from the Zhabei Salt
245 Lake is suitable for recovery of borax via evaporation at 25^{o}C. The brine from the
246 western Sichuan Province is suitable for extraction of potassium as sylvite via
247 evaporation at 25^{o}C.
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251 SUMMARY
252 In this study, a thermodynamic model with high precision is developed for the
253 Na^+–$B(OH)_3$–Cl^-–SO_4^{2-} system, based on new experimental data. This model is
254 validated by independent experimental data in ternary mixtures of NaCl and Na_2SO_4.
255 With this model, solubilities of borax in concentrated NaCl, Na_2SO_4, and NaCl+Na_2SO_4
256 solutions can be accurately modeled.
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371
372 Table 1. Experimental results produced in this study at 22.5 ± 1.5 ^{o}C.
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Experimental Number	Supporting Medium, NaCl, molal	Experimental time, days	pmH	Molal total boron concentrations, $m_{\Sigma B}$, in equilibrium with sodium tetraborate
$Na_2B_4O_7$-NaCl-0.01-1	0.010	132	9.10	0.515
$Na_2B_4O_7$-NaCl-0.01-2	0.010	132	9.03	0.509
$Na_2B_4O_7$-NaCl-0.1-1	0.10	132	8.97	0.435
$Na_2B_4O_7$-NaCl-0.1-2	0.10	132	8.95	0.417
$Na_2B_4O_7$-NaCl-1.0-1	1.0	132	8.70	0.179
$Na_2B_4O_7$-NaCl-1.0-2	1.0	132	8.72	0.194
$Na_2B_4O_7$-NaCl-2.0-1	2.1	132	8.66	0.157
$Na_2B_4O_7$-NaCl-2.0-2	2.1	132	8.81	0.147
$Na_2B_4O_7$-NaCl-3.0-1	3.2	132	8.81	0.139
$Na_2B_4O_7$-NaCl-3.0-2	3.2	132	8.77	0.143
$Na_2B_4O_7$-NaCl-4.0-1	4.4	132	8.88	0.165
$Na_2B_4O_7$-NaCl-4.0-2	4.4	132	8.89	0.151
$Na_2B_4O_7$-NaCl-5.0-1	5.0	132	8.80	0.145
$Na_2B_4O_7$-NaCl-5.0-2	5.0	132	8.79	0.146
$Na_2B_4O_7$-NaCl-0.01-1	0.010	278	9.28	0.488
$Na_2B_4O_7$-NaCl-0.01-2	0.010	278	9.28	0.495
$Na_2B_4O_7$-NaCl-0.1-1	0.10	278	9.26	0.411
$Na_2B_4O_7$-NaCl-0.1-2	0.10	278	9.24	0.415
$Na_2B_4O_7$-NaCl-1.0-1	1.0	278	9.04	0.190
$Na_2B_4O_7$-NaCl-1.0-2	1.0	278	9.03	0.099
$Na_2B_4O_7$-NaCl-2.0-1	2.1	278	9.00	0.155
$Na_2B_4O_7$-NaCl-2.0-2	2.1	278	8.98	0.152
$Na_2B_4O_7$-NaCl-3.0-1	3.2	278	8.96	0.143
$Na_2B_4O_7$-NaCl-3.0-2	3.2	278	8.93	0.140
$Na_2B_4O_7$-NaCl-4.0-1	4.4	278	9.06	0.139
$Na_2B_4O_7$-NaCl-4.0-2	4.4	278	9.05	0.142
$Na_2B_4O_7$-NaCl-5.0-1	5.0	278	8.96	0.141
$Na_2B_4O_7$-NaCl-5.0-2	5.0	278	8.96	0.142
$Na_2B_4O_7$-NaCl-0.01-1	0.010	327	9.33	0.482
$Na_2B_4O_7$-NaCl-0.01-2	0.010	327	9.28	0.508
$Na_2B_4O_7$-NaCl-0.1-1	0.10	327	9.26	0.436

$Na_2B_4O_7$-NaCl-0.1-2	0.10	327	9.22	0.430
$Na_2B_4O_7$-NaCl-1.0-1	1.0	327	9.09	0.207
$Na_2B_4O_7$-NaCl-1.0-2	1.0	327	9.10	0.210
$Na_2B_4O_7$-NaCl-2.0-1	2.1	327	8.99	0.160
$Na_2B_4O_7$-NaCl-2.0-2	2.1	327	9.00	0.161
$Na_2B_4O_7$-NaCl-3.0-1	3.2	327	9.00	0.151
$Na_2B_4O_7$-NaCl-3.0-2	3.2	327	8.95	0.157
$Na_2B_4O_7$-NaCl-4.0-1	4.4	327	9.10	0.151
$Na_2B_4O_7$-NaCl-4.0-2	4.4	327	9.11	0.147
$Na_2B_4O_7$-NaCl-5.0-1	5.0	327	8.97	0.151
$Na_2B_4O_7$-NaCl-5.0-2	5.0	327	9.01	0.158
$Na_2B_4O_7$-NaCl-0.01-1	0.010	377	9.39	0.513
$Na_2B_4O_7$-NaCl-0.01-2	0.010	377	9.38	0.509
$Na_2B_4O_7$-NaCl-0.1-1	0.10	377	9.32	0.468
$Na_2B_4O_7$-NaCl-0.1-2	0.10	377	9.33	0.482
$Na_2B_4O_7$-NaCl-1.0-1	1.0	377	9.09	0.214
$Na_2B_4O_7$-NaCl-1.0-2	1.0	377	9.09	0.231
$Na_2B_4O_7$-NaCl-2.0-1	2.1	377	9.03	0.168
$Na_2B_4O_7$-NaCl-2.0-2	2.1	377	9.03	0.171
$Na_2B_4O_7$-NaCl-3.0-1	3.2	377	9.01	0.153
$Na_2B_4O_7$-NaCl-3.0-2	3.2	377	9.00	0.149
$Na_2B_4O_7$-NaCl-4.0-1	4.4	377	9.08	0.152
$Na_2B_4O_7$-NaCl-4.0-2	4.4	377	9.09	0.146
$Na_2B_4O_7$-NaCl-5.0-1	5.0	377	9.00	0.152
$Na_2B_4O_7$-NaCl-5.0-2	5.0	377	9.02	0.149
$Na_2B_4O_7$-NaCl-0.01-1	0.010	425	9.35	0.514
$Na_2B_4O_7$-NaCl-0.01-2	0.010	425	9.31	0.532
$Na_2B_4O_7$-NaCl-0.1-1	0.10	425	9.26	0.531
$Na_2B_4O_7$-NaCl-0.1-2	0.10	425	9.25	0.458
$Na_2B_4O_7$-NaCl-1.0-1	1.0	425	9.04	0.221
$Na_2B_4O_7$-NaCl-1.0-2	1.0	425	9.03	0.222
$Na_2B_4O_7$-NaCl-2.0-1	2.1	425	8.96	0.171
$Na_2B_4O_7$-NaCl-2.0-2	2.1	425	8.97	0.171
$Na_2B_4O_7$-NaCl-3.0-1	3.2	425	8.95	0.161
$Na_2B_4O_7$-NaCl-3.0-2	3.2	425	8.93	0.156
$Na_2B_4O_7$-NaCl-4.0-1	4.4	425	9.02	0.158
$Na_2B_4O_7$-NaCl-4.0-2	4.4	425	9.04	0.154
$Na_2B_4O_7$-NaCl-5.0-1	5.0	425	8.96	0.159

$Na_2B_4O_7$-NaCl-5.0-2	5.0	425	8.97	0.162
$Na_2B_4O_7$-NaCl-0.01-1	0.010	567	9.28	0.489
$Na_2B_4O_7$-NaCl-0.01-2	0.010	567	9.28	0.497
$Na_2B_4O_7$-NaCl-0.1-1	0.10	567	9.24	0.429
$Na_2B_4O_7$-NaCl-0.1-2	0.10	567	9.23	0.426
$Na_2B_4O_7$-NaCl-1.0-1	1.0	567	9.00	0.199
$Na_2B_4O_7$-NaCl-1.0-2	1.0	567	9.00	0.203
$Na_2B_4O_7$-NaCl-2.0-1	2.1	567	8.94	0.157
$Na_2B_4O_7$-NaCl-2.0-2	2.1	567	8.94	0.167
$Na_2B_4O_7$-NaCl-3.0-1	3.2	567	8.93	0.160
$Na_2B_4O_7$-NaCl-3.0-1R	3.2	567	8.92	0.155
$Na_2B_4O_7$-NaCl-3.0-2	3.2	567	8.90	0.154
$Na_2B_4O_7$-NaCl-4.0-1	4.4	567	8.99	0.148
$Na_2B_4O_7$-NaCl-4.0-2	4.4	567	9.01	0.152
$Na_2B_4O_7$-NaCl-5.0-1	5.0	567	8.93	0.158
$Na_2B_4O_7$-NaCl-5.0-2	5.0	567	8.93	0.154

374
375

Table 2. Felmy and Weare (1986) model for the Na–$B(OH)_3$–Cl–SO_4 system

Pitzer Binary Interaction Cofficients				
Species, *i*	Species, *j*	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
Na^+	$B(OH)_4^-$	–0.0427	0.089	0.0114
Na^+	$B_3O_3(OH)_4^-$	–0.056	–0.910	
Na^+	$B_4O_5(OH)_4^{2-}$	–0.11	–0.40	
Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	Cl^-	Na^+	–0.065	–0.0073
$B(OH)_4^-$	SO_4^{-2}		–0.012	
$B_3O_3(OH)_4^-$	Cl^-	Na^+	0.12	–0.024
$B_3O_3(OH)_4^-$	SO_4^{-2}		0.10	
$B_4O_5(OH)_4^{-2}$	Cl^-	Na^+	0.074	0.026
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}		0.12	
$B(OH)_3$(aq)	Cl^-		0.091	
$B(OH)_3$(aq)	SO_4^{-2}	Na^+	0.018	0.046
$B(OH)_3$(aq)	$B_3O_3(OH)_4^-$		–0.20	
$B(OH)_3$(aq)	Na^+		–0.097	
Equilibrium Constant for Solubility Reaction				
Reaction			log K	
$Na_2B_4O_7{\bullet}10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.49	

Table 3. The revised thermodynamic model for the Na–$B(OH)_3$–Cl–SO_4 system developed in this study*.

Pitzer Mixing Parameters and Interaction Parameters Involving Neutral Species				
Species, *i*	Species, *j*	Species, *k*	θ_{ij} or λ_{ij}	Ψ_{ijk} or ζ_{ijk}
$B(OH)_4^-$	SO_4^{-2}		0.17 ± 0.03	
$NaB(OH)_4$(aq)	Na^+		0.093 ± 0.005	
$B_4O_5(OH)_4^{-2}$	SO_4^{-2}	Na^+		0.1 ± 0.2
Equilibrium Constants for Solubility and Complex Formation Reactions				
Reaction			log *K* or log β_1 at 25 °C unless otherwise noted	
$Na_2B_4O_7 \cdot 10H_2O = 2Na^+ + 4B(OH)_4^- + 2H^+ + H_2O$			–24.80 ± 0.10 (2σ)	
$Na^+ + B(OH)_4^- = NaB(OH)_4$(aq)			0.29 ± 0.01 (10 °C) 0.25 ± 0.01 (25 °C) with $\Delta\varepsilon$ = -0.04 ± 0.02 0.24 ± 0.01 (40 °C) 0.26 ± 0.02 (50 °C)	

*Unless otherwise noted, other parameters, which are not listed, are the same as those in Felmy and Weare (1986) model.

386 Table 4. Comparison of independent, experimental equilibrium compositions for
387 multiple equilibrium assemblages containing sodium tetraborate ($Na_2B_4O_7$•$10H_2O$)
388 (borax) with predicted compositions in mixtures of NaCl and Na_2SO_4 at 25 ^oC

Experimental data for equilibrium compositions					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage*	References
6.967	5.516	0.694	0.125	BRX+HLT+THNDT	Van't Hoff and Blasdale (1905)
6.355	5.925	0.183	0.128	BRX+HLT	Grushvitski and Flerinskava (1932)
6.527	5.408	0.526	0.134	BRX+HLT	*ibid.*
6.716	5.286	0.673	0.167	BRX+HLT	*ibid.*
6.939	5.441	0.716	0.132	BRX+HLT+THNDT	*ibid.*
6.603	4.723	0.903	0.149	BRX	*ibid.*
6.477	3.168	1.619	0.141	BRX+MRBLT+THNDT	*ibid.*
3.774	0.248	1.734	0.117	BRX+MRBLT	*ibid.*
Equilibrium compositions predicted by the Felmy and Weare (1986) model					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage*	
6.971	5.484	0.691	0.212	BRX+HLT+THNDT	
6.364	5.896	0.182	0.206	BRX+HLT	
6.532	5.381	0.523	0.209	BRX+HLT	
6.704	5.260	0.670	0.211	BRX+HLT	
6.943	5.413	0.712	0.212	BRX+HLT+THNDT	
6.602	4.699	0.898	0.214	BRX	
6.367	3.229	1.512	0.229	BRX+MRBLT+THNDT	
3.833	0.246	1.721	0.289	BRX+MRBLT	
Equilibrium compositions predicted by the model developed in this study					
m_{Na}	m_{Cl}	m_{SO4}	$m_{\Sigma B}$	Equilibrium Assemblage*	
6.947	5.494	0.692	0.136	BRX+HLT+THNDT	
6.347	5.906	0.183	0.151	BRX+HLT	
6.512	5.393	0.524	0.141	BRX+HLT	
6.683	5.272	0.671	0.137	BRX+HLT	
6.922	5.426	0.714	0.136	BRX+HLT+THNDT	
6.577	4.711	0.900	0.131	BRX	
6.284	3.273	1.475	0.120	BRX+MRBLT+THNDT	
3.780	0.247	1.728	0.151	BRX+MRBLT	
Difference in %** between experimental values and those predicted by the FW86 model					
ΔNa in %	ΔCl in %	ΔSO_4 in %	$\Delta\Sigma$B in %	Equilibrium Assemblage*	

0.060	-0.586	-0.507	69.788	BRX+HLT+THNDT
0.133	-0.483	-0.482	60.851	BRX+HLT
0.084	-0.496	-0.497	55.925	BRX+HLT
-0.170	-0.504	-0.503	26.362	BRX+HLT
0.072	-0.508	-0.507	60.305	BRX+HLT+THNDT
-0.016	-0.514	-0.515	43.776	BRX
-1.701	1.941	-6.656	62.343	BRX+MRBLT+THNDT
1.555	-0.725	-0.725	145.848	BRX+MRBLT
Difference in %** between experimental values and those predicted by the model developed in this study				
ΔNa in %	ΔCl in %	ΔSO_4 in %	ΔΣB in %	Equilibrium Assemblage*
-0.290	-0.402	-0.274	9.240	BRX+HLT+THNDT
-0.121	-0.309	-0.308	18.448	BRX+HLT
-0.227	-0.284	-0.285	5.249	BRX+HLT
-0.495	-0.275	-0.274	-18.006	BRX+HLT
-0.245	-0.273	-0.272	2.587	BRX+HLT+THNDT
-0.392	-0.259	-0.260	-11.967	BRX
-2.974	3.327	-8.884	-14.637	BRX+MRBLT+THNDT
0.145	-0.307	-0.307	28.758	BRX+MRBLT

*Abbreviations for minerals: BRX, borax ($Na_2B_4O_7 \cdot 10H_2O$); HLT, halite (NaCl); MRBLT, mirabilite ($Na_2SO_4 \cdot 10H_2O$); THNDT, thenardite (Na_2SO_4).

**Difference in % is defined as, using concentrations of sodium on molal scale as an example,

$$\Delta\text{Na in \%} = 100 \times \frac{m_{Na,Model} - m_{Na,Experimental}}{m_{Na,Experimental}}$$

Table 5. Chemical composition of the brine from the Zhabei Salt Lake, Xizang (Tibet) Autonomous Region, China (from Gao et al., 2012)

Composition	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	ΣCO_3	SO_4^{2-}	$B_4O_7^{2-}$
mol•kg^{-1}	0.738	0.0660	0.00203	0.188	0.404	0.124	0.933	0.0864
Other parameters	pH		Density, g/cm^3			Total Dissolved Salts, mg/L		
Value	9.19		1.046			61,740		

*Original compositions are converted to molal concentrations by this work, based on density and total dissolved salts.

Table 6. Chemical composition of the brine from the western Sichuan gas field, China (from Lin et al., 2000)*

Composition	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	ΣCO_3	SO_4^{2-}	$B_4O_7^{2-}$
mol•kg^{-1}	4.90	1.59	0.105	0.152	6.90	0.0215	0.0169	0.0184
Other parameters	pH		Density, g/cm^3			Total Dissolved Salts, mg/L		
Value	6.18		1.2359			377,270		

*Original compositions are converted to molal concentrations by this work, based on density and total dissolved salts.

Figure Captions

Figure 1. A plot showing experimental total boron concentrations in equilibrium with sodium tetraborate produced in this study as a function of experimental time.

Figure 2. A plot showing experimental total boron concentrations in equilibrium with sodium tetraborate produced in this study as a function of molalities of NaCl.

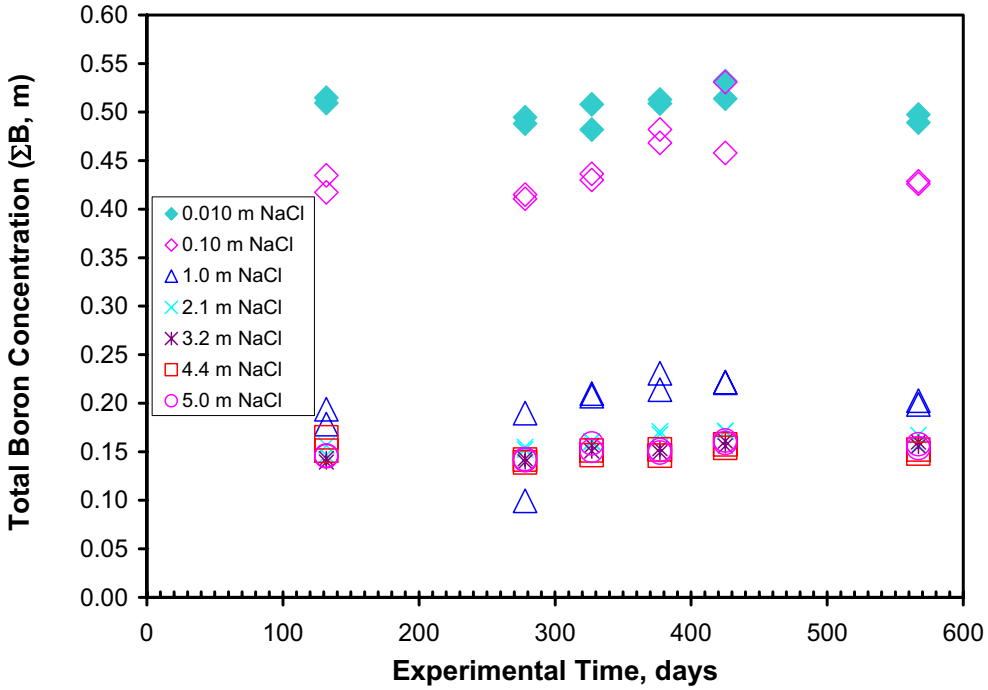
Figure 3. A plot showing [$\log \beta_1^I$ + 2D] as a function of ionic strengths, where $\log \beta_1^I$ denotes conditional formation constants of $NaB(OH)_4(aq)$ at certain ionic strengths from Reardon (1976).

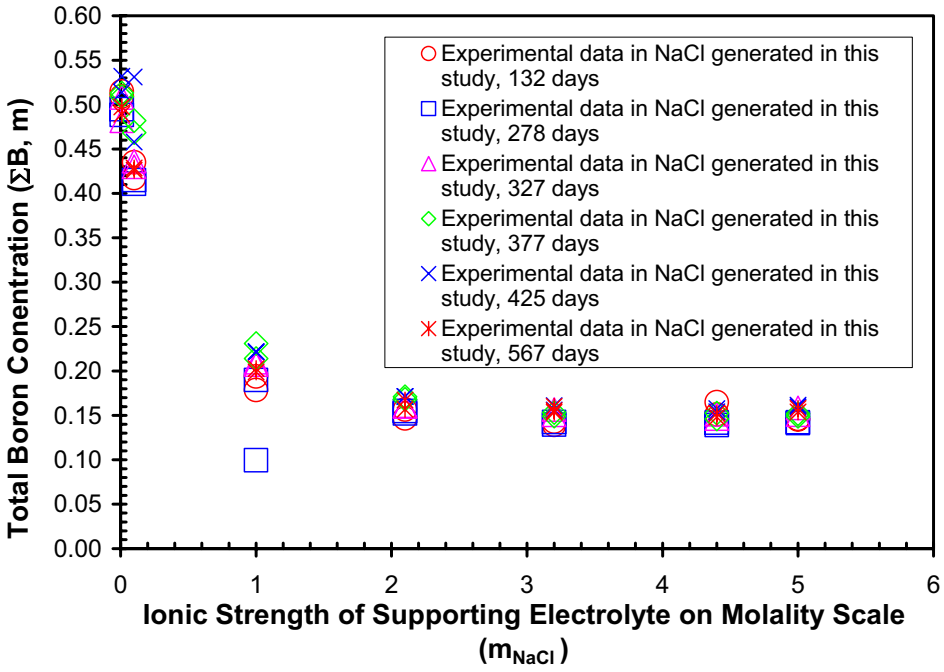
Figure 4. A plot showing a comparison of experimental total boron concentrations in equilibrium with sodium tetraborate in NaCl and Na_2SO_4 solutions with predicted total boron concentrations as a function of ionic strengths.

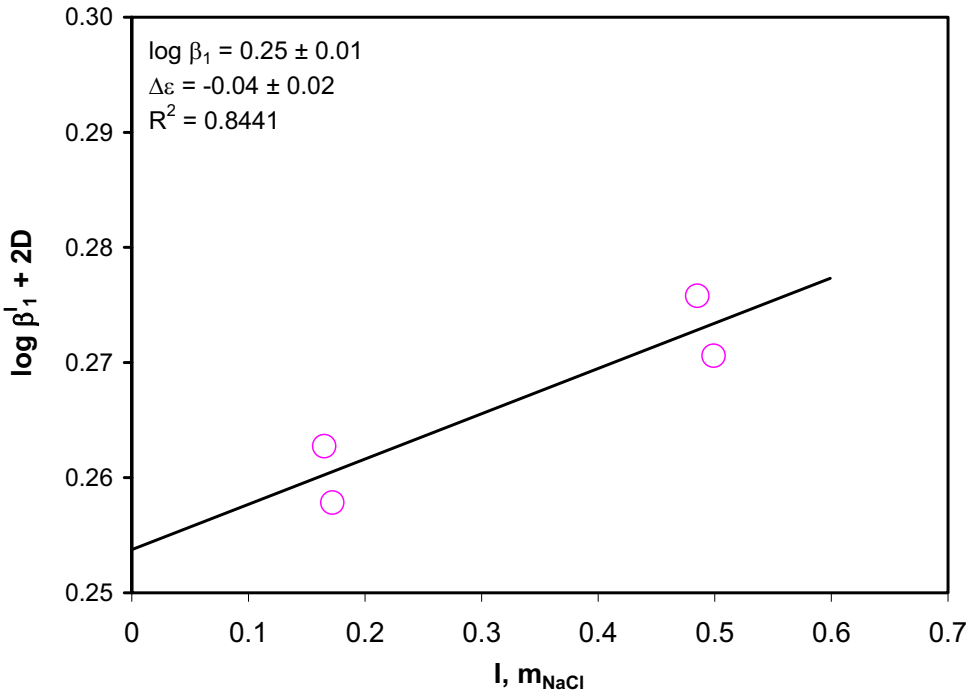
Figure 5. A plot showing differences in total boron concentrations in equilibrium with sodium tetraborate between experimental and predicted values in NaCl + Na_2SO_4 solutions as a function of ionic strengths.

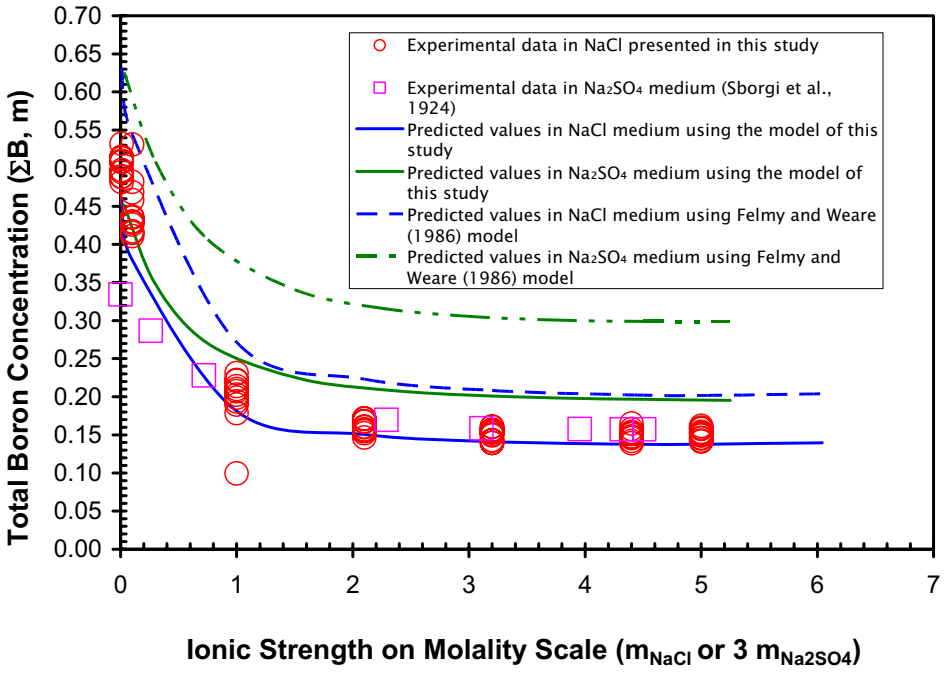
Figure 6. A plot showing mineral precipitation as a function of degree of evaporation (DE).

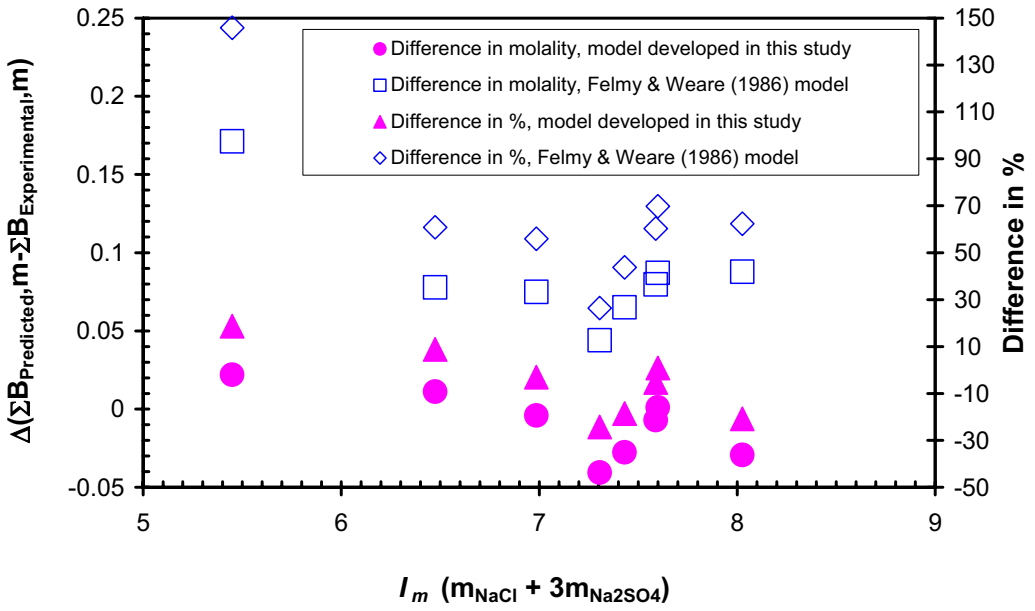
Figure 7. A plot showing chemical evolution of the brine as a function of degree of evaporation (DE). A. the brine from the Zhabei Salt Lake, China; B. the brine from the western Sichuan Province, China

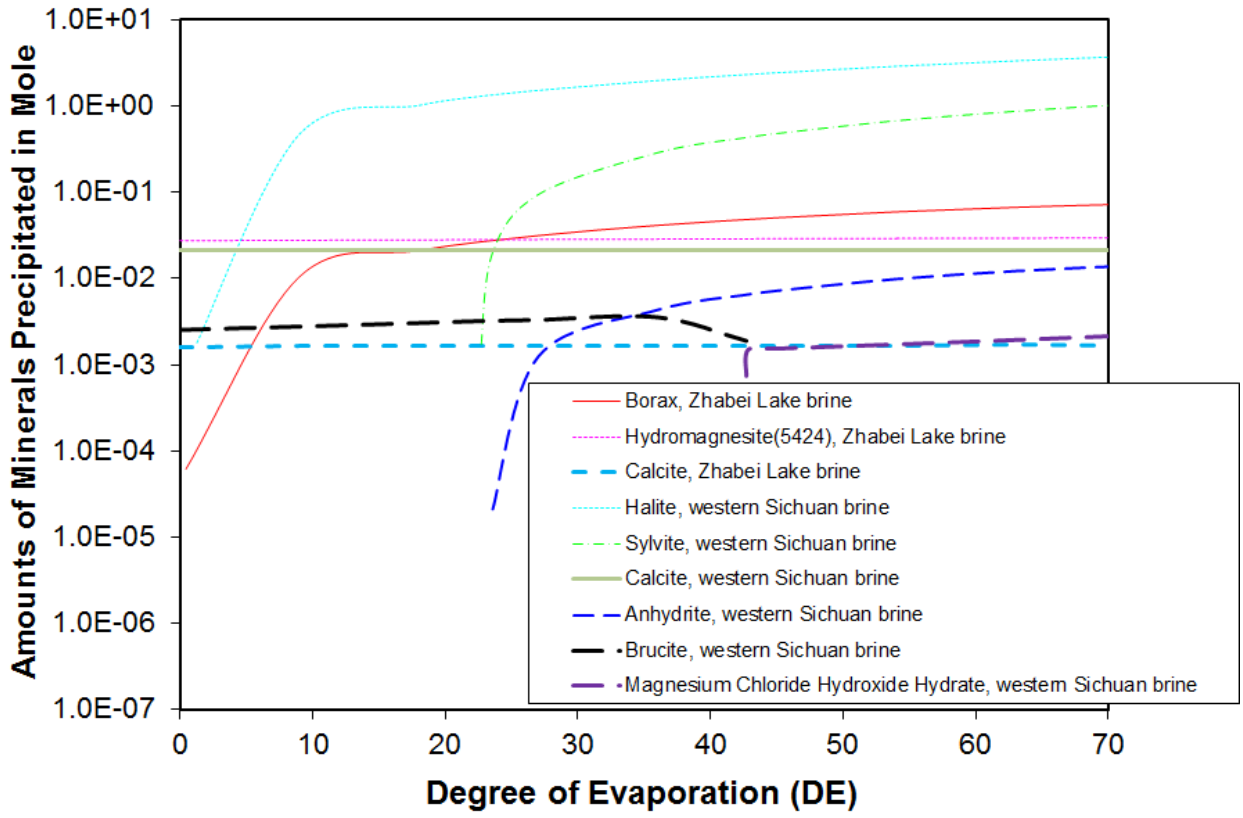

Total Boron Concentration (ΣB, m)
Experimental Time, days
0.010 m NaCl
0.10 m NaCl
1.0 m NaCl
2.1 m NaCl
3.2 m NaCl
4.4 m NaCl
5.0 m NaCl
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0
100
200
300
400
500
600

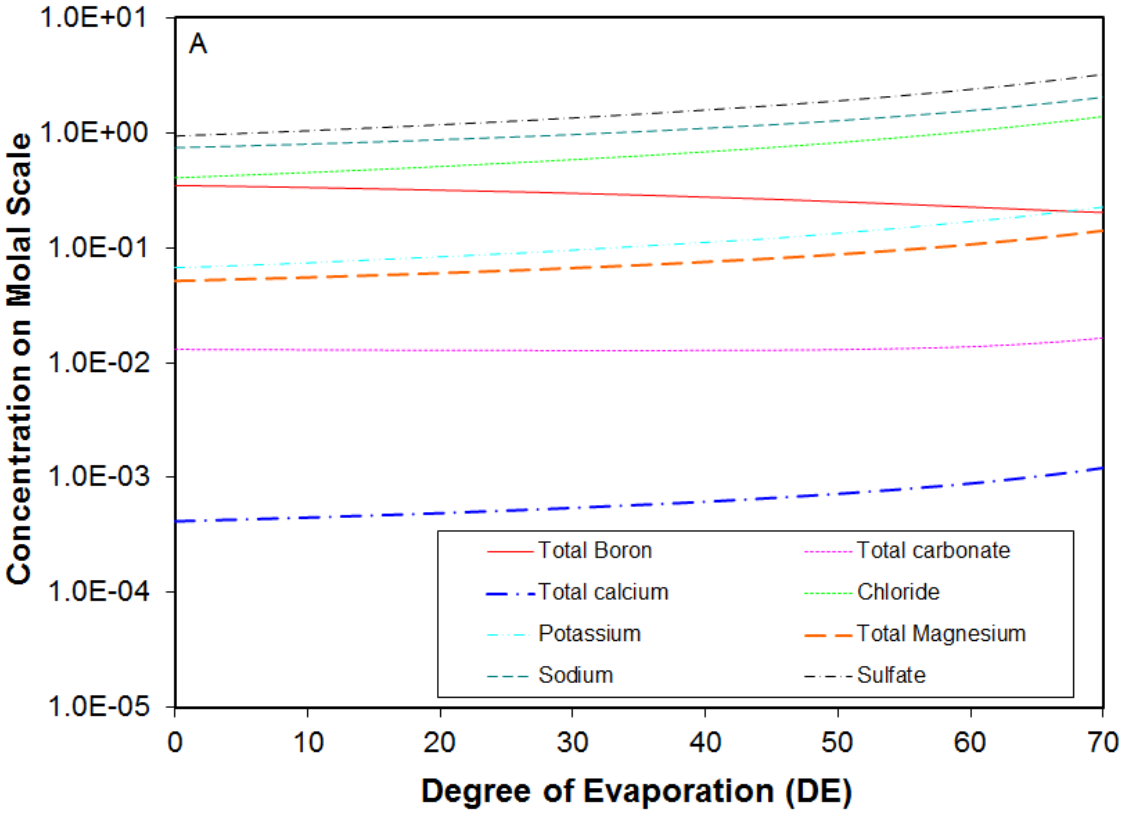

Total Boron Conentration (ΣB, m)
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
1
2
3
4
5
6
Ionic Strength of Supporting Electrolyte on Molality Scale
(m NaCl)
Experimental data in NaCl generated in this study, 132 days
Experimental data in NaCl generated in this study, 278 days
Experimental data in NaCl generated in this study, 327 days
Experimental data in NaCl generated in this study, 377 days
Experimental data in NaCl generated in this study, 425 days
Experimental data in NaCl generated in this study, 567 days

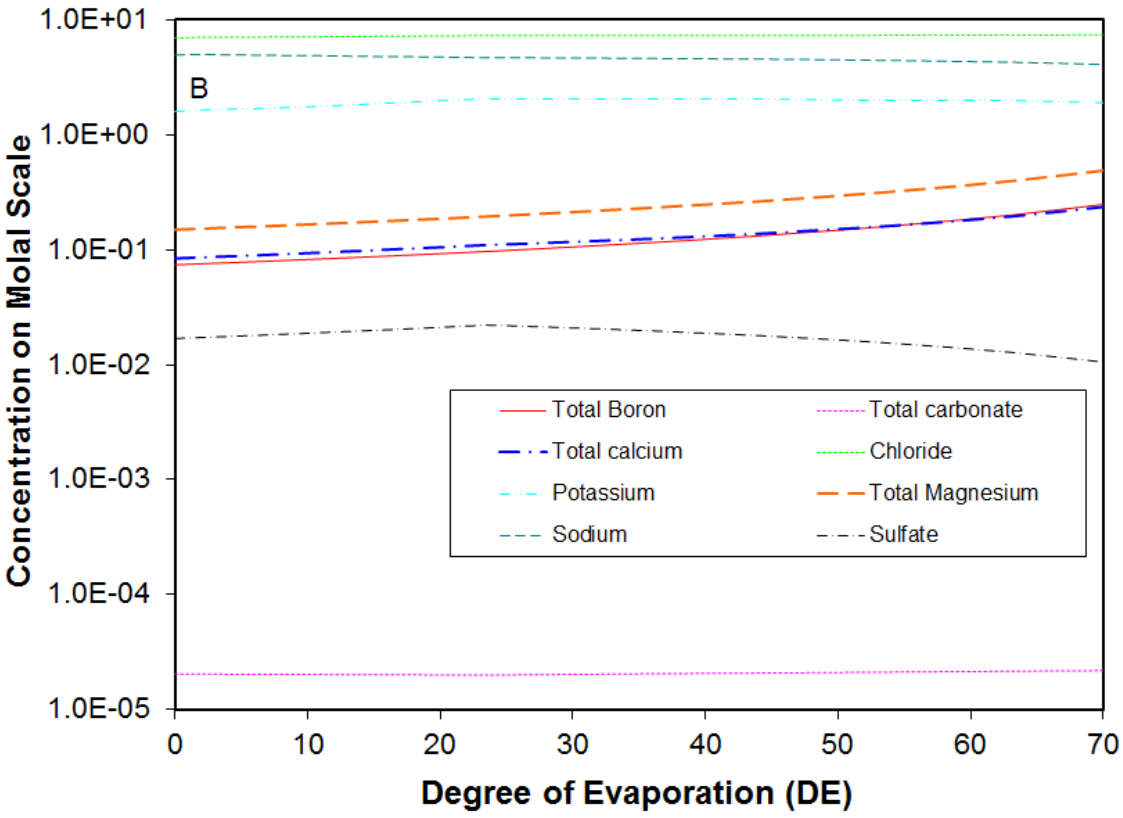

log β_1 = 0.25 ± 0.01
$\Delta\varepsilon$ = -0.04 ± 0.02
R^2 = 0.8441
0.30
0.29
0.28
0.27
0.26
0.25
log β^I_1 + 2D
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
I, m_{NaCl}


Experimental data in NaCl presented in this study
Experimental data in Na2SO4 medium (Sborgi et al., 1924)
Predicted values in NaCl medium using the model of this study
Predicted values in Na2SO4 medium using the model of this study
Predicted values in NaCl medium using Felmy and Weare (1986) model
Predicted values in Na2SO4 medium using Felmy and Weare (1986) model
Total Boron Concentration (ΣB, m)
Ionic Strength on Molality Scale (m_NaCl or 3 m_Na2SO4)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0
1
2
3
4
5
6
7


Difference in molality, model developed in this study
Difference in molality, Felmy & Weare (1986) model
Difference in %, model developed in this study
Difference in %, Felmy & Weare (1986) model
Δ(ΣB Predicted, m-ΣB Experimental, m)
Difference in %
I m (m NaCl + 3m Na2SO4)
0.25
0.2
0.15
0.1
0.05
0
-0.05
150
130
110
90
70
50
30
10
-10
-30
-50
5
6
7
8
9


Amounts of Minerals Precipitated in Mole
1.0E+01
1.0E+00
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
0
10
20
30
40
50
60
70
Degree of Evaporation (DE)
Borax, Zhabei Lake brine
Hydromagnesite(5424), Zhabei Lake brine
Calcite, Zhabei Lake brine
Halite, western Sichuan brine
Sylvite, western Sichuan brine
Calcite, western Sichuan brine
Anhydrite, western Sichuan brine
Brucite, western Sichuan brine
Magnesium Chloride Hydroxide Hydrate, western Sichuan brine


A
1.0E+01
1.0E+00
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
Concentration on Molal Scale
0
10
20
30
40
50
60
70
Degree of Evaporation (DE)
Total Boron
Total carbonate
Total calcium
Chloride
Potassium
Total Magnesium
Sodium
Sulfate


B
Concentration on Molal Scale
1.0E+01
1.0E+00
1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
0
10
20
30
40
50
60
70
Degree of Evaporation (DE)
Total Boron
Total carbonate
Total calcium
Chloride
Potassium
Total Magnesium
Sodium
Sulfate