# Phase Equilibria of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O + 3.0\ \% H_3BO_3 + H_2O$ System at Various Temperatures

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Solid−liquid phase equilibria of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O + 3.0\ \% H_3BO_3 + H_2O$ system have been studied at various temperatures of (0 to 200) °C. The solid phase equilibria identified by infrared spectra and X-ray powder diffraction were $MgO \cdot 2B_2O_3 \cdot 9H_2O$ at (0 to 27) °C, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (kurnakovite) at (27 to 50) °C, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (inderite) at (50 to 72) °C, $MgO \cdot B_2O_3 \cdot 3H_2O$ at (72 to 98.5) °C, $2MgO \cdot B_2O_3 \cdot 2H_2O$ at (98.5 to 190) °C, and $2MgO \cdot B_2O_3 \cdot 1.5H_2O$ at (190 to 200) °C, respectively. The pH values of the liquid phase equilibria and the solubility data of the corresponding solid phases were determined. The formation mechanisms of the solid phases were proposed and discussed.

## Introduction

There are a large variety of salt minerals in the salt lakes on the Qinghai-Xizang plateau in China, which includes five kinds of magnesium borates, $2MgO \cdot 3B_2O_3 \cdot l5H_2O$ (inderite), $2MgO \cdot 3B_2O_3 \cdot l5H_2O$ (kurnakovite), $MgO \cdot 2B_2O_3 \cdot 9H_2O$, $MgO \cdot 3B_2O_3 \cdot 7.5H_2O$, and $MgO \cdot B_2O_3 \cdot 3H_2O$. A borate double salt $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O$ named chloropinnoite was obtained from the natural concentrated salt lake brine containing boron.[1] Gao et al.[2] investigated its crystallization kinetics. Xia et al.[3] and Liu et al.[4] studied the kinetics of dissolution and phase transformation of chloropinnoite in water, and the final transformation product was inderite ($2MgO \cdot 3B_2O_3 \cdot l5H_2O$) at 30 °C and pinnoite ($MgO \cdot B_2O_3 \cdot 3H_2O$) at 60 °C, which showed that the temperature had an influence on the existing form of boron-containing species in solution. To find the relation of formation between this double salt and magnesium borate minerals in the salt lakes and considering the fact that there exists $H_3BO_3$ in the natural concentrated salt lake brine, we studied the phase equilibria of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O + H_3BO_3 + H_2O$ system at 30 °C[5] and 0 °C.[6] The corresponding solid phase equilibria were formed from magnesium triborate to hexaborate, which showed that the concentration of boron in solution had an influence on the form of boron-containing species in solution.

On the basis of this work and considering the existing forms of polyborate anions depend on both temperature and the concentration of boron in solution, we further investigated the phase equilibria of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O + 7.8\ \%/3.0\ \% H_3BO_3 + H_2O$ system at various temperatures. This paper reports the results for the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O + 3.0\ \% H_3BO_3 + H_2O$ system at various temperatures and compares the results with those of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O + 7.8\ \% H_3BO_3 + H_2O$ system.[7] The obtained results can further provide physicochemical data for preparation of borates, extraction of borates from salt lake brine containing boron, and explaining the formation of hydrated borate minerals in the salt lakes.

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## Experimental Section

***Reagents.*** Analytical-grade $H_3BO_3$ (purity ≥ 99.5 %), $MgCl_2 \cdot 6H_2O$ (purity ≥ 99 %), and $Mg(OH)_2 \cdot 4MgCO_3 \cdot 6H_2O$ (purity ≥ 99 %) were produced by the Xi'an Chemical factory, China. Active MgO which dissolves in solution relatively quickly was obtained by thermal decomposition of $Mg(OH)_2 \cdot 4MgCO_3 \cdot 6H_2O$ in an electric furnace at 873 K for 3 h.

***Procedure.*** Amounts of 1.860 g of $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O$ (synthesized by a literature method[2]), 1.304 g of $H_3BO_3$, and 40.0 mL of redistilled water were taken and placed in a three-necked flask, which was set in an isothermal water bath at (0 to 95) °C, or electric jacket for circumfluence (bp 98.5 °C of solution at the barometric pressure of 96.39 kPa in Xian, China), or Teflon-lined stainless steel vessels at (100 to 200) °C. After a few days, a 2.00 mL solution sample was withdrawn with a syringe pipet carrying a filter cartridge (taking the room-temperature solutions obtained by centrifugal separation for the reaction systems from (80 to 200) °C) for chemical analysis: EDTA titration for $Mg^{2+}$, $Hg(NO_3)_2$ standard solution for $Cl^-$, and NaOH standard solution in the presence of mannitol for total boron concentration (expressed as $B_2O_3$)). After an additional day, a sample of the solution was taken again in the same way. When the concentrations of all three ions remained constant, the equilibrium liquid and solid phases were separated. The pH values of the liquid phases were determined with a PHSJ-4A pH meter (Shanghai, China). The solid phases were washed with absolute ethyl alcohol until there was almost no $Cl^-$ in the mother liquor. Thereafter, the solids were washed again with absolute ether. The obtained solids were dried in a vacuum dryer to a constant mass at room temperature and were identified by IR spectra (a Bruker Equinox 55 FT-IR spectrometer recorded over the (400 to 4000) $cm^{-1}$ region with KBr pellets at room temperature), XRD (a Rigaku D/max- IIIC X-ray diffractiometer with Cu target ($\lambda = 1.54178$ Å) at $8° \cdot min^{-1}$), and chemical analysis.

## Results and Discussion

The double salt $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot l4H_2O$ dissolved instantaneously in ($H_3BO_3 + H_2O$) solution to form a clear solution because of the relatively greater acidity of solution. The reactions are as follows:

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$$H_3BO_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \quad (1)$$

$$2[MgB_2O(OH)_6 \cdot H_2O] \cdot [Mg(H_2O)_6Cl_2] \rightarrow 2B_2O(OH)_6^{2-} + 3Mg^{2+} + 2Cl^- + 8H_2O \quad (2)$$

$$2B(OH)_4^- \rightleftharpoons B_2O(OH)_6^{2-} + H_2O \quad (3)$$

Because the temperature and concentration of boron in solution had a strong influence on the existing forms and interaction of polyborate anions, different magnesium borates would crystallize out with an increase of temperature. The crystallizing solid phases were identified by combining the recorded FT-IR spectra with those of ref 8. All data from the XRD of one product corresponded with those of a known borate JCPDS Card (File Nos. 16-392 for $MgO \cdot 2B_2O_3 \cdot 9H_2O$, 24-700 for kurnakovite, 11-583 for inderite, and 25-1119 for $MgO \cdot B_2O_3 \cdot 3H_2O$; for the reported XRD data of $2MgO \cdot B_2O_3 \cdot nH_2O$ ($n = 2$, 1.5), see the literature[7]). It needed to indicate that the solid phase was a mixture when the *d* values of the XRD pattern included those of two substances; for example, the *d* values of the XRD pattern at 50 °C included (0.5064, 0.5824, 0.3368, 0.2927, and 0.2677) nm, which were assigned to $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (inderite), and (0.7345, 0.4223, 0.318, and 0.3048) nm, which were assigned to $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (kurnakovite). The experimental results of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O + 3.0\ \% H_3BO_3 + H_2O$ system at various temperatures are listed in Table 1, and the solubility curves are shown in Figure 1. The XRD patterns of the solid phases are shown in Figure 2.

***Formation of $MgO \cdot 2B_2O_3 \cdot 9H_2O$.*** Because the low temperature of solution was in favor of the formation of a large degree of the polyborate anion, $MgO \cdot 2B_2O_3 \cdot 9H_2O$ could be crystallized out when a certain concentration of $B_4O_5(OH)_4^{2-}$ was formed at (0 to 27) °C. Its solubility increased gradually with the rise of temperature, which is shown as curve *AB* in Figure 1.

$$B(OH)_4^- + B_2O(OH)_6^{2-} \rightleftharpoons B_3O_3(OH)_4^- + 2OH^- + 2H_2O \quad (4)$$

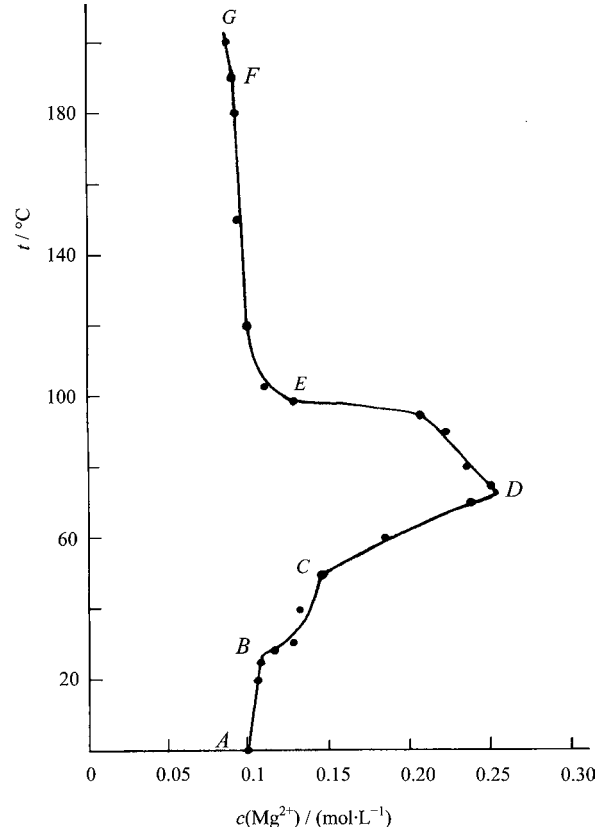


**Figure 1.** Solubility curves of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O + 3.0\ \% H_3BO_3 + H_2O$ system at various temperatures.

$$B_3O_3(OH)_4^- + B(OH)_4^- \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H_2O \quad (5)$$

$$B_4O_5(OH)_4^{2-} + Mg^{2+} + 7H_2O \rightleftharpoons Mg[B_4O_5(OH)_4] \cdot 7H_2O\downarrow \quad (6)$$

***Formation of $2MgO \cdot 3B_2O_3 \cdot 15H_2O$.*** With an increase of the temperature of solution, the polyborate anion with a relatively lower polymerization degree would be the main existing form. So, the solid phases of $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (kurnakovite) were

**Table 1. Phase Relation of the $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O + 3.0\ \% H_3BO_3 + H_2O$ System at Various Temperatures**

| | equilibrium liquid phases | | | | equilibrium solid phases[a] | |
|---|---|---|---|---|---|---|
| *t* °C | pH | $c(Cl^-)$ / (mol·L$^{-1}$) | $c(Mg^{2+})$ / (mol·L$^{-1}$) | $c(B_2O_3)$ / (mol·L$^{-1}$) | $n(MgO):n(B_2O_3):n(H_2O)$ | chemical formula |
| 0 | 7.29 | 0.1882 | 0.0994 | 0.1185 | | s1 |
| 20 | 7.46 | 0.1734 | 0.1063 | 0.1436 | | s1 |
| 25 | 7.36 | 0.1753 | 0.1068 | 0.1651 | | s1 |
| 28 | 7.40 | 0.1836 | 0.1146 | 0.2357 | | s2 |
| 30 | 7.35 | 0.1789 | 0.1274 | 0.2395 | | s2 |
| 40 | 7.28 | 0.1852 | 0.1286 | 0.2405 | | s2 |
| 50 | 7.51 | 0.2076 | 0.1443 | 0.2886 | | s2 + s3 |
| 60 | 7.30 | 0.1978 | 0.1831 | 0.2975 | | s3 |
| 70 | 7.50 | 0.1921 | 0.2375 | 0.3108 | | s3 |
| 75 | 7.99 | 0.2051 | 0.2507 | 0.4589 | | s3 |
| 80 | 7.92 | 0.2152 | 0.2345 | 0.4244 | | s4 |
| 90 | 7.76 | 0.2035 | 0.2225 | 0.4043 | | s4 |
| 95 | 6.98 | 0.2045 | 0.2074 | 0.4024 | | s4 |
| 98.5 | 6.48 | 0.1973 | 0.1297 | 0.3684 | | s4 + s5 |
| 103 | 6.28 | 0.1827 | 0.1099 | 0.3665 | 1.96:1.00:1.91 | s5 |
| 120 | 6.13 | 0.1846 | 0.1002 | 0.3650 | 1.96:1.00:2.06 | s5 |
| 150 | 5.92 | 0.1890 | 0.0934 | 0.3614 | | s5 |
| 180 | 5.77 | 0.1778 | 0.0923 | 0.3611 | 1.93:1.00:2.03 | s5 |
| 190 | 5.74 | 0.1744 | 0.0907 | 0.3637 | 2.01:1.00:1.64 | s5 + s6 |
| 200 | 5.70 | 0.1797 | 0.0895 | 0.3581 | 1.96:1.00:1.56 | s6 |

[a] s1, $MgO \cdot 2B_2O_3 \cdot 9H_2O$; s2, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (Kurnakovite); s3, $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (Inderite); s4, $MgO \cdot B_2O_3 \cdot 3H_2O$; s5, $2MgO \cdot B_2O_3 \cdot 2H_2O$; s6, $2MgO \cdot B_2O_3 \cdot 1.5H_2O$.

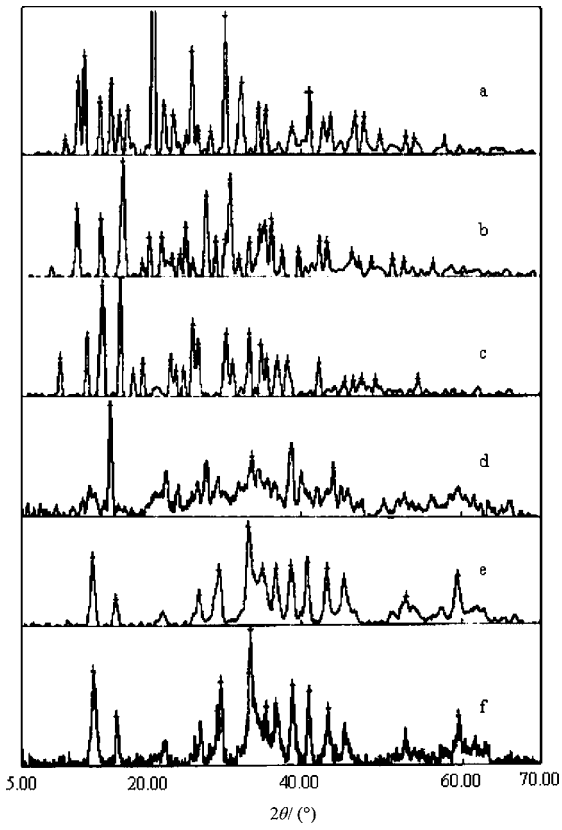


**Figure 2.** XRD patterns of the solid phases (a) $MgO\cdot 2B_2O_3\cdot 9H_2O$, (b) $2MgO\cdot 3B_2O_3\cdot 15H_2O$ (kurnakovite), (c) $2MgO\cdot 3B_2O_3\cdot 15H_2O$ (inderite), (d) $MgO\cdot B_2O_3\cdot 3H_2O$, (e) $2MgO\cdot B_2O_3\cdot 2H_2O$, and (f) $2MgO\cdot B_2O_3\cdot 1.5H_2O$.

formed at (27 to 50) °C and $2MgO\cdot 3B_2O_3\cdot 15H_2O$ (inderite) at (50 to 72) °C, respectively. Their solubilities increased gradually with the rise of temperature, which are shown as curves *BC* and *CD* in Figure 1, respectively.

$$B(OH)_4^- + B_2O(OH)_6^{2+} \rightleftharpoons B_3O_3(OH)_4^- + 2OH^- + 2H_2O \quad (7)$$

$$B_3O_3(OH)_4^- + Mg^{2+} + 6H_2O \rightleftharpoons Mg[B_3O_3(OH)_5]\cdot 5H_2O\downarrow + H^+ \quad (8)$$

Inderite and kurnakovite are isomeric minerals. Their structure contains $[B_3O_3(OH)_5]^{2-}$ groups, but the relationship between Mg and the B−O group occurs in inderite in a way quite different from kurnakovite. The borate group can be considered as less regular in inderite than in kurnakovite if the ideal regular group is defined as one in which the ring plane is a plane of symmetry.[9] This result shows that inderite is more stable than kurnakovite.

***Formation of $MgO\cdot B_2O_3\cdot 3H_2O$.*** At the relatively higher temperatures of (72 to 98.5) °C, the original polyborate anion $B_2O(OH)_6^{2-}$ was difficult to further polymerize and combined with $Mg^{2+}$ directly, forming $MgO\cdot B_2O_3\cdot 3H_2O$. Its solubility decreased distinctly with an increase of temperature, which is shown as curve *DE* in Figure 1.

$$B_2O(OH)_6^{2-} + Mg^{2+} \rightleftharpoons Mg[B_2O(OH)_6]\downarrow \quad (9)$$

***Formation of $2MgO\cdot B_2O_3\cdot nH_2O$ ($n = 2, 1.5$).*** At even higher temperatures, the original polyborate anion of $B_2O(OH)_6^{2-}$ might dehydrate forming $B_2O_4(OH)_2^{4-}$. It combined with $Mg^{2+}$ forming $2MgO\cdot B_2O_3\cdot 2H_2O$ at (98.5 to 190) °C and $2MgO\cdot B_2O_3\cdot 1.5H_2O$ at (190 to 200) °C. Their solubilities decreased gradually with the increase of temperature, which are shown as curves *EF* and *FG* in Figure 1, respectively.

$$B_2O(OH)_6^{2-} + 2OH^- \rightleftharpoons B_2O_4(OH)_2^{4-} + 3H_2O \quad (10)$$

$$B_2O_4(OH)_2^{4-} + 2Mg^{2+} + nH_2O \rightleftharpoons Mg_2[B_2O_4(OH)_2]\cdot nH_2O\ (n = 1, 0.5) \quad (11)$$

As compared to the results of the system containing 7.8 % $H_3BO_3$,[7] the solid phases of triborate appeared, and the hexaborates of $MgO\cdot 3B_2O_3\cdot nH_2O$ ($n = 7.5, 7, 5$) were not formed in the present system containing 3.0 % $H_3BO_3$, indicating that the concentration of boron in solution had a strong effect on the formation of borates. Higher concentration of boron in solution is helpful in the formation of borate with higher polymerization degree.

## Conclusions

Solid−liquid phase equilibria of the $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O$ + 3.0 % $H_3BO_3$ + $H_2O$ system at various temperatures have been studied. The results showed that temperature and concentration of boron in solution had a strong effect on the formation of borates. Higher boron concentration and lower temperature of solution are helpful in the formation of borate with higher polymerization degree, respectively.

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