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钠硼解石——水体系溶解和相平衡的研究

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Study on Dissolution and Phase Equilibrium in Ulexite-water System

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Ulexite dissolution in water has been studied in the wide temperature range from 10℃ to 93 ℃ and two higher temperatures at 120 ℃ and 240 ℃. The analytical results showed that ulexite dissolved congruently from 10 ℃ to 35 ℃ and incongruently from 40 to 68 ℃. The solid component of ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ was dehydrated to form $NaCaB_5O_6(OH)_6 \cdot H_2O$ from 50 to 68 ℃ and finally amorphous solid at 68 ℃. This amorphous solid converted into priceite at 71 ℃ and then converted completely to priceite at the boiling point(93 ℃) of the solution. At both 120 and 240 ℃, the dissolution of ulexite was an incongruent process. Above 120 ℃, ulexite became amorphous solid and then transformed into priceite. In addition to the solid to solid transformation, crystallization of priceite from the solution has also been observed. Based on our experimental results, mechanisms of dissolution, transformation, and crystallization of borate in ulexite-water system are discussed.

Keywords:　　**ulexite**　　　**dissolution**　　　**phase equilibrium**　　　**transformation**

0   Introduction

Ulexite $NaCa(B_5O_6(OH)_6) \cdot 5H_2O$ is an important economical borate mineral. This material is always in association with other minerals, such as pinnoite, kur-nakovite, inderite, sometimes hydroboracite, etc.[1,2] Ulexite is used as a raw material to produce boric acid and borax for many years. Nowadays, ulexite is also commonly used for the production of fireproof chemical substances, insulator and fiberglass[3,4]. Ulex-

ite is found in salt lakes of many places in the world, such as, ulexite of Mg-sulfate sub-type on the Qing-hai-xizang plateau (Tibet in China)[5], Kazakhstan region, Inder Lake of Turkmenistan, the north of Chile, the dessert of California (United States) and Turkey[6].

Solubility of ulexite in various solutions has been studied. These solutions include acids, alkali medium, CO_2-containing aqueous solution, ammonium chloride solution and EDTA solution[7~16], However, not too many studies of ulexite in the most common solvent, water, have been reported[14]. The interaction of ulexite with water and aqueous solution could be used to synthesize other calcium borates. Various calcium borates products, such as $2CaO \cdot 3B_2O_3 \cdot 13H_2O$, $3CaO \cdot 3B_2O_3 \cdot 6H_2O$, $3CaO \cdot 5B_2O_3 \cdot 9H_2O$, $4CaO \cdot 5B_2O_3 \cdot 7H_2O$, and $4CaO \cdot 5B_2O_3 \cdot 9H_2O$ were obtained by treating ulexite with different aqueous solutions[17]. The products obtained depended on the temperature, the presence of salts and the composition of solution etc. For instance, it was found that ulexite in KCl aqueous solution would transform into meyerhofferite in the beginning and then into priceite at 50 ℃. Early study of the solubility of ulexite in water at room temperature was reported[18]. In the present article, we report our systematic study of the dissolutions of ulexite in water at temperatures from 10 ℃ to 240 ℃. The main goal of this study is manifold. We attempt to elucidate the reason why there is only ulexite but no priceite in salt lakes on Qinghai-Xizang (Tibet) plateau. The topic of interest because the thermodynamic properties and stability relations of boron minerals are virtually unknown. No one has ever studied this system extensively in such wide temperature range. The study of the structures, stability, solubility and transformation mechanisms of this particular ulexite-water system may help for the understanding of boron minerals.

1　Experimental

1.1　Sample Treatment

Our ulexite sample was collected from a mining field in Dachaidam salt lake in Chaidamu Basin, Qinghai province, P. R. China. The sample was purified by hydraulic-gravity separation followed by washing thoroughly with distilled water. The sample was then washed by 50% alcohol and further washed by high purity alcohol (99%). After that, the sample was dried to constant weight at 40 ℃ in a vacuum dryer. This purified ulexite was identified by using X-ray diffraction, IR-spectroscopy and microscopic observation. Compositions of calcium and boron of the sample were analyzed by standard analytical methods described as follows. Calcium with little magnesium was titrated by a Na_2-EDTA solution using erichrome black T as an indicator under an alkaline condition of $NH_3 + H_2O + NH_4Cl$ buffer solution. Boron was titrated by a standard solution of NaOH in the presence of mannitol. The composition of sodium was determined by spectrophotometric method[19]. The composition of H_2O in the sample was obtained by taking the difference between the total weight and the weight of all ions analyzed. The precision of analysis Ca^{2+} and B_2O_3 are within ±0.3%, and Na^+ is within ±0.5%. The determined composition of our sample: Na_2O:CaO:B_2O_3:MgO:H_2O is 7.58:13.86:42.96:0.20:35.40 by weight. According to the analysis, the sample is in conformity with ulexite formula $Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$. The theoretical value of composition of corresponding components is 7.65:13.85:42.95:0.0:35.55. The size of our sample was controlled by mesh gauze filter with 40~60 mesh holes.

1.2　Instrument

Given in Fig.1 is the instrument used for the dissolution experiment of ulexite in water. The sample was placed into a special designed glass bottle with a cover of six necks with holes as shown in the figure. The capacity of the bottle was 500 mL. An agitator was fixed on the neck in the central position on the cover. The other four necks were a pH-electrode connected to a pH-meter (PHS-10A-model, Xiaoshan Scientific Instrument Factory), a sodium ion selective electrode, a calcium ion selective electrode and a Hg-Hg_2Cl_2 reference electrode, respectively. Except pH electrode, all other electrodes were connected to an ion meter (Model-93-20, Orion Company). All necks were sealed to insulate the system from CO_2.

To analyze solid sample, XRD diffraction meter (Rigaku D/MAX-2400, Ni-filtered, Cu-radiation), and IR-spectrometer (Nicolet 170sx FTIR spectrometer, KBr pellets) were used.

1.3　Experiment
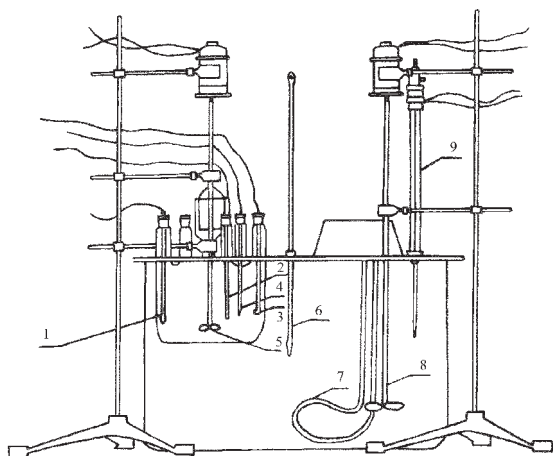
The concentrations of various ions below and

Fig.1　Instrument used for the dissolution experiment of
　　　ulexite in water from 10 to 35 ℃

　　　1: pH electrode; 2: Ca²⁺ selective electrode;

　　　3: Na⁺ selective electrode; 4: Hg-Hg₂Cl₂ reference

　　　electrode; 5: agitator; 6: thermometer; 7: heater;

　　　8: stirring device in isothermal water bath;

　　　9: thermo-regulator.

above 40 ℃ were determined by electrode and chemical analysis, respectively except concentration of B_2O_3 and Na^+ were measured by chemical analysis for both temperature ranges. For electrode analysis, measurements were taken from 10 ℃ to 35 ℃ with 5 ℃ increments. At each measurement, 250 mL water was placed into the glass bottle first. The water was controlled at a given temperature within ±0.2 ℃ by placing the bottle into an isothermal water bath. A 5.00 g ulexite sample was then added into the bottle. The ulexite-water mixture was stirred at 500 rpm to allow the reaction occurred. Ion selective electrodes are used to analyze the concentrations of Ca^{2+}, Na^+ and H^+. Then, the liquid sample was taken through a glass-sintered filter in a given interval of time. The concentration of boron in the solution was then obtained from the standard titration method. The system was then separated into solid and solution phases. The solid sample was washed with water and dried. This dried sample was further analyzed by spectroscopic and chemical methods.

　　Above 40 ℃, a sealed 100 mL glass vessel containing 1.00 g ulexite sample and 50.0 mL H_2O was set in an isothermal water bath. The temperature accuracy was controlled within ±0.2 ℃. After the ulex-

ite-H_2O mixtures reached an equilibrium at given temperatures from 40 to 93 ℃ (about 3~7 days). The samples of liquid and solid should be taken for analysis and identification. The measurements were taken at temperatures as listed in Table 1. The system was boiling at 93 ℃. This specific boiling point was due to the atmosphere of 580 mmHg at the Qinghai-xizang plateau. Above boiling point, analysis was made at two different temperatures i,e. 120 and 240 ℃(±1.0 ℃). The sample was placed into a sealed stainless steel bottle, "autoclave". The inner wall of this bottle was coated with Teflon. The capacity of the autoclave was 40 mL. For the hydrothermal dissolution experiment of ulexite, 0.500 g sample and 25.0 mL H_2O was placed into the autoclave. The autoclave was heated to a given temperature in the oven for different periods of time. After heated at each period of time the sample was take out and allowed to cool to the room temperature. The liquid and solid were then analyzed. The time to reach to the equilibrium state was determined from 40~93 ℃. To analyze our solid sample, the solution was cooled to room temperature and separated. The solid phase was washed with water then dried at 100 ℃. The solid sample was analyzed by chemical and spectroscopic method. The liquid phase was analyzed by standard chemical method.

2　Results

2.1　Results of Isothermal Dissolution of Ulexite from 10 ℃ to 35 ℃

　　The concentration vs. temperature (*C-T*) curve of ulexite solution at given temperatures from 10 ℃ to 35 ℃ is shown in Fig.2. The corresponding solubility
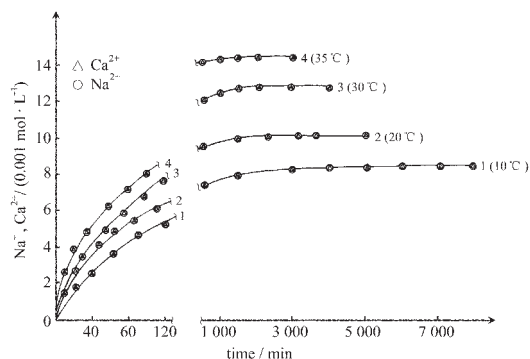

Fig.2　Solution composition as functions of time at temperature
　　　range from 10 to 35℃

Table 1　Chemical Composition of Liquid and Solid Phase of Ulexite-H₂O in Equilibrium at Different Temperature

temp. / ℃	composition								solid phase
	liquid phase				solid phase				
	Ca^{2+} / (mol· L^{-1}) (×10⁻²)	B_2O_3 / (mol· L^{-1}) (×10⁻²)	Na^+ / (mol· L^{-1}) (×10⁻²)	pH	CaO / wt.%	B_2O_3 / wt.%	Na_2O / wt.%	B_2O_3/CaO+Na_2O / (mol ratio)	
10	0.84	3.05	0.84	9.48	13.86	43.00	7.55	1.67	ulexite
20	1.05	3.85	1.06	9.52	13.87	43.00	7.55	1.67	ulexite
30	1.30	4.74	1.32	9.56	13.90	43.02	7.52	1.67	ulexite
35	1.45	5.43	1.46	9.58	13.90	43.02	7.52	1.67	ulexite
40	3.32	6.89	3.95		16.20	43.22	5.10	1.67	$NaCaB_5O_6(OH)_6·H_2O$
50	3.48	7.35	4.30		18.00	44.10	3.50	1.68	$NaCaB_5O_6(OH)_6·H_2O$
60	2.91	7.80	4.60		19.70	45.90	2.09	1.67	$NaCaB_5O_6(OH)_6·H_2O$
65	2.46	9.85	4.94		21.80	45.20	—	1.67	$NaCaB_5O_6(OH)_6·H_2O$
68	2.26	9.34	4.94		25.40	45.45	—	1.44	amorphous
71	1.64	8.14	4.94		25.60	44.44	—	1.40	priceite
75	1.43	7.80	4.94		28.70	46.20	—	1.30	priceite
93	0.21	5.32	4.94		30.50	47.40	—	1.25	priceite

of ulexite in water at every given temperature is given in Table 1.

Fig.2 shows that Ca^{2+} and Na^+ in solution have the same mole values within the given temperature range. The analysis of the solid sample showed that the insoluble residues were ulexite only. The result indicates that ulexite dissolves congruently in water in the temperature range from 10 to 35 ℃. The concentration of B_2O_3 in the liquid phase in this temperature range is shown in Fig.3.
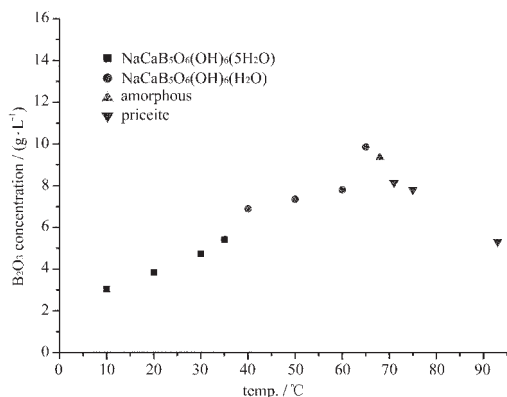

Fig.3　B_2O_3 concentration in equilibrium liquid at different temperature

2.2　Results of Dissolution of Ulexite from 40 to 65 ℃

Given in Fig.4 is XRD result. The result shows that the equilibrium structure of residual in solid phase is $NaCaB_5O_6(OH)_6·H_2O$. This substance has lower hy-
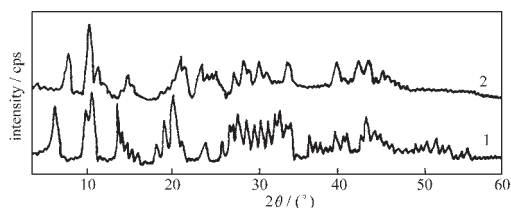

Fig.4　XRD patterns of $NaCaB_5O_6(OH)_6·5H_2O$ (ulexite) and $NaCaB_5O_6(OH)_6·H_2O$
　　　1: $NaCaB_5O_6(OH)_6·5H_2O$ (ulexite)
　　　2: $NaCaB_5O_6(OH)_6·H_2O$

dration number than ulexite $NaCaB_5O_6(OH)_6·5H_2O$. From the chemical analysis we found that different amount of Na^+ and Ca^{2+} were presented in the liquid phase. This indicates that Na^+ and Ca^{2+} of ulexite dissolved into solution with different ratio. The concentration of $B_2O_3(aq)$ in this temperature range is shown in Fig.3. We found that the concentration of $B_2O_3(aq)$ increased with temperature from 10 ℃ to 65 ℃. At 65 ℃, the concentration of $B_2O_3(aq)$ reaches its maximal value and then decreases rapidly with the increasing of temperature.

2.3　Results of Dissolution of Ulexite Higher than 65 ℃

At temperature range from 65 to 93 ℃, the analysis of solid phase showed several changes. From 68 ℃ to 71 ℃, the XRD result indicated that our solid ulexite sample became amorphous. At 71 ℃, XRD analysis showed that a new substance was formed in

the solid phase. The structure of this new substance was identified to be priceite according to the diffraction pattern. The ideal chemical formula of priceite, $4CaO \cdot 5B_2O_3 \cdot 7H_2O$, that gives B_2O_3:CaO = 1.25:1. However, the chemical analysis of our solid sample showed different molar ratio of B_2O_3:CaO=1.41:1. This B_2O_3 to CaO ratio was found to approach to the ideal ratio 1.25:1 at higher temperature. At 93 ℃, these two ratios were identical. Further analysis showed at this temperature, the hydration number of our solid sample was nine instead of ideal value of seven for priceite. To confirm this, we did this analysis at different time after the sample was prepared. The longest time duration was one month. Nevertheless, the exact identical result was obtained for each analysis. Therefore, we believed that our sample was in the equilibrium states at each measured temperature.

The chemical compositions of solution and solid phase at 120 ℃ and 240 ℃ are shown in Table 2. The solid phase was identified as purely priceite $(4CaO \cdot 5B_2O_3 \cdot 7H_2O)$ at these two temperatures. We did not found any $NaCaB_5O_6(OH)_6 \cdot H_2O$ in the solid

phase above 120 ℃. At high temperature the concentration of Ca^{2+}(aq.) was too small to determine by traditional volumetric titration method. Therefore, it was determined by atomic absorption spectrometric method. To examine the conversion from ulexite to the priceite at these high temperatures, XRD analysis
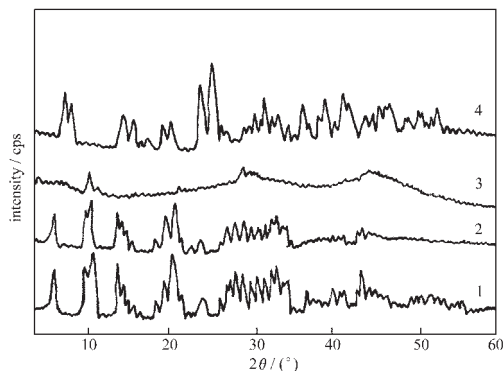

Fig.5　XRD patterns of solid phase during dissolution process
　　　at temperature 120℃
　　　1: sample (ulexite)
　　　2: the residual solid phase at 2 hrs
　　　3: the residual solid phase at 6 hrs
　　　4: the residual solid phase at 12 hrs

Table 2　Chemical Composition of Liquid and Solid Phase in Ulexite-H₂O System at Different Measured Time during Dissolution of Ulexite at 120 ℃ and 240 ℃

| reaction time / h | composition | | | | | | | solid phase |
| | liquid phase | | | solid phase | | | | |
	Na^+/(mol·L⁻¹) (×10⁻²)	Ca^{2+}/(mol·L⁻¹) (×10⁻³)	B_2O_3 /(mol·L⁻¹) (×10⁻²)	CaO / wt.%	B_2O_3 / wt.%	Na_2O / wt.%	$CaO:B_2O_3$ / (mol ratio)	
120 ℃								
2	3.66	1.67	3.40	17.00	42.20	1.90	1:2.00	ulexite
4	4.88	2.86	5.03	24.80	46.20	0.50	1:1.60	amophorous phase
6	4.88	2.64	5.17	28.60	47.30	0.05	1:1.30	amophorous phase
8	4.90	2.42	5.31	30.3	48.90	—	1:1.25	priceite
12	4.92	1.98	5.52	32.00	49.80	—	1:1.25	priceite
18	4.94	0.88	5.39	32.10	49.82	—	1:1.25	priceite
24	4.90	0.53	5.20	32.10	49.40	—	1:1.25	priceite
32	4.94	—	4.96	32.10	49.80	—	1:1.25	priceite
48	4.94	—	4.96	32.10	49.80	—	1:1.25	priceite
240℃								
1	4.80	3.30	5.13	22.3	42.40	1.90	1:1.53	amophorous phase
2	4.90	1.32	5.06	31.8	49.60	0.50	1:1.25	priceite
6	4.90	1.10	5.03	32.1	49.90	0.05	1:1.25	priceite
12	4.90	0.55	4.97	32.1	49.90	—	1:1.25	priceite
24	4.90	—	4.96	32.1	49.90	—	1:1.25	priceite
32	4.90	—	4.96	32.1	49.90	—	1:1.25	priceite

of solid phase at different period of time were carried out. The result was shown in the Table 2 and Fig.5.

3　Discussion

3.1　Low Temperature Dissolution

The analysis result showed that the dissolution of ulexite below 35 ℃ was a congruent process for Na^+ and Ca^{2+}. On the other hand, the structure of boron-oxygen anion in the solution needed to be clarified. At 10 to 35 ℃, the constant pH values were obtained within 9.47~9.58 for our liquid sample. Valyasko[20] had reported that the structure of boron-oxygen of borate depends on pH value in the solution. The reported structures of borate ions were $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$ in the pH range 9.0~9.5. Adams[1] did similar experiment to analyze the structures of boron-oxygen of borates. This experiment indicated that $B_5O_6(OH)_6^{3-}$ might be depolymerized to $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$ in the aqueous ulexite solution. In fact, all the minerals which contain $B_3O_3(OH)_5^{2-}$ (e.g. inyoite, meyerhofferite) and $B_4O_5(OH)_4^{2-}$ (e.g. borax) are very stable in nature. Based on the Valyasko and Adams works, the following dissolution reaction might be suggested for the borate in our ulexite sample in the temperature from 10~35 ℃,

$$2[B_5O_6(OH)_6]^{3-} + H_2O =$$
$$2B_3O_3(OH)_5^{2-} + B_4O_5(OH)_4^{2-} \qquad (1)$$
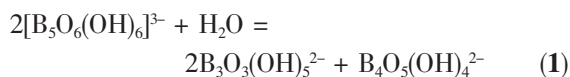
The constant pH value in our solution indicated the equilibrium between $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$. The following reaction may be suggested,

$$4B_3O_3(OH)_5^{2-} =$$
$$3B_4O_5(OH)_4^{2-} + 2OH^- + 3H_2O \qquad (2)$$
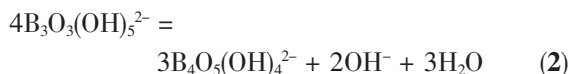
3.2　Dissolution form 40 to 65 ℃

The experimental studies in the temperature range from 40 ℃ through 65 ℃ indicated that the dissolution of Na^+ and Ca^{2+} in ulexite resulted in different mole ratios (non-stoichiometric dissolution or incongruent dissolution). In the solid phase, $[B_5O_6(OH)_6]^{3-}$ was found to be existed in a stable form. Our analysis results showed that ulexite had lost 4 water molecules forming mono-hydrated complex in this temperature range. This indicates that penta-hydrated ulexite could not be stable above 40 ℃. Ghose et al.[21] pointed out that different coordination forms of waters in ulexite. Each coordination form associated with different bind-ing energy. This agrees with our observation, that is, the weakly bind water would dissociate when temperature increases.

The incongruent dissolution of Na^+ and Ca^{2+} may be explained as follows. According to the discussion from Ghose[21], Na^+ is lighter than Ca^{2+} and less charged and has lower coordination number (six for Na^+ and eight for Ca^{2+}) in ulexite. Therefore, the dissolution of Na^+ is easier than Ca^{2+} when temperature increases. In our experiment, we found this temperature effect was only significant above 40 ℃. Since we did not found any significant change in the structure of $[B_5O_6(OH)_6]^{3-}$ framework, therefore, Na^+ sites must be replaced by Ca^{2+} due to exchange process. The leaving Na^+ creates a negative charged site in the solid. Ca^{2+} in solution then occupies this negative charged site naturally. Table 1 shows that the exchanging ratio increased with temperature and all Na^+ were completely replaced by Ca^{2+} at 65 ℃. The constant ratio between cation and anion in the table also indicates the fact of exchanging between Na^+ and Ca^{2+}.

3.3　Dissolution Above 65 ℃

The frame structure of $B_5O_6(OH)_6^{3-}$ in solid was found to be remained stable till 65 ℃. At 68 ℃, this frame structure was found to be destroyed and turned into amorphous phase. At temperature range from 71 ℃ to 75 ℃, the X-ray result showed priceite pattern of the residual solid. On the other hand, the solid showed different composition than priceite by the chemical analysis. Although in our experiment, the ulexite-water system in these two temperature points were kept in a long period of time (about a month), the composition of solid and liquid phase did not changed. We could not confirm whether the system reached equilibrium or not. The residual solid phase is most likely a mixture of amorphous borate and pri-ceite. Nevertheless, we found that the concentration of B_2O_3 in the solution phase decreased as the temperature increased. This means that polyborate ions in the liquid phase participated in the form of solid $[B_5O_8(OH)_3]^{4-}$, which is the B-O structure of priceite.

3.4　High Temperature Studies

Ulexite is occurred in the earth surface within depth of few hundred meters. At such depth, this mineral might be interacted with hot ground water.

Therefore, it is interesting to study this system at high temperature. We did analysis at two temperatures, 120 ℃ and 240 ℃. The analytical result as function of time is listed in Table 2. At both temperatures, we found that solid had only priceite component after 12 hours. However, the concentrations of Ca^{2+} and B_2O_3 in the liquid phase still decreased. The decreased amounts of Ca^{2+} and B_2O_3 in the liquid phase were in consistent of composition priceite. This clearly indicates crystallization of priceite from solution at high temperature. After all Ca^{2+} in the liquid precipitated, the system reached to the equilibrium and we found no composition change in solid or liquid.

Kemp[6] had found that $Na_2[B_4O_5(OH)_4] \cdot 3H_2O$ was very stable at the higher temperature. Hart and co-workers[22] reported their studies of a similar system of B_2O_3-CaO-H_2O in the temperature range from 200 to 400 ℃. They detected solid compound $Ca[B_3O_3(OH)_5] \cdot 4H_2O$ but no priceite at high temperature. These two studies showed that $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$ were very stable at high temperature. Because both of the anions were detected in our system at lower temperature, therefore, the following reaction is suggested of forming priceite at high temperature.

$$2[B_3O_3(OH)_5]^{2-} + [B_4O_5(OH)_4]^{2-} + 2OH^- =$$
$$[B_5O_8(OH)_3]^{4-} + 5H_2O \qquad (3)$$
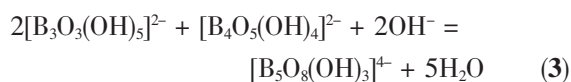
Priceite crystal has layered structure. Our experiment indicated that this crystal was formed first from the transformation of amorphous solid. This serves as seed for crystal growing. The crystal was then grown up at the active sites.

The salt lakes on Qinghai-xizang (Tibet) plateau are the highest in altitude in the world. The annual average temperature is about 0 ℃ and no hot spring in any of the salt lake. According to our experiment, it is impossible for ulexite to transform into priceite in these saline lakes. In fact, priceite has never been found in the salt lakes on Qinghai-xizang plateau. In other areas of the world with high terrestrial heat, for example, Turkey, ulexite and priceite are commonly discovered. Our analysis indicates a possible origin of forming priceite from ulexite.

References

[1] Adams R. M. *Boron, Metal-Boron Compounds and Boranes*, Interscience Publishers: New York, **1964**,p130.

[2] XIE Xian-De(谢先德) *Mineral of Borate*(硼酸盐矿物), Beijing: Science Press, **1965**,p32.

[3] Celik M. S., Suner F. *Thermochim. Acta*, **1995**,**245**,167.

[4] Hurriyet E., Mehmet T. *Thermochim. Acta*, **1995**,**250**,125.

[5] GAO Shi-Yang, CHEN Jing-Qing, ZHENG Mian-Ping *Advances in Science of China*, "Chemistry" Vol.4, Science Press: New York, **1992**,p163.

[6] Kemp P. H. *The Chemistry of Borate*, Part 1, Consolidated Limited S. W. I.: London, **1956**,p68.

[7] Gamze T., Onganer Y., Alkan M. *Canadian Metallurgical Quarterly*, **1998**,**37**(2),91.

[8] Gulensoy H. *Bull. Miner. Res. Explor. Inst. Turk*, **1976**,**86**,7.

[9] Gulensoy H. *Bull. Miner. Res. Explor. Inst. Turk*, **1976**,**89**, 36.

[10] Imamutdinova V. M. *Zh. Prikl. Khim.*, **1967**,**40**(8),3593.

[11] Imamutdinova V. M., Gode H. *Latv. PRS Zinat. Akad. Vestis, Kim. Ser.*, **1981**,**2**,156.

[12] Imamutdinova V. M. *Boraty Sist*, Zinatne: Riga, **1978**,p137.

[13] Mehmet T., Kocakerim M., Yapici S., Bayrakceken S. *Hydrometallurgy*, **1999**,**51**,359.

[14] Mehmet T., Yapici S., Kocakerim M., Yartas A. *Chem. Biochem. Eng., Q*, **2001**,**15**(4),175.

[15] Nakamura H., Nishida H. *Anal. Chim. Acta*, **1982**,**139**,219.

[16] Zdanovskii A. B. *Zh. Prikl. Khim.*, **1982**,**40**(12),2659.

[17] Vinogaradov E. E., Azarova L. A. *Zh. Nerog. Khim.*, **1995**, **40**(3),418.

[18] Spryagina D. *Trudy Vesesoyuz Nauch-Issledovatel Inst. Galurgii.*, No.271953,77, **1956**.

[19] Navak M. *Chem. Prum*, **1982**,**32**(16),633.

[20] Valyashko G. M., Wlassowa E. V. *Jena Rev.*, **1969**,**14**(1),3.

[21] Ghose S., Cheng W. *Am. Mineralogist*, **1978**,**63**(1~2),160.

[22] Hart P. B., Brown C. S. *J. Inorg. Nucl. Chem.*, **1962**,**24**, 1057.