

## SYNTHESES OF ZEOLITES OF THE GISMONDINE GROUP

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### ABSTRACT

The synthetic glasses for the experiments are constituted of three chemical systems, namely,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $n=2\sim 8$ ),  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $n=2\sim 10$ ) and  $x\text{CaO} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $x=0.25\sim 0.75$ ,  $n=3\sim 5$ ). Experiments were carried out in autoclaves using the synthetic glasses and alkaline solutions as starting materials, under the conditions of 110°C, 150°C, 180°C and 210°C; at autogeneous pressures; and in durations from 1 day to 60 days. Synthetic products were examined by an X-ray diffractometer, scanning electron microscope and electron microprobe.

Experimental results show that gismondine, garronite, gobbinsite and amicitite have been synthesized in the  $x\text{CaO} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $x=0.25\sim 0.75$ ,  $n=3\sim 5$ ) system; gismondine, garronite and gobbinsite in the  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $n=2\sim 4$ ) system; and, only gobbinsite in the  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $n=4\sim 8$ ) system. The synthetic gismondine and amicitite exhibit little variation, but garronite and gobbinsite a greater variation in terms of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  and  $\text{Ca}/(\text{Ca}+\text{Na}+\text{K})$  ratios.

$\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of the synthesized zeolites are generally close to those of the starting glasses. As to cationic compositions of synthetic zeolites, compositions of liquid media seem more influential than those of glasses during syntheses of gobbinsite and amicitite. Contrarily, gismondine is essentially related with the initial compositions of glasses, and garronite seemingly with those of both glasses and liquid media.

**Key words:** synthetic glasses, alkaline solutions, autoclaves, gismondine group

## INTRODUCTION

Zeolites of the gismondine group include gismondine ( $\text{Ca}_4\text{Al}_8\text{Si}_8\text{O}_{32}\cdot 16\text{H}_2\text{O}$ ), garronite ( $\text{NaCa}_2\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 13\text{H}_2\text{O}$ ), gobbinsite ( $\text{Na}_5\text{Al}_5\text{Si}_{11}\text{O}_{32}\cdot 11\text{H}_2\text{O}$ ) and amicitite ( $\text{Na}_4\text{K}_4\text{Al}_8\text{Si}_8\text{O}_{32}\cdot 10\text{H}_2\text{O}$ ) (Gottardi and Galli, 1985; Ghobarkar and Schaf, 1999; Armbruster and Gunter, 2001). They are Ca-, Na- or Ca-Na-bearing zeolites except amicitite which is K-Na-bearing. It has generally been considered that natural zeolites are essentially derived from minerals of the plagioclase group with excess or deficient  $\text{SiO}_2$  during rock alteration (Hay, 1966; Boles, 1988).

This study is an attempt to relate minerals of the plagioclase group with the formation of zeolites of the gismondine group under hydrothermal conditions. Experiments using natural minerals are impracticable because of a slow reaction rate for the one reason and of difficulty to obtain natural samples for the other. So, synthetic glasses with the bulk compositions equivalent to those of the plagioclase group minerals were used for solid starting materials in the experiments. The solid starting materials in this study include three chemical systems, namely,  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  and  $x\text{CaO}\cdot(1-x)\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$ . The former two systems describe anorthite with excess  $\text{SiO}_2$  and albite with deficient and excess  $\text{SiO}_2$ , respectively, and the last one represents the general compositions of plagioclase.

In addition to NaOH solution of the conventional use,  $\text{Na}_2\text{CO}_3$  and NaCl solutions were used for the sake of simulating the salt lake water (Surdam and Sheppard, 1978) and sea water (Chen, 1994), respectively, since these natural waters are very important liquid media in geneses of natural zeolites (Hay, 1978; Iijima, 1978; Langella *et al.*, 2001). A systematic study on syntheses of zeolites of the gismondine group has rarely been taken though a few synthetic results have been reported (Taylor and Roy, 1964; Ghobarkar and Schaf, 1999; Alberti and Cheetham, 2000). On the other hand, synthetic studies have not been correlated with natural occurrences (Iijima and Harada, 1969; Nawaz and Malone, 1982; Artioli and Foy, 1994) as well. So, the results of this investigation are separated into two parts. The synthetic results are going to be reported in this paper, whereas those correlated with natural occurrences will be reported in a separate one.

## EXPERIMENTAL METHOD

The starting materials used in the experiments include two fractions: one is a solid and the other is a liquid. Chemical compositions of the solid materials were analyzed by X-ray fluorescence and are listed in Table 1. Presumably, the trace amount of impurities including  $\text{Fe}_2\text{O}_3$  and MgO shown in the Table 1 is inherited from the chemical reagents as given following. Actually, solid materials are constituted of three chemical systems, namely,  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  ( $n=2, 4, 6$  and  $8$ ),  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  ( $n=2, 4, 6, 8$  and  $10$ ), and  $x\text{CaO}\cdot(1-x)\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  ( $x=0.75, 0.50$  and  $0.25$ ;  $n=3, 4$  and  $5$ ). Each starting material was prepared by mixing of  $\text{CaCO}_3$  (Baker analyzed, 98%) and/or  $\text{Na}_2\text{CO}_3$  (Baker analyzed, 99%),  $\text{Al}_2\text{O}_3$  (Baker analyzed, 99.4%) and quartz ( $\text{SiO}_2$ ) powder in a required proportion. The well-mixed mixture was put into a graphite crucible, and then was melted in a high temperature furnace with temperatures ranging from  $1400^\circ\text{C}$  to  $1600^\circ\text{C}$ , depending on the composition of the mixture. The melt was quenched in the air to become homogeneous glass which was ground to powder for experiments. The liquid media include  $\text{NH}_4\text{OH}$ ,  $\text{Na}_2\text{CO}_3$ , NaCl, NaOH and KOH of Merck's reagents prepared into solutions of required concentrations as shown in Table 2. Teflon-lined autoclaves with a

Table 1. Chemical compositions of the synthetic glasses of different chemical systems by XRF.

Chem. systems	Oxides							Total
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O		
	Weight (%)							
CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	42.44	37.71	n.d.*	0.18	20.23	n.d.	n.d.	100.56
CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	59.62	26.13	n.d.	0.11	14.03	n.d.	n.d.	99.89
CaO·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	70.18	18.90	n.d.	0.15	9.88	n.d.	n.d.	99.11
CaO·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub>	75.25	15.89	n.d.	0.13	8.61	n.d.	n.d.	99.88
Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	43.00	36.52	0.65	0.02	0.15	20.49	100.83	
Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	58.61	25.33	0.67	n.d.	0.08	14.71	99.40	
Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	67.26	19.44	0.68	n.d.	0.05	11.48	98.91	
Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub>	73.08	15.81	0.60	n.d.	0.02	9.13	98.64	
Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·10SiO <sub>2</sub>	77.09	13.22	0.57	n.d.	n.d.	7.62	98.50	
0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	46.60	36.52	0.04	n.d.	10.86	5.13	99.15	
0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	56.17	28.35	0.29	n.d.	5.60	8.38	98.79	
0.25CaO·0.75Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·5SiO <sub>2</sub>	62.35	23.33	0.44	n.d.	2.30	10.18	98.60	

\* n.d.: not detectable

Table 2. The liquid media used in different chemical systems.

Liquid media	Chemical systems
NH <sub>4</sub> OH 1.0M	CaO·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
Na <sub>2</sub> CO <sub>3</sub> 0.1M	CaO·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
NaOH 0.1M	CaO·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
NaOH 0.1M (+) NaCl 0.36M	CaO·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
NaOH 1.0M	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
NaOH 0.5M (+) KOH 0.5M	xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
KOH 0.1M	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
KOH 0.5M	CaO·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>
KOH 1.0M	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub> xCaO·(1-x)Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·nSiO <sub>2</sub>

capacity of 35ml for each and temperature-calibrated oven with the maximum temperature attaining 300°C are the main pieces of the equipment used in experiments. Experiments were started with 2g solid and 20ml liquid for each, and then were carried out in autoclaves under the conditions of 110°C, 150°C, 180°C and 210°C, at autogeneous pressures, and in durations from 1 day to 60 days.

Synthetic products were examined by an X-ray diffractometer (XRD) and scanning electron microscope (SEM) for phase identification. Chemical compositions of the synthetic minerals were obtained through the electron probe microanalysis (EPMA) with accelerating potential of 15kV, beam current of 10nA, counting-time of 10-sec, and feldspars as standards.

## RESULTS

Experimental results are listed in Table 3. It should be noted that only those which are relevant to the syntheses of zeolites of the gismondine group are shown in the table. As indicated

Table 3. Experimental results.

Run no.	Chemical systems	Temp. (°C)	Liquid media	Duration (days)	Products*	
A-01	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	180	NH <sub>4</sub> OH 1M	12~60	Gis + t	
A-02	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	150		30~60	Gis	
A-03	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		6~30	G	
A-04	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		12~30	G	
A-05	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	150	Na <sub>2</sub> CO <sub>3</sub> 0.1M	17	ca + Gis + o	
A-06	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		1~3	G + a + ca	
A-07	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		6~12	a + G + ca	
A-08	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		7	Go + p + ca	
A-09	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		30	p + Go + a + ca	
A-10	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	110	NaOH 0.1M	30	Gis	
A-11	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		3~12	a + G	
A-12	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		6	Go	
A-13	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		12	a + G	
A-14	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		12	Go	
A-15	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		30	G	
A-16	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	150	NaOH 0.1M (+)	12~30	Gis + a + o	
A-17	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		12	a + G	
A-18	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		NaCl 0.36M	12	a + Go
A-19	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		12	Go + p	
B-01	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180	Na <sub>2</sub> CO <sub>3</sub> 0.1M	12	a + Go	
B-02	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		12	Go	
B-03	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180	NaOH 0.1M	12	a + Go	
B-04	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		12	Go	
B-05	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	110		30	Go	
B-06	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		NaOH 0.1M (+)	12	a + Go
B-07	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	110		NaCl 0.36M	30	Go
B-08	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	110	NaOH 1M	20	Go	
B-09	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·6SiO <sub>2</sub>	110		20	Go	
B-10	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub>	150		7	a + Go	
B-11	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·8SiO <sub>2</sub>	110		20	Go	
C-01	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	210	Na <sub>2</sub> CO <sub>3</sub> 0.1M	7	Go + p + ca + a	
C-02	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	180		12	Go + p + ca	
C-03	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210		7	Go + a	
C-04	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		12	Go + ca	

Table 3. continued.

C-05	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		31	Go + ca
C-06	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	210		7	G
C-07	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	180		12	Gis
C-08	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	150		17~33	Gis
C-09	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	110	NaOH 0.1M	30	Gis
C-10	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180		12	a + Go
C-11	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150		17~33	Go
C-12	0.5CaO·0.5Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	110		30	Go
C-13	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	210	NaOH 0.1M (+)	7	G + a
C-14	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	180	NaCl 0.36M	12	Gis
C-15	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	150		17~33	Gis
C-16	0.25CaO·0.75Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·5SiO <sub>2</sub>	150	NaOH 1M	7	a + Go
C-17	0.25CaO·0.75Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·5SiO <sub>2</sub>	110		14	a + Go
C-18	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	150	NaOH 0.5M (+)	7	o + Am
C-19	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	150	KOH 0.5M	7	o + Am
C-20	0.75CaO·0.25Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	110		14	Am

\* Gis: gismondine, G: garronite, Go: gobbinsite, Am: amicitte, t: thomsonite, a: analcime, p: zeolite P, ca: calcite, o: other synthetic minerals

in Table 3, gismondine, garronite, gobbinsite and amicitte; and the associated zeolitic (analcime, thomsonite and zeolite P) and non-zeolitic (calcite and others) minerals have been synthesized. The X-ray powder diffraction data of zeolites synthesized in this study and of those reported in literature (Gottardi and Galli, 1985; Nawaz and Malone, 1982; Barrer *et al.*, 1959; Alberti and Vezzalini, 1979) are compared in Tables 4-1 to 4-4. Obviously, they agree well with each other for a given zeolite.

The synthetic results in the system of CaO·Al<sub>2</sub>O<sub>3</sub>·nSiO<sub>2</sub> (n=2, 4, 6 and 8) are illustrated in Figure 1-1. Certainly, gismondine, garronite and gobbinsite have been synthesized. Gismondine can be produced in CaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>, and 1M NH<sub>4</sub>OH, 0.1M Na<sub>2</sub>CO<sub>3</sub>, 0.1M NaOH and 0.1M NaOH (+) 0.36M NaCl solutions at 110°C, 150°C and 180°C. Garronite appears in CaO·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, and 1M NH<sub>4</sub>OH and 0.1M NaOH solutions at 150°C, 180°C and 210°C; but in CaO·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, and 0.1M Na<sub>2</sub>CO<sub>3</sub> and 0.1M NaOH (+) 0.36M NaCl solutions only at 210°C. On the other hand, gobbinsite can only be yielded in CaO·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, and 0.1M Na<sub>2</sub>CO<sub>3</sub> and 0.1M NaOH (+) 0.36M NaCl solutions at 150°C and 180°C.

As illustrated in Figure 1-2 of the system of Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·nSiO<sub>2</sub> (n=2, 4, 6, 8 and 10), it is obvious that, at 110°C, 150°C and 180°C, only gobbinsite or gobbinsite associated with others has been synthesized in Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, and 0.1M Na<sub>2</sub>CO<sub>3</sub>, 0.1M NaOH and 0.1M NaOH (+) 0.36M NaCl solutions; but also in Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·nSiO<sub>2</sub> (n=4, 6 and 8), and 1M NaOH solution.

Table 4-1. X-ray powder diffraction data of gismondine.

Gismondine (this study)		JCPDS files 39-1373 (Gottardi and Galli, 1985)		
d (Å)	I / I <sub>0</sub>	d (Å)	I / I <sub>0</sub>	hkl
7.28	55	7.30	63	110
5.92	7	5.94	7	111
5.76	15	5.77	15	111
5.01	8	5.00	17	200
4.91	39	4.91	52	002
4.67	19	4.68	17	021
4.26	100	4.27	100	121
4.21	26	4.21	51	121
4.19	49	4.18	34	211
4.05	18	4.05	30	211
3.42	11	3.43	16	122
3.34	54	3.34	47	031
3.18	51	3.19	90	310
3.12	39	3.13	71	013
2.74	45	2.74	76	321
2.71	39	2.71	59	123
2.69	46	2.69	78	321
2.66	82	2.66	69	123
2.62	11	2.62	17	312
2.34	14	2.34	16	042

Table 4-2. X-ray powder diffraction data of garronite.

Garronite (this study)		JCPDS files 16-0148 (Barrer <i>et al.</i> , 1959)		
d (Å)	I / I <sub>0</sub>	d (Å)	I / I <sub>0</sub>	hkl
7.13	85	7.15	80	101
4.95	54	4.95	80	200
4.13	76	4.12	100	112
4.07	22	4.07	60	211
3.23	39	3.22	60	103
3.14	100	3.14	100	301
2.67	63	2.66	100	312

Table 4-3. X-ray powder diffraction data of gobbinsite.

Gobbinsite (this study)		JCPDS files 35-0559 (Nawaz and Malone, 1982)		
d (Å)	I / I <sub>0</sub>	d (Å)	I / I <sub>0</sub>	hkl
7.10	69	7.11	100	101
5.03	41	5.05	50	020
4.11	79	4.11	100	121
		3.32	30	122
3.19	100	3.20	100	031
3.11	59	3.11	80	013
2.69	47	2.69	80	132
		2.65	40	123

Table 4-4. X-ray powder diffraction data of amicitite.

Amicitite (this study)		JCPDS files 33-1273 (Alberti and Vezzalin, 1979)		
d (Å)	I / I <sub>0</sub>	d (Å)	I / I <sub>0</sub>	hkl
7.23	73	7.29	55	110
5.11	40	5.11	40	200
4.95	23	4.94	30	002
		4.22	90	211
4.19	73	4.18	40	121
3.29	16	3.29	30	130
3.23	72	3.24	45	310
3.14	70	3.14	80	013
2.97	23	2.97	10	222
2.76	21	2.76	35	321
2.72	100	2.72	100	132
		2.70	50	123
2.60	20	2.61	40	040
2.48	5	2.47	5	004
2.39	6	2.39	7	033



Figure 1-3 indicates the synthetic results of the system of  $x\text{CaO} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $x=0.75, 0.50$  and  $0.25$ ;  $n=3, 4$  and  $5$ ). In this system, all members of the gismondine group, namely, gismondine, garronite, gobbinsite and amicite have been synthesized. It is noted that gismondine appears in  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and  $0.1\text{M Na}_2\text{CO}_3$ ,  $0.1\text{M NaOH}$  and  $0.1\text{M NaOH (+)}$   $0.36\text{M NaCl}$  solutions at  $110^\circ\text{C}$  and  $150^\circ\text{C}$ . It also occurs in  $0.75\text{CaO} \cdot 0.25\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , and  $0.1\text{M NaOH}$  and  $0.1\text{M NaOH (+)}$   $0.36\text{M NaCl}$  solutions at  $110^\circ\text{C}$ ,  $150^\circ\text{C}$  and  $180^\circ\text{C}$ ; but

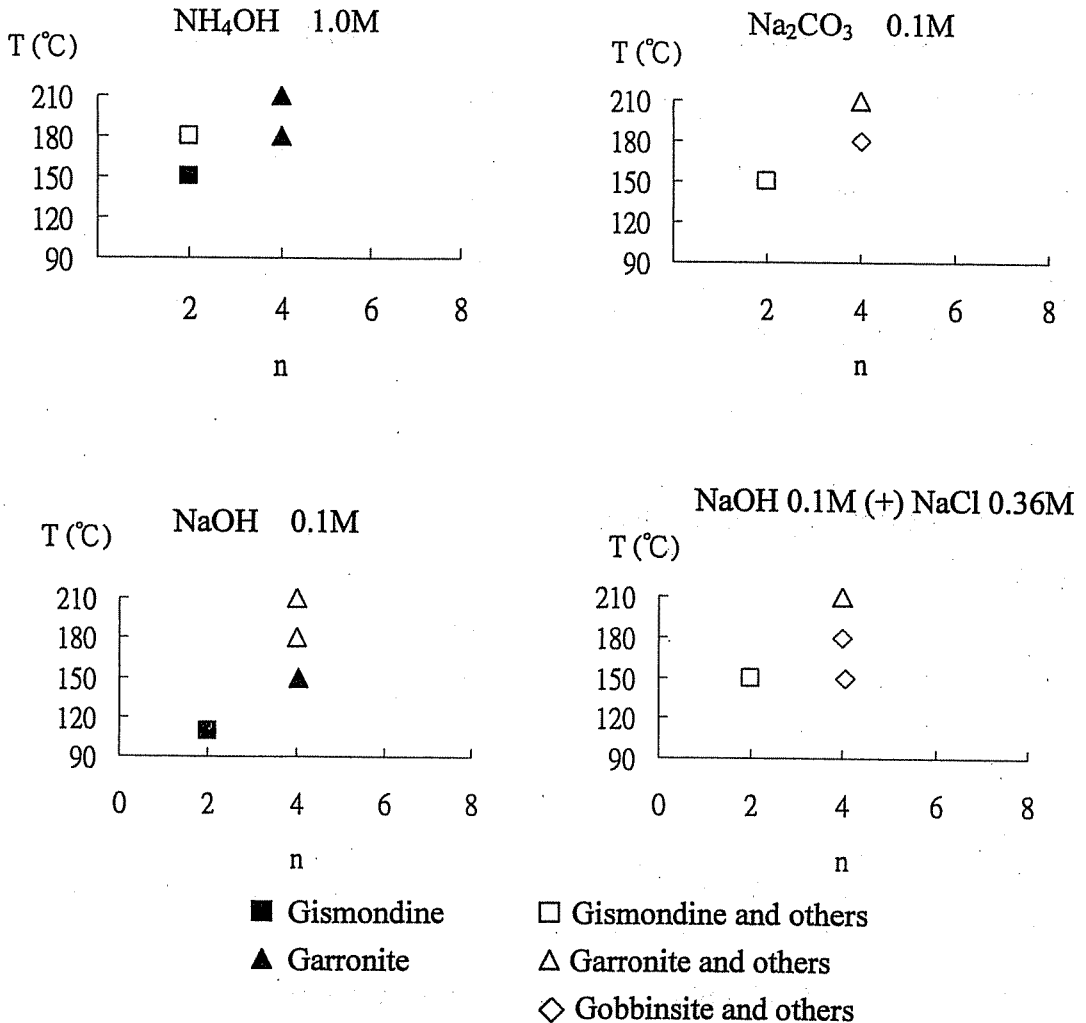


Figure 1-1. Zeolites of the gismondine group and others synthesized in the  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $n = 2, 4, 6$  and  $8$ ) system.

garronite appears instead of gismondine in the same starting materials at 210°C. Meanwhile, gobbinsite can be synthesized in  $0.75\text{CaO}\cdot 0.25\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$ , and 0.1M  $\text{Na}_2\text{CO}_3$  solution at 180°C and 210°C; in  $0.5\text{CaO}\cdot 0.5\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ , and 0.1M  $\text{Na}_2\text{CO}_3$  solution at 150°C, 180°C and 210°C, and 0.1M NaOH solution at 110°C, 150°C and 180°C; in  $0.25\text{CaO}\cdot 0.75\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$  and  $\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ , and 1M NaOH solution at 110°C and 150°C. Specially, amicite only appears in  $\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$  and  $0.75\text{CaO}\cdot 0.25\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$ , and 0.5M NaOH (+) 0.5M KOH solution at 110°C and 150°C.

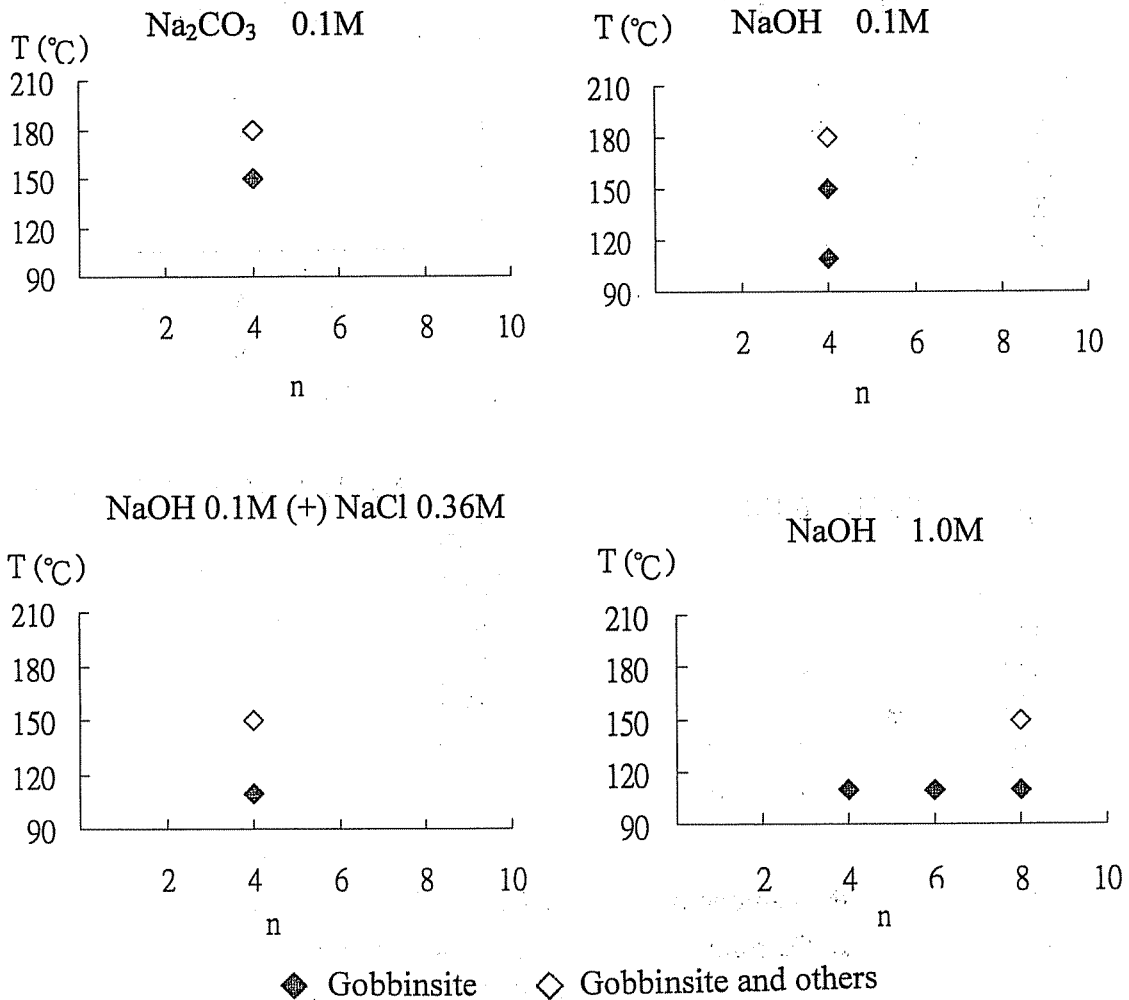


Figure 1-2. Zeolites of the gismondine group and others synthesized in the  $\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot n\text{SiO}_2$  ( $n = 2, 4, 6, 8$  and  $10$ ) system.

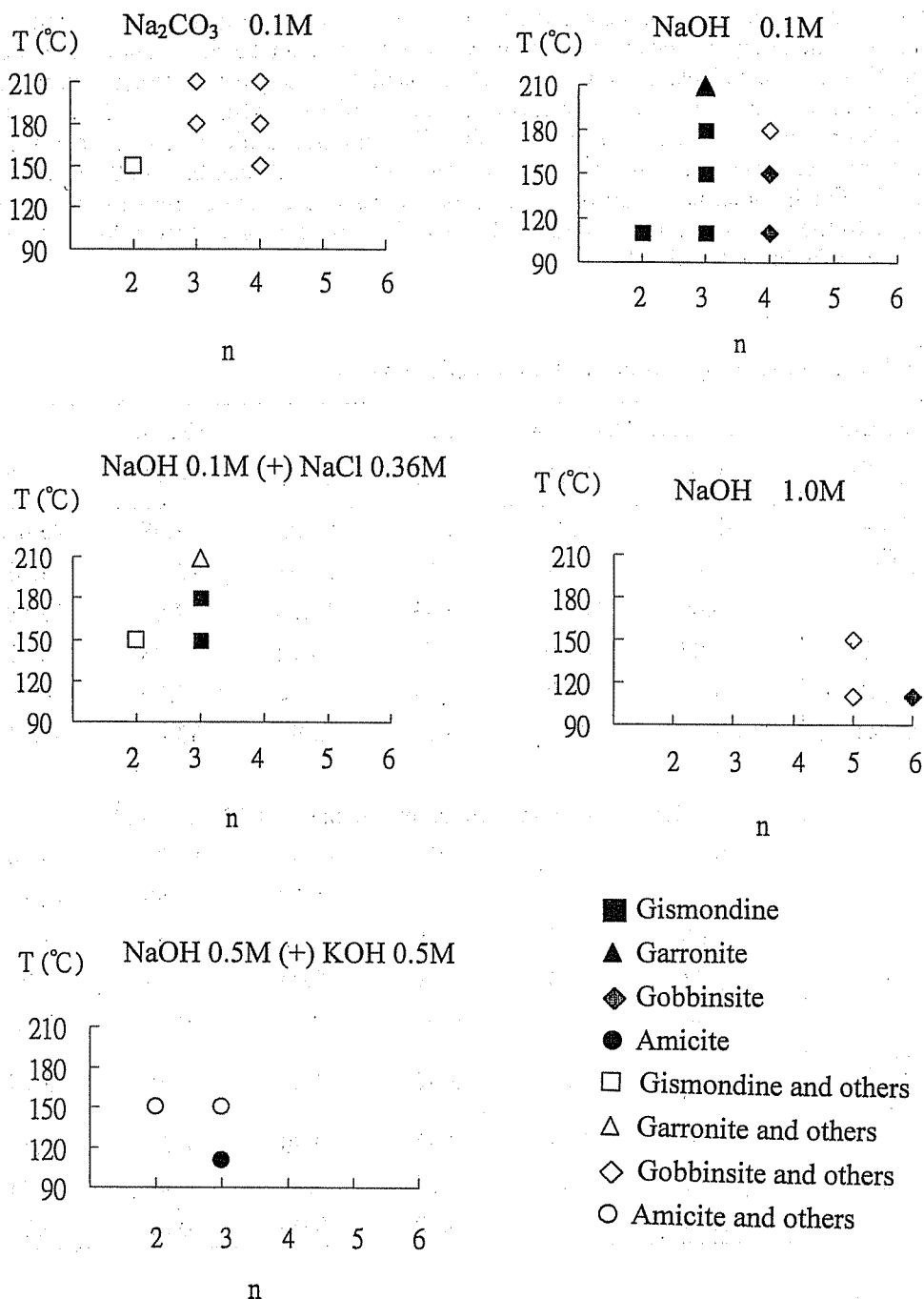


Figure 1-3. Zeolites of the gismondine group and others synthesized in the system of  $x\text{CaO} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$  ( $x = 1, 0.75, 0.50, 0.25$  and  $0$ ;  $n = 2, 3, 4, 5$  and  $6$ ). 2:  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , 3:  $0.75\text{CaO} \cdot 0.25\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ , 4:  $0.5\text{CaO} \cdot 0.5\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ , 5:  $0.25\text{CaO} \cdot 0.75\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ , 6:  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$

Chemical compositions of the zeolites synthesized in this investigation are given in Tables 5-1 and 5-2. The analytical errors are estimated to be lower than  $\pm 2\%$ , except that of sodium oxide of  $\pm 3\%$ . Figure 2 displays Ca/(Ca+Na+K) versus SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> plots of the synthetic zeolites. Clearly, gismondine shows little variation in terms of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (2.25~2.32) and Ca/(Ca+Na+K) ratios (0.93~1.00) (Table 5-1, Fig. 2). Similarly, amicitte also indicates a near constant composition (Fig. 2) with the above two ratios of 2.15~2.21 and 0.02~0.04, respectively (Table 5-2). On the other hand, garronite and gobbinsite give a greater compositional variation (Fig. 2) with the two ratios, just stated, of 3.15~4.12, 3.02~4.33 and 0.54~0.98, 0.02~0.13, respectively (Tables 5-1 and 5-2).

Table 5-1. Chemical compositions of the synthetic zeolites.

Zeolites Run no.	Gismondine			Garronite		
	A-02	A-10	C-15	A-03	A-15	C-13
SiO <sub>2</sub>	38.86	37.44	39.66	53.22	47.99	45.49
Al <sub>2</sub> O <sub>3</sub>	28.47	28.31	29.00	21.51	23.34	24.53
CaO	16.40	16.99	15.93	11.10	7.87	13.58
Na <sub>2</sub> O	0.04	0.09	0.66	0.12	3.78	2.25
K <sub>2</sub> O	n.d.	0.02	0.01	0.02	0.06	0.06
Total (wt.%)	83.77	82.85	85.26	85.97	83.04	85.91
Unit cell compositions (on the basis of 32 oxygens)						
Si	8.54	8.37	8.56	10.89	10.29	9.64
Al	7.36	7.45	7.37	5.18	5.89	6.11
Ca	3.86	4.07	3.69	2.43	1.81	3.08
Na	0.02	0.04	0.28	0.05	1.57	0.92
K	0.00	0.01	0.00	0.01	0.02	0.02
<u>SiO<sub>2</sub></u>	2.32	2.25	2.32	4.21	3.50	3.15
<u>Al<sub>2</sub>O<sub>3</sub></u>						
Ca*	1.00	0.99	0.93	0.98	0.54	0.77
Na*	0.00	0.01	0.07	0.02	0.46	0.23
K*	0.00	0.00	0.00	0.00	0.00	0.00

$$\text{Ca}^* = \text{Ca}/(\text{Ca}+\text{Na}+\text{K})$$

$$\text{Na}^* = \text{Na}/(\text{Ca}+\text{Na}+\text{K})$$

$$\text{K}^* = \text{K}/(\text{Ca}+\text{Na}+\text{K})$$

Table 5-2. Chemical compositions of the synthetic zeolites.

Zeolites Run no.	Gobbinsite					Amicite	
	A-08	B-04	B-08	C-04	C-11	C-19	C-20
SiO <sub>2</sub>	55.70	56.14	46.07	60.42	57.90	38.33	38.86
Al <sub>2</sub> O <sub>3</sub>	24.16	22.89	25.95	24.70	22.73	29.54	30.72
CaO	1.40	0.40	0.38	1.16	2.18	0.57	0.88
Na <sub>2</sub> O	8.12	8.94	10.25	7.99	7.65	6.99	4.93
K <sub>2</sub> O	0.49	1.08	0.50	0.66	0.20	10.80	10.94
Total (wt.%)	89.87	89.45	83.15	94.93	90.65	86.23	86.33
Unit cell compositions (on the basis of 32 oxygens)							
Si	10.89	11.06	9.92	11.12	11.18	8.57	8.60
Al	5.56	5.30	6.58	5.35	5.16	7.77	8.00
Ca	0.29	0.08	0.09	0.23	0.45	0.14	0.21
Na	3.07	3.41	4.27	2.85	2.86	3.03	2.11
K	0.12	0.27	0.14	0.16	0.05	3.08	3.09
SiO <sub>2</sub>	3.92	4.17	3.02	4.16	4.33	2.21	2.15
Al <sub>2</sub> O <sub>3</sub>							
Ca*	0.08	0.02	0.02	0.07	0.13	0.02	0.04
Na*	0.88	0.91	0.95	0.88	0.85	0.49	0.39
K*	0.04	0.07	0.03	0.05	0.02	0.49	0.57

$$\text{Ca}^* = \text{Ca}/(\text{Ca}+\text{Na}+\text{K})$$

$$\text{Na}^* = \text{Na}/(\text{Ca}+\text{Na}+\text{K})$$

$$\text{K}^* = \text{K}/(\text{Ca}+\text{Na}+\text{K})$$

## CONCLUSIONS AND DISCUSSION

The zeolites synthesized in the experiments are presumably related with compositions of starting materials and with temperature. It is considered that they are primarily determined by SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of the starting glasses. In other words, the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of a given zeolite is usually close to that of the glass. For instances, gismondine has the ratio 2.25~2.32 (2 or 3), garronite 3.15~4.21 (3 or 4), gobbinsite 3.02~4.33 (mostly 3 or 4), and amicite 2.15~2.21 (3) with the initial ratios of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> indicated in parentheses (Table 6). An exception is noted for gobbinsite synthesized in 1M NaOH solution. In this situation, gobbinsite can be synthesized in glasses with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios from 3 or 4 (in other liquid media) and then extending to 6

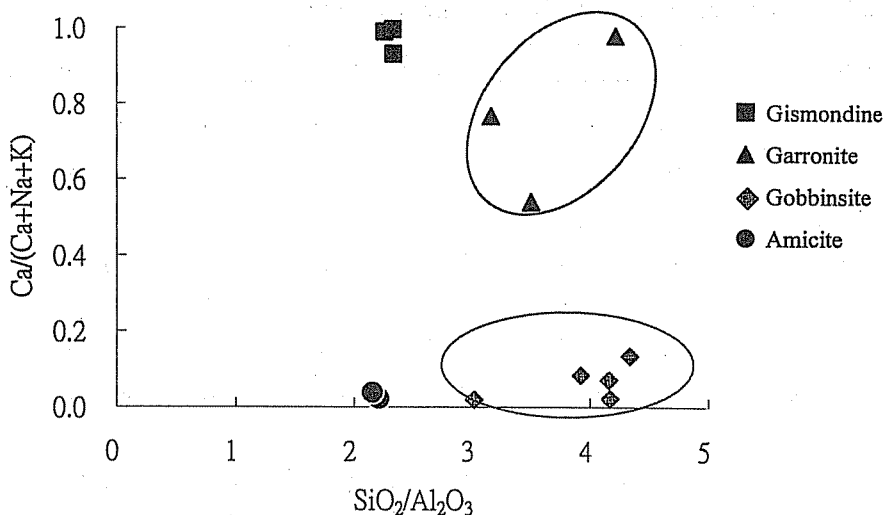


Figure 2. Ca/(Ca+Na+K) vs. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> plots of the synthetic zeolites.

and 8 (Figures 1-1, 1-2 and 1-3) in 1M NaOH solution. So, the closeness of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of gobbinsite synthesized to that of the starting glass seems to be ruled out for this mineral in a liquid medium of high alkalinity such as 1M NaOH solution.

As to cationic compositions, zeolites synthesized are controlled strongly by compositions of glasses and liquid media. Gobbinsite of low Ca/(Ca+Na+K) ratios (0.02~0.13) can be synthesized with Ca-rich glasses (CaO·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub> and 0.5CaO·0.5Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>) in 0.1 M Na<sub>2</sub>CO<sub>3</sub> or 0.1M NaOH solution (Table 6). Similarly, amicitte of low Ca/(Ca+Na+K) ratios (0.02~0.04) can be produced with the Ca-rich glass (0.75CaO·0.25Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub>) in 0.5M NaOH (+) 0.5M KOH solution (Table 6). Therefore, cationic compositions of liquid media seem more influential than those of glasses during syntheses of gobbinsite and amicitte. To the contrary, gismondine of high Ca/(Ca+Na+K) ratios (0.93~1.00) is essentially related with Ca-rich glasses (CaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and 0.75CaO·0.25Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub>) rather than compositions of liquid media (Table 6). In the meantime, the Ca/(Ca+Na+K) ratios of garronite seem to be influenced by compositions of both glasses and liquid media (Table 6).

Temperature may also play a role in the syntheses. It is found that garronite (150°C~210°C) and gobbinsite (110°C~210°C) can be synthesized up to higher temperatures than gismondine (110°C~180°C) and amicitte (110°C~150°C) (Table 3). In addition, at 210°C, garronite appears instead of gobbinsite in CaO·Al<sub>2</sub>O<sub>3</sub>·4SiO<sub>2</sub>, and 0.1M Na<sub>2</sub>CO<sub>3</sub> and 0.1M NaOH (+) 0.36M NaCl solutions (Fig. 1-1) or instead of gismondine in 0.75CaO·0.25Na<sub>2</sub>O·3SiO<sub>2</sub>, and 0.1M NaOH and 0.1M NaOH (+) 0.36M NaCl solutions (Fig. 1-3). Therefore, garronite is more stable than gobbinsite and gismondine at higher temperature, and this is consistent with the synthetic results of Taylor and Roy (1964).

As for chemical compositions of zeolites, gismondine and amicitte show little variation with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CaO/(Ca+Na+K) ratios in the ranges of 2.25~2.32, 2.15~2.21, and 0.93~1.00, 0.02~0.04, respectively (Table 6). On the other hand, garronite and gobbinsite show a greater compositional variation with the above two ratios in the ranges of 3.15~4.21, 3.02~4.33, and 0.54~0.98, 0.02~0.13, respectively (Table 6). It is generally considered that the chemical

Table 6. The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Ca/(Ca+Na+K) ratios of the zeolites synthesized under different conditions in the gismondine group.

Minerals	SiO <sub>2</sub>	Ca	Glass comp.	T (°C)	Liquid media
	Al <sub>2</sub> O <sub>3</sub>	(Ca+Na+K)			
Gismondine	2.32	1.00	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	150	NH <sub>4</sub> OH 1M
	2.25	0.99	CaO·Al <sub>2</sub> O <sub>3</sub> ·2SiO <sub>2</sub>	110	NaOH 0.1M
	2.32	0.93	0.75CaO·0.25Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	150	NaOH 0.1M (+) NaCl 0.36M
Garronite	4.21	0.98	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	210	NH <sub>4</sub> OH 1M
	3.50	0.54	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150	NaOH 0.1M
	3.15	0.77	0.75CaO·0.25Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	210	NaOH 0.1M (+) NaCl 0.36M
Gobbinsite	3.92	0.08	CaO·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180	Na <sub>2</sub> CO <sub>3</sub> 0.1M
	4.17	0.02	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150	NaOH 0.1M
	3.02	0.02	Na <sub>2</sub> O·Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	110	NaOH 1M
	4.16	0.07	0.5CaO·0.5Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	180	Na <sub>2</sub> CO <sub>3</sub> 0.1M
	4.33	0.13	0.5CaO·0.5Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·4SiO <sub>2</sub>	150	NaOH 0.1M
Amicite	2.21	0.02	0.75CaO·0.25Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	150	NaOH 0.5M (+) KOH 0.5M
	2.15	0.04	0.75CaO·0.25Na <sub>2</sub> O· Al <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub>	110	NaOH 0.5M (+) KOH 0.5M

composition of a mineral may be essentially related with its crystal structure, especially the distribution of Si and Al (Gottardi and Galli, 1985). Presumably, little variation of the chemical compositions of gismondine and amicite may probably be due to an ordered (Si, Al) distribution of their crystal structures (Fishcher and Schramm, 1971; Alberti and Vezzalini, 1979). Contrarily, a greater compositional variation of garronite and gobbinsite may be accounted for by their disordered (Si, Al) distribution of the two minerals (Baerlocher and Meier, 1972; Gottardi and Alberti, 1974; Artioli, 1992).

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