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THE SYNTHESIS OF MERLINOITE

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ABSTRACT

Syntheses of merlinoite were carried out in autoclaves using glasses with compositions representing feldspathic minerals in the presence of alkaline solutions. Experimental conditions were set with temperatures from 110°C to 210°C, at autogeneous pressures, and in durations from 3 to 140 days.

Merlinoite, merlinoite (+) orthoclase, merlinoite (+) montmorillonite, merlinoite (+) orthoclase (+) analcime, merlinoite (+) analcime, and merlinoite (+) chabazite have been synthesized. It is shown that mineral associations of merlinoite (+) orthoclase, merlinoite (+) montmorillonite, merlinoite (+) orthoclase (+) analcime, and merlinoite (+) analcime generally appear in the highest temperatures (180°C~210°C); merlinoite occurs as a single phase in the intermediate temperatures (150°C~180°C); and merlinoite associated with chabazite takes place in the lowest temperatures (110°C~150°C). Chemical analyses indicate that Si/Al ratios are in ranges of 1.56~2.49, 2.24~2.26, 1.62~1.65, and 1.66~2.62; and K/(K+Na+Ca) ratios are in ranges of 0.39~0.70, 0.65~0.85, 0.47~0.84 and 0.93~0.96 for the merlinoite synthesized in systems of $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$, orthoclase-albite, albite-anorthite, and $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$, respectively.

Merlinoite seems favorable to be produced with both K-bearing and K-free glasses, especially the former ones, in the presence of liquids with high concentration of K^+ like 1M KOH in this study at low temperatures. The Si/Al ratio of merlinoite is primarily determined by that of the starting glass. For cationic compositions of merlinoite, though Na content appears to be related with the starting glass, Ca content seems irrespective to its amount in the starting glass; and K content is mainly supplied from KOH solution. Available chemical data suggest that the highest content of Ca, Na, and K of merlinoite may be up to 20%, 60%, and 100%, respectively among the cationic components.

Key words: glasses, alkaline solutions, autoclaves, merlinoite, mineral associations

INTRODUCTION

Merlinoite was recognized as a new zeolitic mineral as late as 1977 by Passaglia *et al.* This mineral has been noted for its rarity in nature (Gottardi and Galli, 1985) and for its excellent capacity of ion-exchange and absorption (Sherman, 1978), especially, the latter one. The chemical formula of natural merlinoite has been given as $(K,Na)_5(Ba,Ca)_2Al_9Si_{23}O_{64}{\cdot}24H_2O$ (Passaglia *et al.*, 1977) or as $K_7Na_5Al_{12}Si_{20}O_{64}{\cdot}24H_2O$ (Yakubovich *et al.*, 1999), suggesting a variation in its cationic components. However, the extent of variation of each cationic component is not clearly known as yet and needs to be clarified through further synthetic studies.

Syntheses of merlinoite have been carried out using gels with compositions of K-aluminosilicate (Barrer and Baynham, 1956; Breck, 1974; Sherman, 1977; Skofteland *et al.*, 2001) and K-Na-aluminosilicate (Bosmans *et al.*, 1973; Donahoe *et al.*, 1984; Belhekar *et al.*, 1995); and using natural rocks such as rhyolitic pumice (Colella *et al.*, 1977), fly ash (Querol *et al.*, 1995), obsidian (Kawano and Tomita, 1997), and andesitic tuff (Lo *et al.*, 1999) in alkaline solutions. Mainly, the former two studies were made of course for the purpose of industrial uses, whereas the latter ones in an attempt to ascertain the natural occurrence of merlinoite. As a result, K-merlinoite and K-Na-merlinoite have been synthesized from the gels; and merlinoite has been prepared from the rocks as well, but no chemical data have been given.

This study attempts to synthesize merlinoite from glasses with compositions representing feldspathic minerals in alkaline solutions and to analyze chemical compositions of the merlinoite synthesized. As a consequence, conditions for the synthesis of merlinoite from the stated starting materials can be delineated; and the correlation between cationic components (K, Na, and Ca) of the synthetic merlinoite and those of the starting materials, and the extent of variation of each cationic component of K, Na, and Ca in merlinoite can be evaluated.

EXPERIMENTAL METHODS

Starting materials for experiments include two fractions: one is solid and the other is liquid. The solid materials include four systems, namely, $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$ (n=2, 4, 6, 8, 10), $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$ (n=2, 4, 6, 8), albite-anorthite, and orthoclase-albite, representing the composition of feldspathic minerals. Synthetic glasses with the compositions of the stated four systems were used as solid materials in experiments. The glasses were prepared by mixing of calcium carbonate, sodium carbonate, potassium carbonate, and aluminum oxide of Baker's reagents; and of quartz powder in a desired proportion. The mixtures were well mixed, and then put into graphite crucibles to melt in a high temperature furnace with a temperature range from 1400°C to 1650°C, depending on compositions of mixtures. The melts were quenched in the air to become homogeneous glasses. Chemical compositions of the glasses are shown in Table 1. It is noted that a trace amount of impurities such as TiO_2, Fe_2O_3, MgO etc. is believed to be inherited from chemical reagents. The liquid media involve sodium carbonate, sodium hydroxide and potassium hydroxide solutions with concentrations ranging from 0.1M to 1M.

Table 1. Chemical compositions of glasses.

Systems \ Oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Total (wt. %)
$Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$	43.00	0.12	36.52	0.65	0.02	0.15	20.49	—	100.95
$Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$	58.61	0.13	25.33	0.67	—	0.08	14.71	—	99.53
$Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$	67.26	0.13	19.44	0.68	—	0.05	11.48	—	99.04
$Na_2O{\cdot}Al_2O_3{\cdot}8SiO_2$	73.08	0.11	15.81	0.60	—	0.02	9.13	—	98.75
$Na_2O{\cdot}Al_2O_3{\cdot}10SiO_2$	77.90	0.13	13.22	0.57	—	—	7.62	—	99.44
$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	42.44	—	37.71	—	0.18	20.23	—	—	100.56
$CaO{\cdot}Al_2O_3{\cdot}4SiO_2$	59.62	—	26.13	—	0.11	14.03	—	—	99.89
$CaO{\cdot}Al_2O_3{\cdot}6SiO_2$	70.18	—	18.90	—	0.15	9.88	—	—	99.11
$CaO{\cdot}Al_2O_3{\cdot}8SiO_2$	75.25	—	15.89	—	0.13	8.61	—	—	99.88
$Ab_{75}An_{25}$	62.35	0.07	23.33	0.44	—	2.30	10.18	—	98.67
$Ab_{50}An_{50}$	56.17	0.04	28.35	0.29	—	5.60	8.38	—	98.83
$Ab_{25}An_{75}$	46.60	—	36.52	0.04	—	10.86	5.13	—	99.15
$Or_{25}Ab_{75}$	66.43	0.09	19.44	0.37	—	—	8.49	4.09	98.91
$Or_{50}Ab_{50}$	65.91	0.01	19.38	0.19	—	—	5.51	8.08	99.08
$Or_{75}Ab_{25}$	65.34	0.03	19.14	0.04	—	—	2.39	11.54	98.48

—: denoted to not detectable.

Each experiment was started with 2 grams of glass powder and 20 milliliters of liquid medium in a teflon-lined autoclave with a capacity of 35 milliliters. Meanwhile, experiments were carried out under the conditions of temperatures from 110°C to 210°C, at autogeneous pressures, and in durations ranging from 3 to 140 days.

Synthetic products were identified by using an X-ray diffractometer and a scanning electron microscope. Chemical compositions of synthetic minerals were analyzed by using an electron microprobe with feldspar standards, 15KV accelerating potential, beam current of 10nA, beam size of 10μm, and exposure duration of 10 seconds.

EXPERIMENTAL RESULTS

Experimental results are shown in Table 2 and are summarized in Figure 1. It is worthy of mention that only those relevant to the synthesis of merlinoite are given in the table. Syntheses of merlinoite in the four chemical systems are described as follows.

In the $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$ system, merlinoite, merlinoite (+) analcime, merlinoite (+) orthoclase, and merlinoite (+) chabazite have been synthesized. Merlinoite can be produced as a single phase in $Na_2O{\cdot}Al_2O_3{\cdot}4{\sim}8SiO_2$ and 0.1M KOH solution at 150°C; and in $Na_2O{\cdot}Al_2O_3{\cdot}6{\sim}10SiO_2$ and 1M KOH solution at 150°C and 180°C. Merlinoite associated with analcime can

Table 2. Experimental results

Run No.	Glass compositions	T (℃)	Liquid	Duration (days)	Products[1,2]
A-1	$Na_2O-Al_2O_3-6SiO_2$	180	NaOH 0.5M (+)KOH 0.5M	5	A+M
A-2	$Na_2O-Al_2O_3-4SiO_2$	180		18	A+M
A-3	$Na_2O-Al_2O_3-4SiO_2$	150		30	M
A-4	$Na_2O-Al_2O_3-6SiO_2$	150	KOH 0.1M	30	M
A-5	$Na_2O-Al_2O_3-8SiO_2$	150		30	M
A-6	$Na_2O-Al_2O_3-6SiO_2$	110		140	M+C
A-7	$Na_2O-Al_2O_3-4SiO_2$	210		3	M+A
A-8	$Na_2O-Al_2O_3-6SiO_2$	210		3	M+Or
A-9	$Na_2O-Al_2O_3-4SiO_2$	180		7	C+M
A-10	$Na_2O-Al_2O_3-6SiO_2$	180		3~7	M
A-11	$Na_2O-Al_2O_3-8SiO_2$	180		3~7	M
A-12	$Na_2O-Al_2O_3-10SiO_2$	180		3~7	M
A-13	$Na_2O-Al_2O_3-4SiO_2$	150	KOH 1M	7	M+C
A-14	$Na_2O-Al_2O_3-6SiO_2$	150		7	M
A-15	$Na_2O-Al_2O_3-8SiO_2$	150		7	M
A-16	$Na_2O-Al_2O_3-10SiO_2$	150		7	M
A-17	$Na_2O-Al_2O_3-4SiO_2$	110		20	C+M
A-18	$Na_2O-Al_2O_3-6SiO_2$	110		20	M+C
A-19	$Na_2O-Al_2O_3-8SiO_2$	110		20	M+C
A-20	$Na_2O-Al_2O_3-10SiO_2$	110		20	M+C
B-1	$CaO-Al_2O_3-4SiO_2$	180	KOH 0.1M	52	M
B-2	$CaO-Al_2O_3-4SiO_2$	210		3~20	M
B-3	$CaO-Al_2O_3-6SiO_2$	210		3	M+Or
B-4	$CaO-Al_2O_3-8SiO_2$	210		3	M+Or
B-5	$CaO-Al_2O_3-6SiO_2$	210		12	Or+M
B-6	$CaO-Al_2O_3-8SiO_2$	210		12	Or+M
B-7	$CaO-Al_2O_3-4SiO_2$	180		5~20	M
B-8	$CaO-Al_2O_3-6SiO_2$	180		5	M
B-9	$CaO-Al_2O_3-6SiO_2$	180	KOH 0.5M	20	M+Or
B-10	$CaO-Al_2O_3-8SiO_2$	180		5~20	M
B-11	$CaO-Al_2O_3-4SiO_2$	150		22	M+C
B-12	$CaO-Al_2O_3-6SiO_2$	150		8~14	M
B-13	$CaO-Al_2O_3-6SiO_2$	150		22	M+Or

Table 2. (continued)

B-14	$CaO-Al_2O_3-8SiO_2$	150		8~22	M + C
C-1	$Ab_{75}An_{25}$	210		3	A + M
C-2	$Ab_{50}An_{50}$	210		3	A + M
C-3	$Ab_{75}An_{25}$	180	NaOH 0.5M	5	M + A
C-4	$Ab_{50}An_{50}$	180	(+)KOH 0.5M	5	M + A
C-5	$Ab_{75}An_{25}$	150		7	M
C-6	$Ab_{50}An_{50}$	210	KOH 0.1M	7	M + A
C-7	$Ab_{50}An_{50}$	180		12	M
C-8	$Ab_{75}An_{25}$	210		3	M
C-9	$Ab_{50}An_{50}$	210		3	M
C-10	$Ab_{75}An_{25}$	180		5	M
C-11	$Ab_{50}An_{50}$	180	KOH 1M	5	M
C-12	$Ab_{75}An_{25}$	150		7	M
C-13	$Ab_{50}An_{50}$	150		7	C + M
C-14	$Ab_{75}An_{25}$	110		14	M
D-1	$Or_{25}Ab_{75}$	180		12	A+M
D-2	$Or_{50}Ab_{50}$	180	Na_2CO_3 0.1M	7	M + A + Or
D-3	$Or_{75}Ab_{25}$	180		12	M + Or + A
D-4	$Or_{25}Ab_{75}$	210		7	A + M
D-5	$Or_{50}Ab_{50}$	210		7	A + M + Or
D-6	$Or_{75}Ab_{25}$	210	NaOH 0.1M	7	M + Or + A
D-7	$Or_{25}Ab_{75}$	180		12	A+M
D-8	$Or_{50}Ab_{50}$	180		12	M + Or + A
D-9	$Or_{75}Ab_{25}$	180		12	M + Or
D-10	$Or_{25}Ab_{75}$	150		33	M
D-11	$Or_{25}Ab_{75}$	210		3	A + M
D-12	$Or_{50}Ab_{50}$	210		3	M
D-13	$Or_{75}Ab_{25}$	210		3	M
D-14	$Or_{25}Ab_{75}$	180	NaOH 0.5M	5	M
D-15	$Or_{50}Ab_{50}$	180	(+)KOH 0.5M	5	M
D-16	$Or_{75}Ab_{25}$	180		5	M
D-17	$Or_{50}Ab_{50}$	150		7	M
D-18	$Or_{75}Ab_{25}$	150		7	M
D-19	$Or_{25}Ab_{75}$	180		12	A + Or + M
D-20	$Or_{50}Ab_{50}$	180		12	Or+ M
D-21	$Or_{75}Ab_{25}$	180	KOH 0.1M	12	Or + M
D-22	$Or_{25}Ab_{75}$	150		40	M
D-23	Or_{50} Ab_{50}	150		40	M + C

Table 2. (continued)

D-24	$Or_{25}Ab_{75}$	210		3	M
D-25	$Or_{50}Ab_{50}$	210		3	M + mon
D-26	$Or_{75}Ab_{25}$	210		3	M + mon
D-27	$Or_{50}Ab_{50}$	210		6	M
D-28	$Or_{75}Ab_{25}$	210		6	M
D-29	$Or_{25}Ab_{75}$	180		5	M
D-30	$Or_{50}Ab_{50}$	180	KOH 1M	5	M
D-31	$Or_{75}Ab_{25}$	180		5	M
D-32	$Or_{25}Ab_{75}$	150		7	M
D-33	$Or_{50}Ab_{50}$	150		7	M
D-34	$Or_{75}Ab_{25}$	150		7	M
D-35	$Or_{25}Ab_{75}$	110		14	M
D-36	$Or_{50}Ab_{50}$	110		14	M
D-37	$Or_{75}Ab_{25}$	110		14	M

1. Abbreviations used: **A**: analcime; **M**: merlinoite; **Or**: orthoclase; **C**: chabazite; **mon**: montmorillonite
2. Synthetic minerals being listed in the order of decreasing amount

be yielded in $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ and 0.5M NaOH (+) 0.5M KOH mixed solution at 180°C; in $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ and 0.1M KOH solution at 180°C; and in $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ and 1M KOH solution at 210°C. Meanwhile, merlinoite together with orthoclase only appears in $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ and 1M KOH solution at 210°C. The association of merlinoite and chabazite occurs in $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ and 0.1M KOH solution at 110°C; in $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ and 1M KOH solution at 110°C, 150°C and 180°C; and in $Na_2O{\cdot}Al_2O_3{\cdot}6{\sim}10SiO_2$ and 1M KOH solution at 110°C [Table 2, Fig.1(a)].

In the $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$ system, merlinoite, merlinoite (+) orthoclase, and melrinoite (+) chabazite have been produced. Merlinoite occurs as a single phase in $CaO{\cdot}Al_2O_3{\cdot}4SiO_2$ and 0.1M KOH solution at 180°C; in $CaO{\cdot}Al_2O_3{\cdot}4SiO_2$ and 0.5M KOH solution at 210°C and 180°C; in $CaO{\cdot}Al_2O_3{\cdot}6SiO_2$ and 0.5M KOH solution at 180°C in 5 days and at 150°C in 8~14 days; and in $CaO{\cdot}Al_2O_3{\cdot}8SiO_2$ and 0.5M KOH solution at 180°C. Merlinoite associated with orthoclase happens in $CaO{\cdot}Al_2O_3{\cdot}6{\sim}8SiO_2$ and 0.5M KOH solution at 210°C; and in $CaO{\cdot}Al_2O_3{\cdot}6SiO_2$ and 0.5M KOH solution at 180°C in 20 days and at 150°C in 22 days. Merlinoite and chabazite can be produced in $CaO{\cdot}Al_2O_3{\cdot}4SiO_2$ and 0.5M KOH solution at 150°C; and in $CaO{\cdot}Al_2O_3{\cdot}8SiO_2$ and 0.5M KOH solution at 150°C [Table 2, Fig. 1(b)].

In the albite-anorthite system, merlinoite, merlinoite (+) orthoclase, merlinoite (+) analcime, and merlinoite (+) chabazite have been yielded. Merlinoite appears as a single phase in $Ab_{75}An_{25}$, and 0.5M NaOH (+) 0.5M KOH mixed solution at 150°C; in $Ab_{50}An_{50}$ and 0.1M KOH solution at 180°C; in Ab_{100} and 0.1M KOH solution at 150°C; in $Ab_{50\text{-}75}An_{50\text{-}25}$ and 1M KOH solution at 110°C~210°C except in $Ab_{50}An_{50}$ at 150°C; and in Ab_{100} and 1M KOH solution at 150°C and 180°C. Merlinoite associated with analcime has been yielded in $Ab_{50\text{-}100}An_{50\text{-}0}$ and 0.5M NaOH

(+) 0.5M KOH mixed solution at 180°C and 210°C; and in $Ab_{50}An_{50}$ and 0.1M KOH solution at 210°C. Merlinoite together with chabazite occurs in $Ab_{50}An_{50}$ and 1M KOH solution at 150°C, and in Ab_{100} and 1M KOH solution at 110°C [Table 2, Fig. 1(c)].

In the orthoclase-albite system, merlinoite, merlinoite (+) analcime (+) orthoclase, merlinoite (+) analcime, merlinoite (+) orthoclase, merlinoite (+) chabazite, and merlinoite (+) montmorillonite have been produced. Merlinoite occurs alone in $Or_{25}Ab_{75}$ and 0.1M NaOH

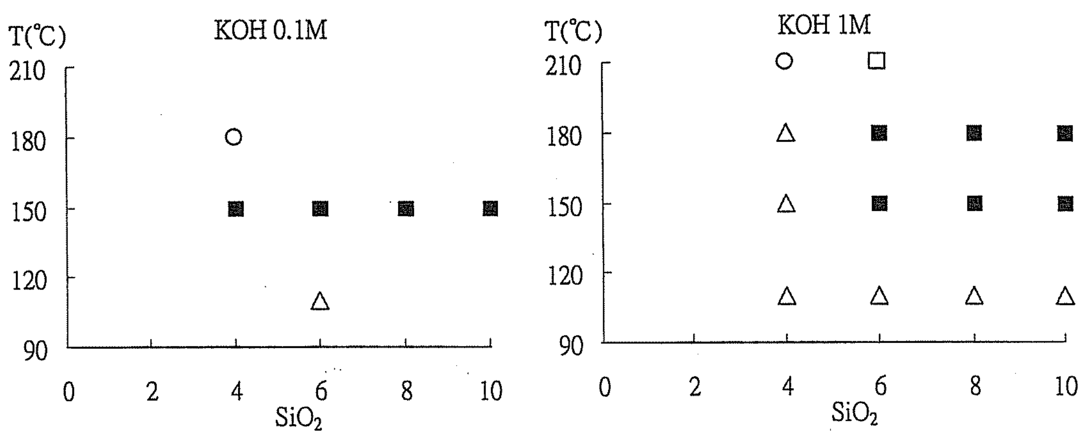


Figure 1(a). $Na_2O \cdot Al_2O_3 \cdot nSiO_2$ system

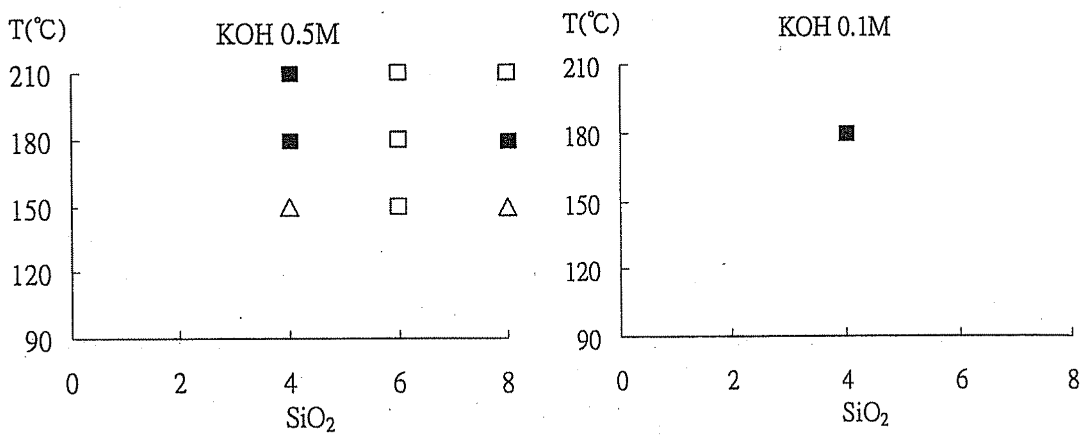


Figure 1(b). $CaO \cdot Al_2O_3 \cdot nSiO_2$ system

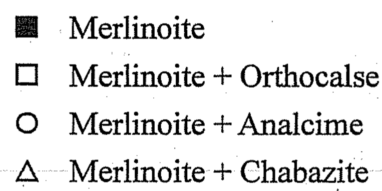
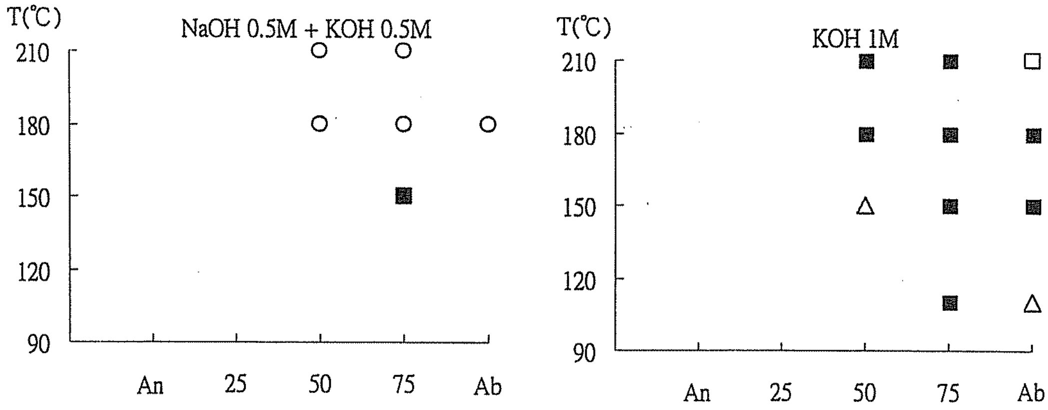


Figure 1. Diagrams illustrating the synthetic results



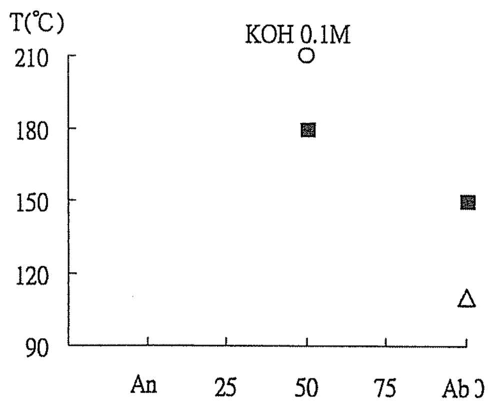


Figure 1. Diagrams illustrating the synthetic results

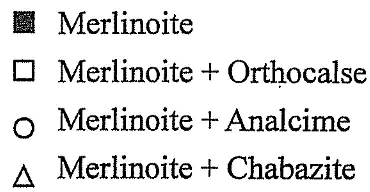
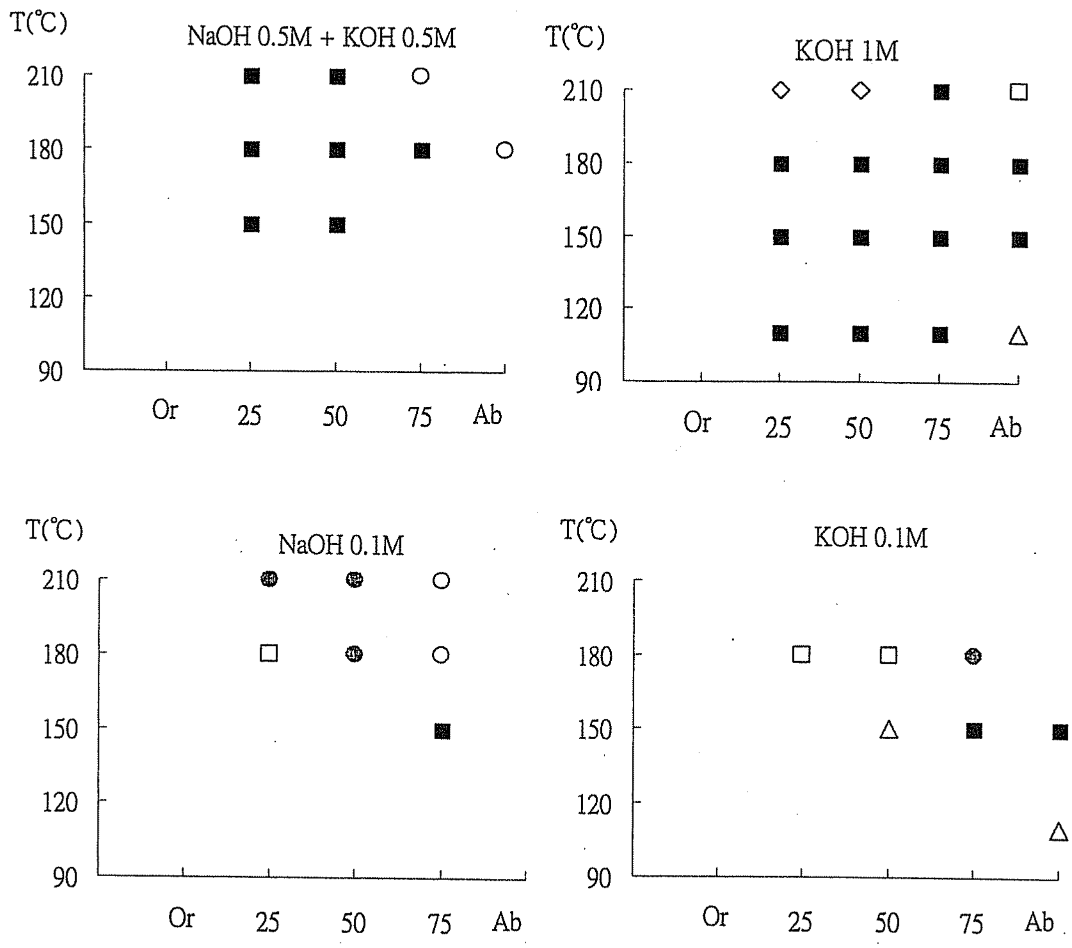


Figure 1(c). Albite-anorthite system

solution at 150°C; in $Or_{25-75}Ab_{75-25}$ and 0.5M NaOH (+) 0.5M KOH mixed solution at 150°C~210°C except in $Or_{25}Ab_{75}$ at 210°C; in $Or_{25-0}Ab_{75-100}$ and 0.1M KOH solution at 150°C; in $Or_{25-75}Ab_{75-25}$ and 1M KOH solution at 110°C~210°C except in $Or_{50}Ab_{50}$ and $Or_{75}Ab_{25}$ at 210°C; and in Ab_{100} and 1M KOH solution at 150°C and 180°C. Merlinoite associated with analcime and orthoclase appears in $Or_{50-75}Ab_{50-25}$ and 0.1M Na_2CO_3 solution at 180°C; in $Or_{50-75}Ab_{50-25}$ and 0.1M NaOH solution at 210°C, and $Or_{50}Ab_{50}$ at 180°C; and in $Or_{25}Ab_{75}$ and 0.1M KOH solution at 180°C. The association of merlinoite and analcime has been yielded in $Or_{25}Ab_{75}$ and 0.1M NaOH solution at 180°C and 210°C; in $Or_{25}Ab_{75}$ and 0.5M NaOH (+) 0.5M KOH mixed solution at 210°C; and in Ab_{100} and 0.5M NaOH (+) 0.5M KOH mixed solution at 180°C. Merlinoite together with orthoclase has been produced in $Or_{75}Ab_{25}$ and 0.1M NaOH solution at 180°C; in $Or_{50-75}Ab_{50-25}$ and 0.1M KOH solution at 180°C; and in Ab_{100} and 1M KOH solution at 210°C. Merlinoite associated with chabazite takes place only in $Or_{50}Ab_{50}$ and 0.1M KOH solution at 150°C; in Ab_{100} and 0.1M KOH solution at 110°C; and in Ab_{100} and 1M KOH solution at 110°C. Merlinoite occurs together with montmorillonite in $Or_{50-75}Ab_{50-25}$ and 1M KOH solution at 210°C [Table 2, Fig. 1(d)].



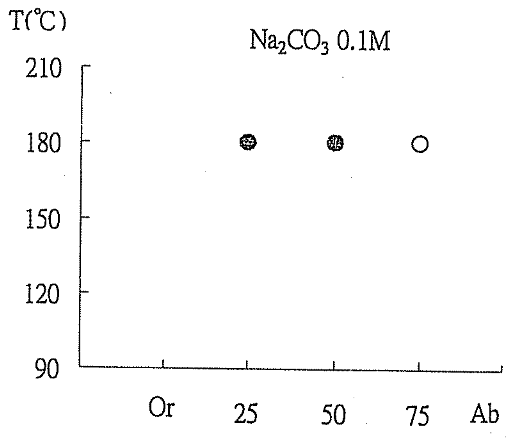


Figure 1. Diagrams illustrating the synthetic results

- ■ Merlinoite
- □ Merlinoite + Orthocalse
- ○ Merlinoite + Analcime
- ◍ Merlinoite + Analcime + Orthoclase
- △ Merlinoite + Chabazite
- ◇ Melrinoite + Montmorillonite

Figure 1(d). Orthoclase-albite system

Chemical compositions of the synthetic merlinoite are indicated in Table 3. The analytical errors were estimated to be less than 3% for Na_2O, and less than 2% for the others of the reported values. It is found that chemical compositions of the synthetic merlinoite vary with wide extent in different conditions. For the analytical data available, Si/Al ratios are in the ranges of 1.56~2.49, 2.24~2.26, 1.62~1.65, and 1.66~2.62; and K/(K+Na+Ca) ratios are in the ranges of 0.39~0.70, 0.65~0.85, 0.47~0.84, and 0.93~0.96 for the merlinoite synthesized in the system of $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$, orthoclase-albite, albite-anorthite, and $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$, respectively (Table 3). It should be noted that a minor amount of cationic components is believed to be inherited from impurities of chemical reagents used. For instances, a minor amount of Ca and Na in the merlinoite synthesized in the system of $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$ and $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$ is inherited from the initial glasses and liquid media, respectively (Table 3).

CONCLUSIONS AND DISCUSSIONS

Experimental results suggest that the synthesis of merlinoite is essentially influenced by the solid composition, liquid medium and temperature. Merlinoite is favorably produced in silica-rich portions in the systems of $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$ (n=4~10) [Fig.1(a)] and of $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$ (n=4~8) [Fig.1(b)]. It can be yielded only in albite-rich portions (Ab=50~100) in the albite-anorthite system [Fig.1(c)], but in the whole compositions of the orthoclase-albite system [Fig.1(d)]. As to the effect of liquid medium, merlinoite can only be produced in KOH solution if starting glasses are K-free as in the system of $Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2$ [Fig.1(a)], $CaO{\cdot}Al_2O_3{\cdot}nSiO_2$ [Fig.1(b)], and albite-anorthite [Fig.1(c)]. On the other hand, merlinoite can be synthesized in NaOH or Na_2CO_3 solution if glasses are K-contained as in the orthoclase-albite system [Fig. 1(d)]. The KOH solution of higher concentration (0.5~1.0M) is generally favorable to the formation of merlinoite as a single phase or in association with other phases in a wider range of glass composition under the given systems [Fig.1(a), (b), (c) and (d)]. It is also noted that merlinoite and its associations only appear in NaOH or Na_2CO_3 solution of low concentration (0.1M) [Fig.1(d)]. Mineral associations synthesized are generally affected by the temperature. The associations of merlinoite (+) orthoclase, merlinoite (+) analcime, and merlinoite (+) orthoclase (+) analcime usually occur above 180°C [Fig. 1(a), (b), (c) and (d)]. On the other hand, the association of merlinoite (+) chabazite generally takes place below 150°C [Fig.1(a), (b), (c) and (d)], while merlinoite associated with montmorillonite only happens at 210°C. Meanwhile, merlinoite seems favorable to appear as a single phase at 150°C and 180°C [Fig.1 (a), (b), (c) and (d)]. So, merlinoite, a K-bearing mineral, can be formed with K-free solid materials in K-bearing liquid media [Fig. 1(a), (b), (c)], or with K-bearing solid materials in K-free liquid media [Fig.1(d)]. Hence, it is easy to see that natural merlinoite can be found in K-rich rocks as nepheline melilitite (Passaglia *et al.*, 1977; Alberti *et al.*, 1979) and granitic pegmatite (Khomyakov *et al.*, 1981), or in low-K pyroxene-rich ejecta (Gottardi and Galli, 1985). Lo *et al.*(1999) reported that merlinoite would be transformed to K-feldspar at 180°C in longer runs. This is also suggested by the present experiments which show that the association of merlinoite (+) orthoclase usually takes place at higher temperatures (210°C and 180°C, Table 2) and longer duration (ex: $CaO{\cdot}Al_2O_3{\cdot}6SiO_2$, 180°C, 5 and 20 days). In these situations, merlinoite should be considered to be metastable. It is believed that merlinoite may be stable below 150°C so far as this study is concerned, since the association of merlinoite (+) orthoclase has been synthesized at 150°C (B-13, Table 2).

Table 3. Chemical compositions of the synthetic merlinoite (microprobe data in wt%)

	$Na_2O·Al_2O_3·nSiO_2$ system				Or–Ab system		Ab-An system	
Run	A-3	A-5	A-10	A-11	D-16	D-31	C-6	C-11
no.	n=4	n=8	n=6	n=8	$Or_{75}Ab_{25}$	$Or_{75}Ab_{25}$	$Ab_{50}An_{50}$	$Ab_{50}An_{50}$
SiO_2	53.93	52.41	45.98	53.25	53.76	53.86	48.93	47.81
Al_2O_3	23.09	17.91	25.03	21.73	20.41	20.23	25.20	25.14
CaO	0.40	0.18	0.85	0.85	0.15	0.17	1.55	0.29
Na_2O	6.65	4.62	2.98	2.90	3.83	1.39	5.50	1.64
K_2O	6.64	9.23	12.16	11.48	10.86	12.59	8.56	14.67
Total	90.71	84.35	87.00	90.21	89.01	88.23	89.73	89.55
	Calculated on the basis of 64 oxygens							
Si	21.61	22.82	19.93	21.86	22.29	22.53	20.23	20.23
Al	10.89	9.17	12.76	10.50	9.96	9.96	12.26	12.52
Ca	0.17	0.08	0.39	0.37	0.07	0.08	0.69	0.13
Na	5.16	3.89	2.50	2.30	3.07	1.13	4.40	1.34
K	3.40	5.13	6.73	6.02	5.75	6.72	4.52	7.92
2Ca+Na+K	8.90	9.18	10.01	9.06	8.96	8.01	10.30	9.52
Si/Al	1.98	2.49	1.56	2.08	2.24	2.26	1.65	1.62
K/(Ca+Na+K)	0.39	0.56	0.70	0.69	0.65	0.85	0.47	0.84

	$CaO·Al_2O_3·nSiO_2$ system				
Run	B-1	B-2	B-7	B-11	B-14
no.	m=4	m=4	m=4	m=4	m=8
SiO_2	49.69	49.02	47.62	45.50	56.48
Al_2O_3	22.48	23.10	24.41	21.87	18.31
CaO	0.20	0.05	0.33	0.19	0.57
Na_2O	0.35	0.46	0.44	0.47	0.35
K_2O	15.82	15.86	17.15	17.96	13.82
Total	88.54	88.49	89.95	86.00	89.53
	Calculated on the basis of 64 oxygens				
Si	21.24	21.00	20.31	20.55	23.31
Al	11.31	11.64	12.25	11.62	8.89
Ca	0.09	0.02	0.15	0.09	0.25
Na	0.29	0.38	0.36	0.41	0.28
K	8.63	8.67	9.34	10.35	7.28
2Ca+Na+K	9.1	9.09	10.00	10.94	8.06
Si/Al	1.88	1.80	1.66	1.77	2.62
K/(Ca+Na+K)	0.96	0.96	0.95	0.95	0.93

Consequently, it seems that merlinoite is favorably produced with both K-bearing and K-free solid materials, especially the former one, in the presence of liquids with high concentration of K^+ (Skofteland *et al.*, 2001) like 1M KOH in this study at a low temperature. Accordingly, it is not surprised to see that merlinoite has been found in rhyolitic tuff of Searles Lake under the condition of high-K water and ambient temperature (Donahoe, 1990).

Chemical analyses show that compositions of the synthetic merlinoite are variable in terms of Si/Al ratio and cationic content (Table 3). As shown in Table 3, Si/Al ratios vary from 1.56 to 2.62. The variation of Si/Al ratios can also be found in natural merlinoite (Table 4), and it is in the range from 1.67 to 2.56 (Donahoe *et al.*, 1990) Hence, the (Si, Al)-disorder in the framework of merlinoite proposed by Galli *et al.* (1979) is thus supported. Meanwhile, it is found that Si/Al ratio of the synthetic merlinoite is positively correlated with that of the starting material as illustrated in Figure 2. So, it is reasonable to assume that Si/Al ratio of merlinoite is primarily determined by that of the starting material.

Table 4. Cationic contents of natural merlinoite (data from literature, calculated on the basis of 64 oxygens).

	Cupello, Italy (Passaglia *et al.*,1977)	Vuonnemiok River, Khibiny (Khomyakov *et al.*,1981)	Kola Peninsula (Baturin *et al.*, 1985)	Kukisvumchorr mountain, Khibn (Yakubovich *et al.*,1999)
Si	22.68	20.15	20	20
Al	9.31	12.71	12	12
Ca	1.49	0	0	0
Na	0.55	1.14	1	5
K	4.21	4.15	5	7
Ba	0.43	1.71	3	0
Si/Al	2.44	1.59	1.67	1.67

In terms of chemical formula based on 64 oxygens, the amount of Ca, Na, and K of the synthetic merlinoite is in the range of 0.02~0.69, 0.28~5.16, and 3.40~10.35, respectively (Table 3). The distribution of its cationic components in a K-Na-Ca plot is indicated in Figure 3. It is clear that Ca content is invariably low (< 10% among the cationic components) and seems irrespective of the amount of this component in starting glasses. On the other hand, Na content may be up to about 60% , the highest content of Na so far reported (Figure 4), and appears to be related with its quantity in starting glasses, while K content may be up to about 96% and is mainly supplied from KOH solution (see also Tables 2 and 3). Combining available chemical data of the synthetic and natural merlinoite as displayed in Figure 4, it is suggested that the highest content of Ca, Na, and K of merlinoite may be up to 20%, 60%, and 100%, respectively among the cationic components. In addition, the total amount of cationic components (2Ca+Na+K) is also variable (8.01~10.94) (Table 3) and is negatively correlated with the Si/Al ratio as illustrated in Figure 5. In other words, the higher Si/Al ratio is, the lower total amount of cationic components will be. Basically, this is on account of charge balance.

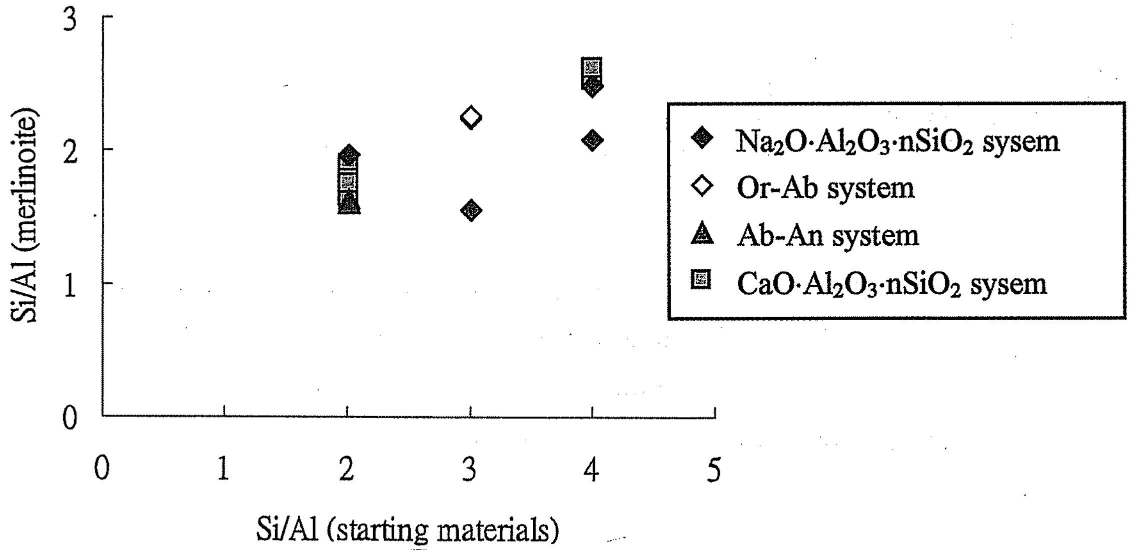


Figure 2. Relationship of Si/Al ratios between the synthetic merlinoite and its starting materials

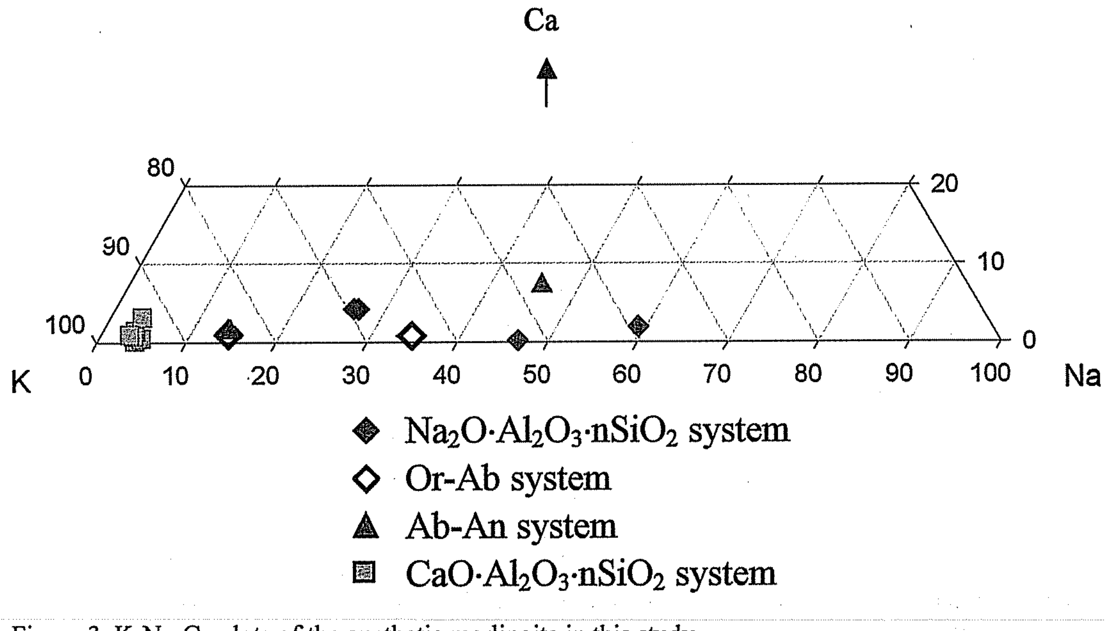
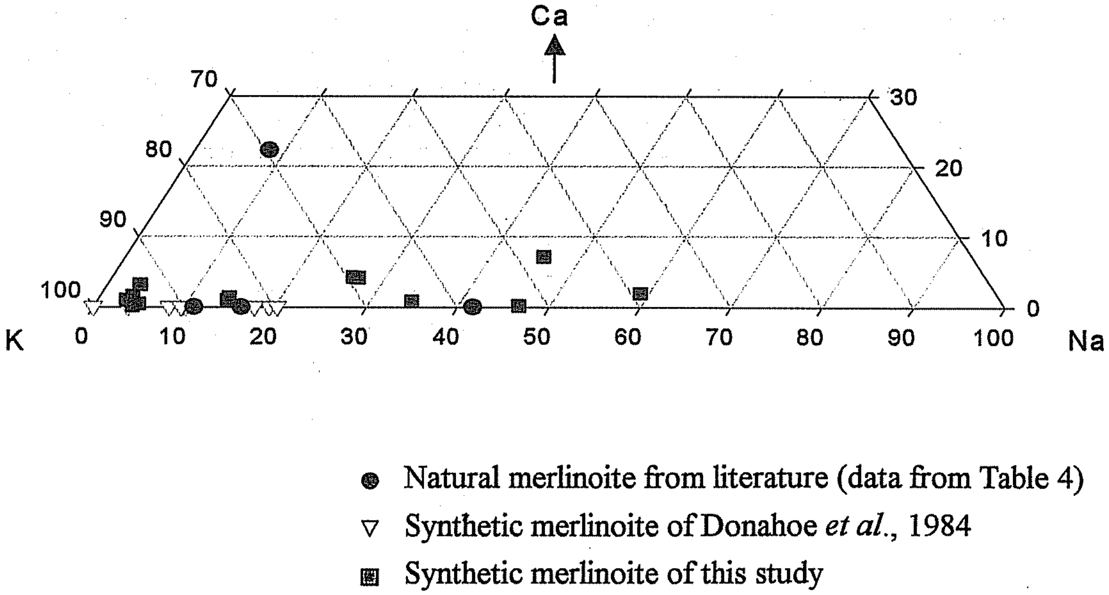


Figure 3. K-Na-Ca plots of the synthetic merlinoite in this study



Fiqure 4. K-Na-Ca plots of the natural and synthetic merlinoite

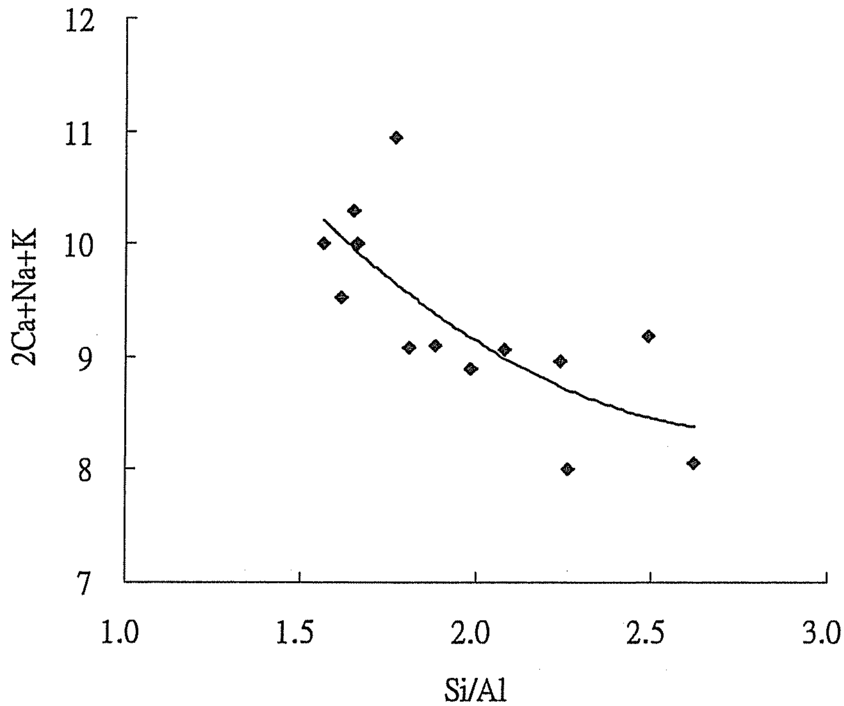


Figure 5. Relationship between the sum of 2Ca+Na+K and the Si/Al ratio of the merlinoite synthesized

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