THE SYNTHESIS OF PHILLIPSITE

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ABSTRACT

Syntheses of phillipsite were carried out in autoclaves using glasses with compositions representing three chemical systems, namely, $Na_2O \cdot Al_2O_3 \cdot nSiO_2$ (n=2~10), albite-anorthite, and orthoclase-albite in the presence of alkaline solutions. Experiments were set under the conditions of temperatures from 110°C to 210°C, autogeneous pressures, and durations from 7 to 53 days. Synthetic products were examined by an X-ray diffractometer, scanning electron microscope and electron microprobe.

The synthetic phillipsite has been designated K-rich, Na-rich, and Ca-rich phillipsite. K-rich phillipsite generally appears in glasses of the Or-Ab system with NaOH solution, and in those of Or-Ab and Ab-An systems with NaOH (+) KOH mixed solution. Na-rich phillipsite occurs in glasses of the Or-Ab system with NaOH (+) NaCl mixed solution, and in those of the $Na_2O \cdot Al_2O_3 \cdot nSiO_2$ system with KOH solution. Ca-rich phillipsite only takes place in the glass of $Ab_{25}An_{75}$ with KOH solution.

Phillipsite occurs as a single phase at temperatures below 150°C, but it usually associates with other phases above that temperature. Chemical analyses show that Si/Al ratios are in ranges of 1.65~2.23, 3.07~3.77, and 1.24~1.28; and K/(Ca+Na+K) ratios are in ranges of 0.48~0.56, 0.21~0.43, and 0.13~0.14 for the synthetic phillipsite being desingnated K-rich, Na-rich, and Ca-rich phillipsite, respectively.

Phillipsite seems favorable to be produced with solid materials of alkali feldspathic compositions in the presence of liquid with high Na^+ concentration at low temperatures. It is found that both the Si/Al ratio and cationic composition of phillipsite are primarily determined by those of solid starting materials.

Key words: Phillipsite, syntheses, autoclaves, glasses, alkaline solutions

INTRODUCTION

Phillipsite is a very common and abundant zeolite of sedimentary origin including sea-water (Bonatti, 1956; Stonecipher, 1976; Bernat and Church, 1978; Honnorez, 1978) and saline-lake environments (Sheppard and Gude, 1968, 1973; Sheppard and Fitzpatrick, 1989). Field studies seem to suggest that the genesis of natural phillipsite may be essentially related with volcanic rocks of basic to acid compositions (Dunham, 1933; Iijima and Harada, 1969; Sheppard et al., 1970; Gottardi and Galli, 1985). Hence, natural phillipsite displays a wide range of chemical composition, perhaps the widest among zeolites (Galli and Loschi Ghittoni, 1972).

Experiments on the synthesis of phillipsite have extensively been carried out on account of its industrial uses and abundance in nature. Sersale et al. (1965) obtained phillipsite starting from an aluminosilicate glass with K, Na, and Ca hydrothermally treated in NaOH (+) KOH mixed solution. Kühl (1969) used phosphate as a complex agent for a batch of metasilicate, and NaOH and KOH to get phillipsite. Colella and Aiello (1975) reported on low temperature (~80°C) synthesis of phillipsite with a rhyolitic pumice reacting in a NaOH (+) KOH mixed solution. Donahoe et al. (1984) claimed that phillipsite was easily synthesized in K- and Na-bearing systems.

In this study, the synthesis of phillipsite is going to be undertaken using synthetic glasses with compositions of feldspathic minerals and liquid media with compositions similar to those of the sea-water and saline-lake water to simulate sedimentary environments. Hence, the purposes of this study are two folds. Firstly, it is attempted to delineate favorable physicochemical conditions for the genesis of phillipsite. Secondly, it is tried to find out factors controlling the wide range of chemical composition of natural phillipsite.

EXPERIMENTAL METHOD

The starting materials used in the experiments include two fractions: one is a solid and the other is a liquid. Solid materials are constituted of three chemical systems, namely, $Na_2O \cdot Al_2O_3 \cdot nSiO_2$ (n=2~10), albite-anorthite, and orthoclase-albite. Each starting material was prepared by mixing of Na_2CO_3 (Baker analyzed, 99%) and/or $CaCO_3$ (Baker analyzed, 98%) or K_2CO_3 (Baker analyzed, 99%), Al_2O_3 (Baker analyzed, 99.4%) and quartz (SiO_2) powder in a required proportion. After well-mixed, the mixtures were put into a graphite crucible, and then were melted in a high temperature furnace with temperatures ranging from 1400°C to 1650°C, depending on the composition of mixtures. The melt was quenched in the air to become homogeneous glass, which was ground to powder for experiments. 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 TiO_2, Fe_2O_3 and MgO shown in Table 1 is inherited from the chemical reagents used. The liquid media include 0.1M and 1M NaOH, 0.1M NaOH (+) 0.36M NaCl, 0.1M and 1M KOH, and 0.5M NaOH (+) 0.5M KOH solutions. Teflon-lined autoclaves with a volume 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 with 2g solid and 20ml liquid for each 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 7 to 53 days.

Table 1. Chemical compositions of synthetic glasses of different systems.

Oxides / Systems	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
Plagioclase An_{100}	42.44	—	37.71	—	0.18	20.23	—	—	100.56
Plagioclase $Ab_{25} An_{75}$	46.60	—	36.52	0.04	—	10.86	5.13	—	99.15
Plagioclase $Ab_{50} An_{50}$	56.17	0.04	28.35	0.29	—	5.60	8.38	—	98.83
Plagioclase $Ab_{75} An_{25}$	62.35	0.07	23.33	0.44	—	2.30	10.18	—	98.67
Alkali feldspar $Or_{25}Ab_{75}$	66.43	0.09	19.44	0.37	—	—	8.49	4.09	98.91
Alkali feldspar $Or_{50}Ab_{50}$	65.91	0.01	19.38	0.19	—	—	5.51	8.08	99.08
Alkali feldspar $Or_{75}Ab_{25}$	65.34	0.03	19.14	0.04	—	—	2.39	11.54	98.48

— : denoted not detectable

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, exposure duration of 10-sec, and feldspars as standards.

EXPERIMENTAL RESULTS

The experimental results relevant to the synthesis of phillipsite are shown in Table 2. For the convenience of description, the synthetic phillipsite has been arbitrarily designated K-rich, Na-rich, and Ca-rich phillipsite based on the chemical composition as displayed in Table 3 and X-ray diffraction data as indicated in Table 4. The synthetic phillipsite is characterized by prismatic crystals [Pl. 1(a)]; and the crystals are usually twins [Pl. 1(b)], and grow into spherical aggregates [Pl. 1(c)].

Syntheses of phillipsite in different liquid media (Table 2) are described as follows. In 1M NaOH solution, K-rich phillipsite appears as a single phase in compositions of $Or_{50 \sim 75}Ab_{50 \sim 25}$ at 110°C and 150°C. In 0.5M NaOH (+) 0.5M KOH mixed solution, K-rich phillipsite and K-rich phillipsite associated with orthoclase have been synthesized. K-rich phillipsite can be produced as a single phase in glasses of Ab_{100} at 110°C and 150°C, $Ab_{50 \sim 75}An_{50 \sim 25}$ at 110°C, and $Or_{25 \sim 75}Ab_{75 \sim 25}$ at 110°C and 150°C. On the other hand, K-rich phillipsite associated with other minerals occurs only in the glass of $Ab_{50}An_{50}$ at 150°C. In 0.1M NaOH (+) 0.36M NaCl mixed solution, Na-rich phillipsite, and Na-rich phillipsite (+) analcime (+) orthoclase have been yielded. Na-rich phillipsite takes place in glasses of $Or_{25 \sim 75}Ab_{75 \sim 25}$ at 110°C, and $Or_{25 \sim 50}Ab_{75 \sim 50}$

Table 2. Experimental results.

Run no.	Glass comp.	Temp (°C)	Solution	Duration (days)	Products[a, b]
A01	$Or_{50}Ab_{50}$	150	1M NaOH	7	P_1
A02	$Or_{50}Ab_{50}$	110		14	P_1
A03	$Or_{75}Ab_{25}$	150		7、14	P_1
A04	$Or_{75}Ab_{25}$	110		14	P_1
B01	Ab_{100}	150		10	P_1
B02	Ab_{100}	110		23	P_1
B03	$Ab_{75}An_{25}$	110		14	P_1
B04	$Ab_{50}An_{50}$	150	0.5M NaOH (+)	7	$P_1 + X$
B05	$Ab_{50}An_{50}$	110	0.5M KOH	14	P_1
B06	$Or_{25}Ab_{75}$	150		7	P_1
B07	$Or_{25}Ab_{75}$	110		14	P_1
B08	$Or_{50}Ab_{50}$	110		14	P_1
B09	$Or_{75}Ab_{25}$	110		14	P_1
C01	$Or_{25}Ab_{75}$	180		12	$A + P_2 + Or$
C02	$Or_{25}Ab_{75}$	150		17	P_2
C03	$Or_{25}Ab_{75}$	110	0.1M NaOH (+)	53	P_2
C04	$Or_{50}Ab_{50}$	180	0.36M NaCl	12	$P_2 + Or + A$
C05	$Or_{50}Ab_{50}$	150		33	P_2
C06	$Or_{50}Ab_{50}$	110		53	P_2
C07	$Or_{75}Ab_{25}$	110		53	P_2
D01	$Ab_{25}An_{75}$	210		7	$P_3 + X$
D02	$Ab_{25}An_{75}$	180		12	P_3
D03	$Ab_{25}An_{75}$	150	0.1M KOH	17	P_3
D04	Ab_{100}	180		18	$P_2 + Or$
D05	$Na_2O \cdot Al_2O_3 \cdot 8SiO_2$	180		18	$P_2 + Or$

a. Abbreviations used: P_1: K-rich phillipsite ; P_2: Na-rich phillipsite ; P_3:Ca-rich phillipsite ; A: analcime; Or: orthoclase; X: other synthetic minerals

b. synthetic minerals listed in the order of decreasing amount

Table 3. Chemical compositions of the synthetic phillipsite.

Zeolite	K-rich Phillipsite				Na-rich Phillipsite			Ca-rich Phillipsite	
Run no.	A03	B02	B03	B04	C02	C03	D04	D01	D02
SiO_2	53.65	54.58	52.31	44.73	66.27	61.97	66.16	41.37	44.09
Al_2O_3	21.43	20.83	20.27	23.02	14.96	17.15	15.64	28.45	29.30
CaO	0.49	0.04	1.19	1.22	0.29	0.24	0.01	11.55	10.20
Na_2O	5.19	5.92	4.46	4.48	4.48	4.02	6.96	3.16	3.06
K_2O	7.61	10.25	8.57	9.91	4.75	4.70	2.88	2.08	2.13
Total wt (%)	88.37	91.62	86.80	83.36	90.75	88.08	91.65	86.61	88.78
Calculated on the basis of 32 oxygens									
Si	11.04	11.04	11.05	10.08	12.73	12.29	12.56	8.84	9.09
Al	5.19	4.96	5.04	6.10	3.38	4.00	3.49	7.15	7.11
Ca	0.11	0.01	0.27	0.29	0.06	0.05	0.00	2.65	2.25
Na	2.07	2.32	1.82	1.95	1.67	1.54	2.56	1.31	1.22
K	2.00	2.65	2.31	2.85	1.16	1.19	0.70	0.57	0.56
Si/Al	2.13	2.23	2.19	1.65	3.77	3.07	3.60	1.24	1.28
Ca*	0.03	0.00	0.06	0.06	0.02	0.02	0.00	0.58	0.56
Na*	0.49	0.47	0.41	0.38	0.58	0.55	0.79	0.29	0.30
K*	0.48	0.53	0.53	0.56	0.40	0.43	0.21	0.13	0.14

Ca*= Ca/(Ca+Na+K)
Na*= Na/(Ca+Na+K)
K*= K/(Ca+Na+K)

at 150°C. In the meantime, the association of Na-rich phillipsite, analcime, and orthoclase occurs in glasses of $Or_{25\sim50}Ab_{75\sim50}$ at 180°C. Finally, in 0.1M KOH solution, Ca-rich phillipsite, Ca-rich phillipiste (+) other minerals, and Na-rich phillipsite (+) orthoclase have been produced. Ca-rich phillipsite happens as a single phase in the glass of $Ab_{25}An_{75}$ at 150°C and 180°C, but Ca-rich phillipsite in association with other minerals occurs in the same glass at 210°C. On the other hand, Na-rich phillipsite together with orthoclase takes place in glasses of Ab_{100} and $Na_2O{\cdot}Al_2O_3{\cdot}8SiO_2$ at 180°C.

Chemical compositions of the synthetic phillipsite are listed in Table 3. The analytical errors were estimated to be less than 3% for Na_2O and 2% for the others of the reported values. It is obvious that the synthetic phillipsite varies to some extent in the chemical composition. For the available chemical data, Si/Al ratios are in the ranges of 1.65~2.23, 3.07~3.77, and 1.24~1.28; and K/(Ca+Na+K) ratios are in the ranges of 0.48~0.56, 0.21~0.43, and 0.13~0.14 for the synthetic phillipsite being designated K-rich, Na-rich, and Ca-rich phillipsite, respectively (Table 3).

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

| Synthetic Phillipsite (this study)						Natural Phillipsite (Gottardi and Galli, 1985)			
P_1		P_2		P_3		Casal Brunori, Italy		Montegalda, Italy	
d (Å)	I / Io	d (Å)	I / Io	d (Å)	I / Io	d (Å)	I / Io	d (Å)	I / Io
8.10	13	8.05	11	8.14	4	8.11	8	8.15	5
7.09	70	6.99	49	7.15	81	7.18	63	7.14	74
6.38	7			6.35	3	6.42	17	6.39	4
5.35	12	5.33	8	5.38	6	5.38	19	5.36	24
5.02	18					5.07	23	5.04	15
4.96	28	4.95	27	4.98	54	4.94	27	4.95	15
4.29	8	4.24	7	4.25	36	4.31	8	4.29	15
4.11	44			4.12	52	4.12	41	4.11	32
		4.06	22	4.06	30	4.06	18	4.07	9
3.26	19			3.32	16	3.27	37	3.26	26
3.23	27							3.22	20
3.19	100	3.21	40	3.18	100	3.21	100	3.19	100
3.15	47	3.15	100	3.15	76	3.14	35	3.14	21
2.94	19	2.93	11	2.92	8	2.93	15	2.93	13
2.75	21			2.74	43	2.75	36	2.74	17
2.69	39	2.72	17	2.70	97	2.70	36	2.69	25
		2.67	20			2.68	21	2.67	13

Notes: P_1: K-rich phillipsite ; P_2: Na-rich phillipsite; P_3: Ca-rich phillipsite
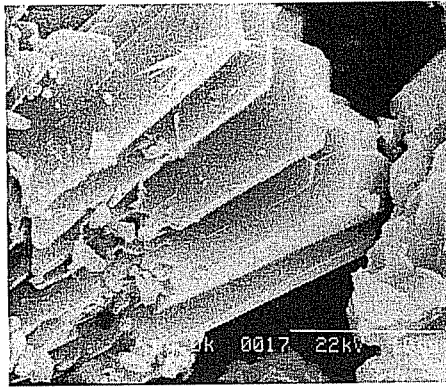
(a)
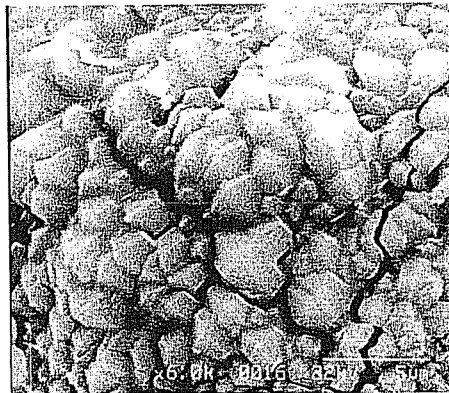
(b)
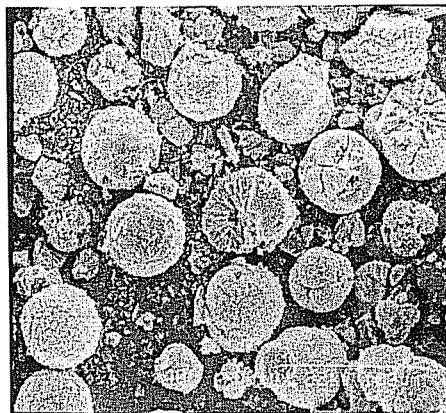
(c)

Plate 1. Micrographs displaying the crystal growth of the synthetic phillipsite.
(a) Prismatic crystals
(b) Twinned crystals
(c) Spherical crystal aggregates

CONCLUSIONS AND DISCUSSION

Experimental results suggest that the synthesis of phillipsite can be affected by the solid composition, liquid medium, and temperature. For the influence of the solid composition, K-rich phillipsite is in favor of being produced from alkali feldspar system owing to the presence of a sufficient amount of potassium in the system (Table 2). Similarly, Na-rich phillipsite is expected to be yielded in the Na-bearing systems of alkali feldspar and $Na_2O \cdot Al_2O_3 \cdot 6 \sim 8SiO_2$, whereas Ca-rich phillipsite is reasonable to be found in the Ca-rich system of plagioclase (Table 2). As to the effect of the liquid medium, K-rich phillipsite can be produced in 1M NaOH solution and in 0.5M NaOH (+) 0.5M KOH mixed solution; Na-rich phillipsite seems favorable to be yielded in 0.1M NaOH (+) 0.36M NaCl mixed solution; and Ca-rich phillipsite only appears in 0.1M KOH solution. It is likely that both the solid composition and liquid medium may mutually determine the composition of synthetic phillipsite. However, liquid medium may also play a critical role to affect the composition of phillipsite. In a given starting solid, $Or_{50}Ab_{50}$ for instance, K-rich phillipsite appears in 1M NaOH, and 0.5M NaOH (+) 0.5M KOH mixed solutions; but Na-rich phillipsite takes place instead in 0.1M NaOH (+) 0.36M NaCl mixed solution (Table 2). In a whole, K-rich, Na-rich, and Ca-rich phillipsites have mostly been synthesized as a single phase in experiments. Noteworthily, the former two happen at temperatures (110°C, 150°C) lower than those (150°C, 180°C) of the latter one. Meanwhile, at higher temperatures ($\geq$ 180°C), phillipsite is usually associated with other minerals (Table 2). In these situations, phillipsite is considered to be synthesized metastably as inferred from DTG analysis which shows an obvious dehydration of phillipsite at 120°C (Reeuwijk, 1974). Consequently, it seems that phillipsite is favorable to be produced with the solid material of alkali feldspathic compositions in the presence of liquids with high concentration of Na^+ at low temperature. Accordingly, it is not surprised to see the common occurrence of phillipsite in deep-sea (Bonatti, 1965; Stonecipher, 1976; Bernat and Church, 1978; Honnorez, 1978), and in saline lake environments (Sheppard and Gude, 1968, 1973; Sheppard and Fitzpatrick, 1989) where the concentration of Na^+ is rather high, namely 0.5M in sea water (Chen, 1994), and 0.6M in saline lake water (Davies, 1996) and the temperature is low. Thus, the predominant sedimentary origin of phillipsite is easily explained.

Chemical analyses indicate that the composition of the synthetic phillipsite is variable in terms of the Si/Al ratio and the cationic content (Table 3). As displayed in Table 3, the Si/Al ratio varies greatly from 1.24 to 3.77 supporting the (Si, Al)-disorder of the framework of phillipsite suggested by Sadanaga *et al.* (1961). Based on the Si/Al ratio, the phillipsite synthesized can arbitrarily be grouped into low Si/Al (1.24~1.28), medium Si/Al (1.65~2.23), and high Si/Al (3.07~3.77) phillipsite. Coincidently, they correspond to Ca-rich, K-rich, and Na-rich phillipsite, respectively. Meanwhile, it is revealed that the Si/Al ratio of the synthetic phillipsite is positively correlated with that of the starting material as illustrated in Figure 1. Presumably, the Si/Al ratio of phillipsite is primarily determined by that of the starting material. This postulate is certainly supported by natural occurrences of phillipsite. It was reported that low Si/Al, medium Si/Al, and high Si/Al phillipsite were found in melilite-nephelinite (Dunham, 1933; Iijima and Harada, 1969), in deep-sea sediments of basaltic composition (Sheppard *et al.*, 1970; Stonecipher, 1978), and in rhyolitic tuffs (Hay, 1964; Sheppard *et al.*, 1970), respectively.

In terms of chemical formula based on 32 oxygens, the amount of Ca, Na, and K of the synthetic phillipsite is in the range of 0~2.65, 1.22~2.56, and 0.56~2.85, respectively (Table
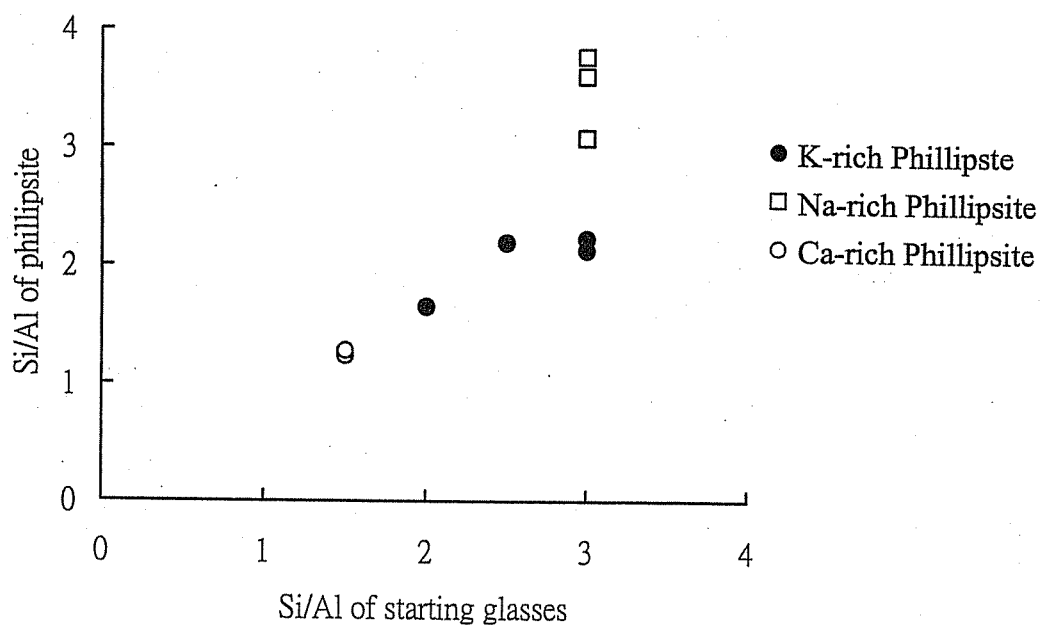
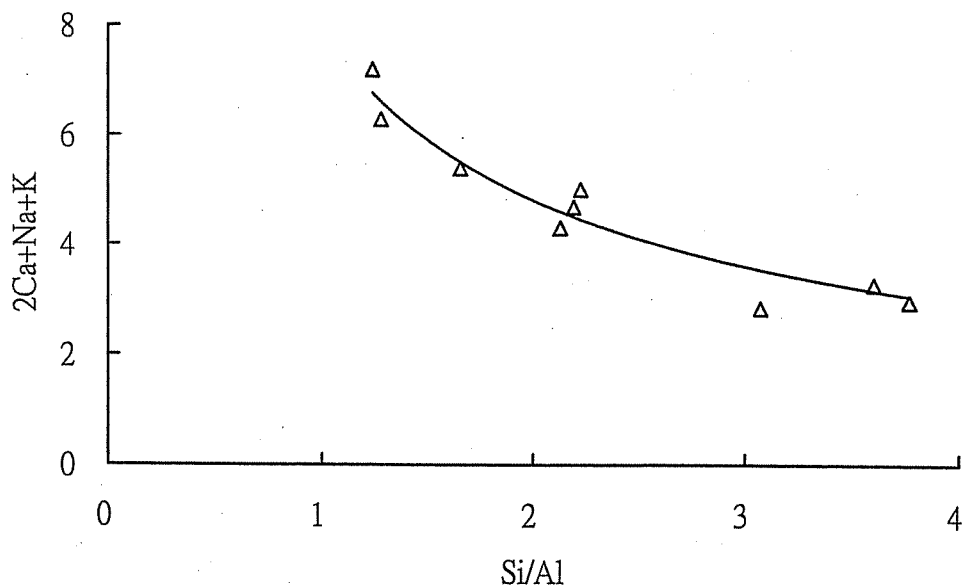Figure 1. The relationship of Si/Al ratios between starting glasses and the synthetic phillipsite.

Figure 2. The relationship between Si/Al ratios and the sum of 2Ca+Na+K of the synthetic phillipsite.
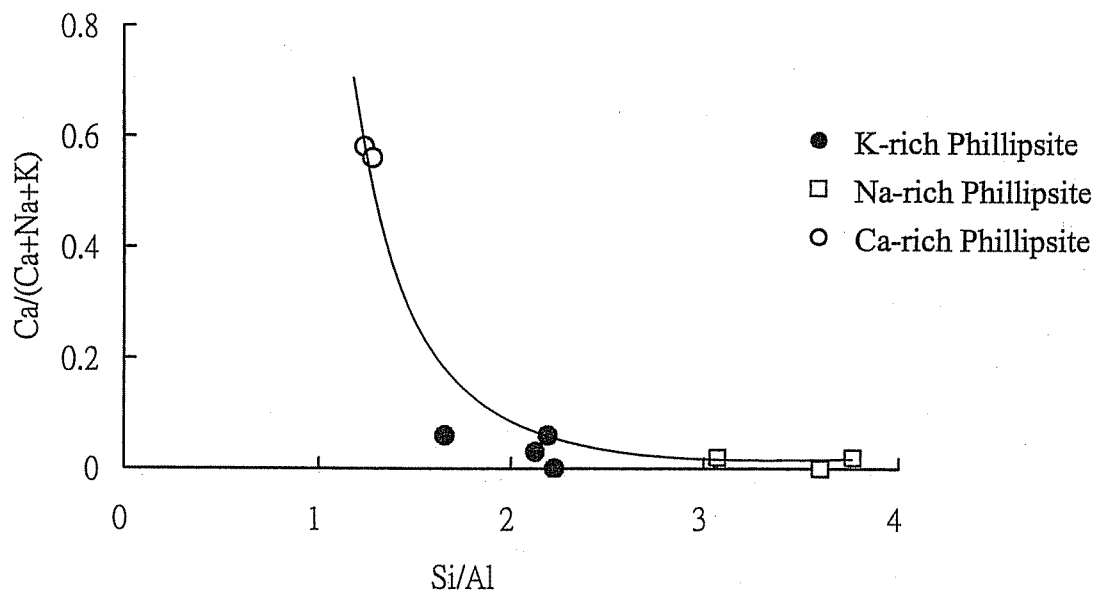
3). Besides, the total amount of cationic components (2Ca+Na+K) is also variable and is inversely correlated with the Si/Al ratio as shown in Figure 2. In other words, the higher the Si/Al ratio is, the lower the total amount of the cationic components will be. This is due to a substitution of Al for Si being coupled with an incorporation of cationic component into the crystal lattice.

The distribution of cationic components of phillipsite in a K-Na-Ca plot is illustrated in Figure 3. Obviously, natural phillipsite shows a wide range of cationic composition, and the phillipsite synthesized only falls in the Ca-poor and Ca-rich field in Figure 3. Surprisingly, phillipsite of intermediate composition (i.e., between Ca-poor and Ca-rich) has not been synthesized in the experiments. As mentioned previously, the Si/Al ratio of phillipsite is essentially determined by that of the solid starting material (Figure 1); and the Ca-rich, K-rich, and Na-rich phillipsite is coincident with low Si/Al, medium Si/Al, and high Si/Al phillipsite (Figure 4), respectively. Accordingly, it is reasonably to assume that the cationic compositions of phillipsite are mainly affected by the starting material as well. As stated above, phillipsite of intermediate compositions has not been synthesized in the experiments suggesting that phillipsite with these compositions may be derived from feldspathic minerals and other aluminosilicate minerals in addition so as to have proper Si/Al ratios as well as suitable Ca content.

● K-rich Phillipsite
□ Na-rich Phillipsite
○ Ca-rich Phillipsite
⬭ Natural phillipsite (Galli and Loschi Ghittoni, 1972)

Figure 3. Ca-Na-K plot of the synthetic and natural phillipsite.

Figure 4. The relationship between ratios of Si/Al and Ca/(Ca+Na+K) of the synthetic phillipsite.

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