ARTIFICIAL CRYSTALLIZATION OF VOLCANIC GLASS TO SODIUM AND POTASSIUM FORM OF CHABAZITE AT ROOM PRESSURE

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Abstract: In this study we used volcanic glass from Kagoshima. In the system of glass+NaOH, initial crystallization of the sodium form of chabazite occurs, followed by a gradual conversion to zeolite X, and finally Na-P zeolite begins to crystallize.

In the system of glass+KOH, the potassium form of chabazite was formed after boiling for 14 hours.

High structure form of albite was formed from the sodium form of chabazite upon heating at 530°C and the potassium form of chabazite was broken upon heating at 1000°C.

There is replacement of the type $\text{Ca} \rightleftharpoons \text{Na}_2 \rightleftharpoons \text{K}_2$ in chabazite.

INTRODUCTION

Chabazite is typically found in crevices and amygdales in basalt and andesite, and related igneous rocks, where it occurs associated with stilbite, mesolite, mordenite, heulandite, apophyllite, etc. Chabazite also occurs in cavities and joints as a result of hydrothermal mineralization.

Many reports have been published concerning the hydrothermal synthesis of zeolites. The synthetic production of the potassium form of chabazite from a potassium aluminosilicate gel with appropriate composition which had been subjected to hydrothermal crystallization, was reported by Barrer and Baynham (1956). Concerning synthesis of zeolite at room pressure only a few experiments have been reported (Sudo and Matsuoka, 1959).

Chabazite is one of the more common low-temperature zeolites. It can be regarded as a hydration product of volcanic glasses and lavas. This fact led to a suggestion that the crystallization of chabazite may occur easily at low temperature and pressure among volcanic glass and various alkaline solutions.

This paper proposes to communicate that the chemical reactions easily occur at room pressure and temperature less than 100°C by digesting volcanic glass

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with NaOH or KOH solution. Such observations have led to the industrial significance of sodium or potassium form of chabazite syntheses from naturally occurring materials, particularly volcanic glasses and pumice, in well defined experimental conditions.

STARTING MATERIAL

The original volcanic glass used for this study is found in widespread occurrence particularly in the southern part of Kyūshū, Japan. The mineral and chemical compositions, and the genesis of the volcanic glass which is so-called "Shirasu" were studied by Ōba, *et al.* (1967a, b). The chemical composition of the specimen collected from Gokoku-zinsha, Kagoshima city, Kagoshima prefecture is listed in Table 4. The microscopic observation revealed that it consists of small amounts of feldspar, hypersthene, hornblende and quartz. After pulverizing to fine powder with an agate mortar, this specimen was used for experiments.

EXPERIMENTAL

One gram of powdered sample was boiled with 5% of NaOH or KOH solution. After boiling for a desired time, the sample was washed with distilled water by filtering until the filtrate showed no alkaline reaction. The washed sample was dried in air and investigated by X-ray, differential thermal, infrared absorption and chemical analyses.

(A) Reaction between volcanic glass and NaOH.

Observation was made on the reaction of one gram of powdered sample with 5% NaOH solution in a glass jar upon heating it at about 100°C for various periods of time. During the first 6 hours none of zeolite phases were crystallized, but after boiling for 7 hours the initial crystallization of the sodium form of chabazite occurred, followed by a gradual conversion to zeolite X, and finally Na-P zeolite of cubic form began to crystallize. Single phases of the sodium form of chabazite and zeolite X could not be obtained. A single Na-P zeolite phase of cubic form was obtained when the run was carried for more than 20 hours. The Na-P zeolite phase of cubic form was stable and persisted up to 150 hours boiling. The X-ray powder data of the specimens of zeolite X and Na-P zeolite are listed in Table I.

(B) Reaction between volcanic glass and KOH.

One gram of powdered sample was boiled in 50 ml of 5% KOH solution for various periods of time. During the first 12 hours any zeolite phase could not be obtained, and the potassium form of chabazite was crystallized after boiling for more than 13 hours. A single phase of the potassium form of chabazite was obtained after boiling for more than 20 hours. At least the single phase

Table 1. X-ray powder diffraction data for zeolite X and Na-P zeolite. (CuK α) = 1.5418Å

hkl	zeolite X		hkl	Na-P zeolite	
	d (Å)	I		d (Å)	I
111	14.4	100	110	7.08	55
220	8.76	65	200	5.01	31
311	7.50	50	211	4.10	54
222			310	3.16	100
400			321	2.68	44
331	5.72	65	400	2.51	8
422			411,330	2.36	7
333,511	4.85	35	422	2.05	3
440	4.37	100	510,431	1.969	9
620	3.90	65	440	1.774	4
533	3.79	65	530,433	1.720	7
622	3.75	*	600,422	1.669	6
444	3.59	*	611,532	1.626	4
551,711	3.50	50			
642	3.34	*			
553,731	3.25	*			
800					
644,820	3.02	50			
660,822	2.93	*			
555,751	2.85	35			
840	2.79	50			
911	2.73	35			
664	2.65	*			
931	2.62	35			

* reflections overlapped by reflections of sodium form of chabazite or Na-P zeolite.

persisted in boiling up to 200 hours.

SYNTHESIZED SODIUM FORM OF CHABAZITE AND POTASSIUM FORM OF CHABAZITE

X-ray analysis

The sodium form of chabazite which was synthesized by 10 hours boiling was analysed. We could not obtain a single phase of sodium form of chabazite and in this sample a small amount of zeolite X was included. The X-ray powder data of the specimen are listed in Table 2 together with those of natural chabazite. Lattice dimensions were obtained from powder data: $a=13.56\text{\AA}$, $c=15.27\text{\AA}$, all being $\pm 0.02\text{\AA}$. The unit cell dimensions of the zeolite were determined by the following method: Peaks were scanned at a rate of $1/4^\circ\ 2\theta$ per minute on chart scale of $1/4^\circ\ 2\theta$ per cm. The silicon peak positions were

Table 2. X-ray powder data of sodium form of chabazite and potassium form of chabazite. ($\text{CuK}\alpha$) = 1.5418 Å

	1		2		3	
hkl	d (Å)	I	d (Å)	I	d (Å)	I
101	9.5	70	9.50	71	9.35	45
110	7.0	40	7.03	21	6.86	16
012	6.4	10	6.46	7		
021	5.6	40	5.61	18	5.54	13
003	5.0	40	5.09	25	5.04	14
211	4.35	90	4.37	53	4.33	51
122,300	3.90	20	3.91	35	3.87	29
*	3.61	50	3.62	62	3.60	16
220,104	3.47	20	3.48	18	3.44	11
401	2.95	100	2.95	100	2.93	100
410	2.62	20	2.62	9	2.61	18
125,232	2.51	30	2.53	16	2.51	19
333	2.10	20	2.10	12	2.09	10
	1.82	30	1.83	14	1.82	10
	1.74	20	1.71	9	1.73	10

1. Chabazite from Herval, Santa Catherina, south-eastern Brazil.
2. Sodium form of chabazite.
3. Potassium form of chabazite.
- *, Not indexed.

used as standards. The cell dimensions were calculated from the Q_{hkl} values. Accuracy of $\pm 0.02 \text{ Å}$ was estimated for the unit cell measurement.

High structure form of albite was derived from the sodium form of chabazite upon heat treatment at 530°C for one hour. The X-ray powder data of the albite are listed in Table 3.

The X-ray powder data of the potassium form of chabazite are given in Table 2 together with those of the sodium form of chabazite and natural chabazite. The X-ray powder data are similar to those of the sodium form of chabazite. The unit cell dimensions for the potassium form of chabazite are $a = 15.12 \text{ Å}$, $c = 13.42 \text{ Å}$. The potassium form of chabazite collapsed on heat treatment at 1000°C .

Differential thermal analysis

Differential thermal analysis curves were taken by an automatic thermal analyser at a heating rate of 10°C per minute for the sodium form of chabazite and the potassium form of chabazite. They are shown in Fig. 1 together with that of the original volcanic glass. The curve of the volcanic glass shows no

Table 3. X-ray powder diffraction data for albite.

$$(\text{CuK}\alpha) = 1.5418 \text{ \AA}$$

hkl	Natural Albite		Synthesized Albite	
	d (Å)	I	d (Å)	I
020	6.37	30	6.37	25
111	5.91	4		
111	5.61	4		
201	4.02	34	4.04	34
111	3.85	12		
130	3.79	43	3.76	36
130	3.66	30	3.66	32
131	3.51	12	3.48	27
112	3.38	15	3.36	65
040			3.20	100
002	3.19	100	3.18	80
220			3.13	25
131	2.97	20	3.02	8
041				
022	2.93	22	2.93	48
222				
131	2.87	15	2.84	15
132	2.64	9	2.65	17
112	2.56	12	2.52	15

Albite : From Amelia, Virginia, U. S. A.

reaction peaks. But the curves of both sodium and potassium forms of chabazite show only a broad endothermic peak between 100°C and 200°C. The curve of the sodium form of chabazite shows an endothermic peak at about 150°C and the curve of the potassium form of chabazite shows an endothermic peak at about 145°C. The broad endothermic peak at about 150°C was identical to that of previous workers (Koizumi, 1953; Koizumi and Kiriya, 1953).

Infrared absorption spectra

Infrared absorption spectra were obtained using a IR-6 type spectrophotometer with the Nujol past method. Fig. 2 shows spectra of the sodium form and potassium form of chabazite. Both spectra are quite similar and the bands of absorption around 3450 cm^{-1} are probably due to adsorbed water as indicated by comparison with montmorillonite data of Wolff (1965). The absorption bands at 3450 cm^{-1} in the water-stretching region are broad and spread toward higher frequencies. This phenomenon has also been described in stilbite by Harada and Tomita (1967). It may be explained if a part of water in these zeolites is structurally bound. The absorption bands around 3600 cm^{-1} may be attributed to structurally bound water. A clear asymmetrical absorption at 1640 cm^{-1} due to adsorbed water is visible.

Fig. 1. Differential thermal analysis curves of volcanic glass (1), sodium form of chabazite (2) and potassium form of chabazite (3).

Chemical compositions

The specimens were analysed chemically. The results are listed in Table 4 together with that of the original volcanic glass. The sodium form of chabazite contains a remarkable amount of sodium. The potassium form of chabazite contains a remarkable amount of potassium. A hershelite variety from Sicily contains over 8 per cent of Na_2O (Irrera, 1949), but such potassium form of chabazite has not previously been reported.

Amounts of Exchangeable Cations

Amounts of exchangeable cations of the sodium form and potassium form of chabazite were measured by the Schollenberger and Simon's method (Schollenberger and Simon, 1945). The Sodium form and potassium form of chabazite were pulverized in an agate mortar and 0.2 g of powdered sample was mixed with 2g of quartz powder, and a complete mixture thus obtained was

Fig. 2. Infrared absorption spectra of sodium form of chabazite (1) and potassium form of chabazite (2)

Note: Dotted line indicates the elimination of the peak due to Nujol.

packed into a glass tube, which is 12 cm in length and 1.3 cm in inner diameter with a stem of 4 cm length and 0.3 cm inner diameter. To prevent loss of the samples, absorbent cotton was placed at the bottom of the tube. Ammonium acetate solution (pH=7, 1N, 100 ml.) was passed through the column for the duration between 7 and 10 hours. The amounts of exchangeable calcium and magnesium ions in the effluent were chemically determined and those of potassium and sodium ions were determined by flame photometer. The results are listed in Table 5. The amount of exchangeable sodium ion in the sodium form of chabazite is larger than that of the potassium form of chabazite, whereas the potassium form of chabazite contains a remarkable

Table 4. Chemical compositions of volcanic glass, sodium form of chabazite and potassium form of chabazite.

No.	1	2	3
SiO ₂	71.40%	46.77%	51.34%
TiO ₂	0.25	0.24	0.46
Al ₂ O ₃	13.65	17.80	19.14
Fe ₂ O ₃	0.76	)	)
FeO	1.55		
MnO	0.04	0.02	—
MgO	0.48	0.93	0.75
CaO	1.88	2.38	3.11
Na ₂ O	3.36	1.54	6.78
K ₂ O	2.70	11.70	1.94
H ₂ O+	3.40	7.82	6.62
H ₂ O—	0.62	7.66	6.20
P ₂ O ₅	0.05	0.03	0.05
Total	100.14%	99.30%	99.50%

1. Volcanic glass.
2. Potassium form of chabazite.
3. Sodium form of chabazite.

amount of exchangeable potassium ion as compared with that of the sodium form of chabazite.

DISCUSSION

The ideal composition of chabazite is $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$. Coombs *et al.* (1959) gave the composition as $(\text{Ca}, \text{Na}_2, \text{K}_2)_5 \text{Al}_{10}\text{Si}_{26}\text{O}_{72} \cdot 36\text{H}_2\text{O}$ to $(\text{Ca}, \text{Na}_2, \text{K}_2)_{6.75} \text{Al}_{13.5}\text{Si}_{22.5}\text{O}_{72} \cdot 36\text{H}_2\text{O}$. Our experimental studies suggest that almost all Ca^{2+} , K^+ and Na^+ in chabazite should be exchangeable, which is in contrast to the wairakite-analcime substitutions. Such replacement is possible from the stand point of the crystal structure of chabazite (Dent and Smith, 1958). This is common phenomenon in zeolites.

The potassium form and sodium form of chabazite were easily crystallized from volcanic glass at room pressure. This experiment suggests that NaOH and KOH seem to behave as catalyst in the course of crystallization of volcanic glass; probably it may take an important role to break the network linkage of Si(Al)-oxygen in volcanic glass and facilitate the rearrangement of atoms toward new crystalline materials. This experiment is interesting from the industrial point of view.

Table 5. Amounts of exchangeable cations of the sodium form of chabazite and the potassium form of chabazite. (me/100g)

sodium form of chabazite		potassium form of chabazite	
Na ⁺	200	Na ⁺	14
K ⁺	3	K ⁺	178
Mg ⁺⁺	7.5	Mg ⁺⁺	9.8
Ca ⁺⁺	7.4	Ca ⁺⁺	7.3

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常圧下での火山ガラスからのナトリウム質リョウ沸石 とカリウム質リョウ沸石人工結晶化

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摘 要

鹿児島県に広く分布する火山ガラスを原料にしてナトリウムに富むリョウ沸石とカリウムに富むリョウ沸石を常圧下で合成した。リョウ沸石において $\text{Ca}_2 \rightleftharpoons \text{Na}_2 \rightleftharpoons \text{K}_2$ の置換が可能であることがわかった。ナトリウムに富むリョウ沸石を 530°C で 1 時間加熱することによって曹長石が生成した。