

SYNTHESIS OF SMECTITE FROM VOLCANIC GLASS AT LOW TEMPERATURE

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Abstract—Smectite and zeolites were formed from a volcanic glass as the products of reaction with NaOH solution at 90°C and 100°C under atmospheric pressure. Formation conditions of smectite and various zeolites were determined by the ratio of the amounts of volcanic glass (g) to NaOH (g) in the solution. Smectite was formed under the condition that the values of weight of volcanic glass (g)/(NaOH(g)/40) are between 0.5 and 6. Fe was an important constituent of the octahedral layer of smectite.

Key Words—Low temperature, Smectite, Sodium hydroxide concentration, Synthesis, Volcanic glass, Zeolites.

INTRODUCTION

Synthesis of smectite at elevated temperatures and pressures from oxides and hydroxides and from various minerals has been carried out by many researchers (Noll, 1930, 1935, and 1936; Bowen and Tuttle, 1949; Yoder, 1952; Sand *et al.*, 1953; Roy and Roy, 1955; Tomita, 1970), but it has been rarely achieved at atmospheric pressure (von Sedleckij, 1937; Farmer *et al.*, 1991). Zeolites are easily formed from volcanic glasses as reaction products with alkali solutions at atmospheric pressure (Sudo and Matsuoka, 1959; Tomita *et al.*, 1969), but formation of smectite from volcanic glass at 1 atm has not yet been reported. Smectite is commonly found as a weathering product in various rocks and sediments. In the pyroclastic flow deposits of southern Kyushu, Japan, smectite is present as a weathering product of volcanic glass (Tomita and Onishi, 1976). This study was undertaken to simulate the alteration of volcanic glass to smectite and zeolites at atmospheric pressure in the laboratory.

EXPERIMENTAL MATERIALS AND METHODS

Starting materials and methods

Volcanic glass in the pumice from the Osumi pumice fall at Kanoya, Kagoshima Prefecture, Japan, was pulverized in an agate mortar, and powdered samples were used for the experiments. It was confirmed by XRD and TEM that the volcanic glass did not contain smectite, and only small amounts of plagioclase and pyroxene were observed by microscopic observation. The X-ray powder diffraction pattern for the starting sample is shown in Figure 1 (curve 1), and no smectite peaks are observed. Chemical composition of the start-

ing volcanic glass is listed in Table 1. The sample was placed in a Teflon flask with various concentration of NaOH solution (0.1 ~ 10 M) and the reaction was carried out while keeping the concentration of NaOH solution constant at 90°C or 100°C. After reaction, the sample was washed with distilled water on filter paper and excess salt thus removed. The product was air-dried, and oriented specimens were made smearing a clay paste onto a glass slide, and investigated by X-ray diffraction analysis. Total chemical analysis, infrared absorption spectroscopy, and scanning electron microscopy were carried out.

RESULTS

Effects of solid/solution ratio on the reaction products

Experiments were carried out changing only the amounts of volcanic glass. Reaction products of volcanic glass and 10 ml of 1 M NaOH solution at 90°C are listed in Table 2. When the amounts of the volcanic glass are small, smectite formed after 3 days of reaction. Zeolite P, zeolite E, and chabazite were formed by increasing the amounts of the volcanic glass.

Relationship between concentration of NaOH solution and reaction products

Experiments were carried out by changing the concentration of NaOH solution against constant weight of volcanic glass. Volcanic glass was reacted in 10 ml of each NaOH solution. Reaction products from 0.02 g of the volcanic glass and various concentration of NaOH solutions after reactions of 3 days, 5 days, and 7 days are listed, respectively, in Table 3. Products of

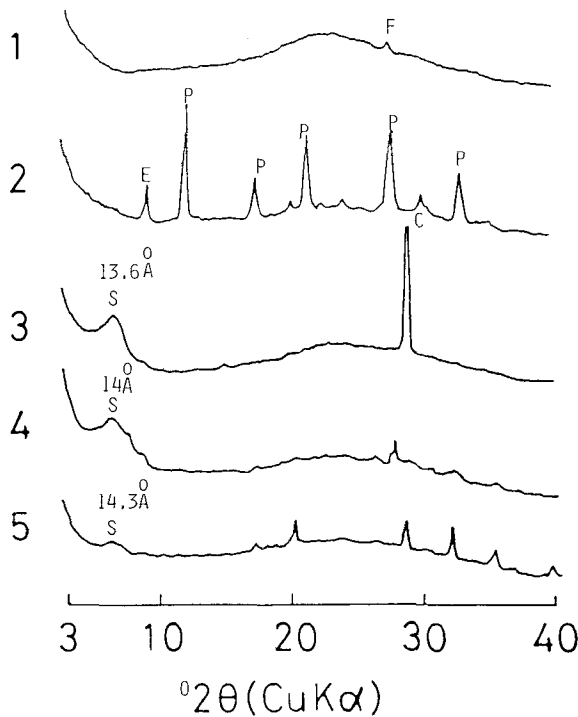


Figure 1. X-ray powder diffraction patterns of the starting volcanic glass and reaction products of 0.02 g of the volcanic glass and with various concentrations of NaOH solution after 7 days: 1) volcanic glass; 2) reaction product with 0.5 M NaOH; 3) reaction product with 1 M NaOH; 4) reaction product with 2 M NaOH; and 5) reaction product with 4 M NaOH. S = smectite, E = zeolite E, P = zeolite P, C = calcite, F = feldspar.

the 5-day reaction were not so different from those of the 7-day reaction. X-ray diffraction patterns for the products after 7 days are shown in Figure 1 together with that of the starting volcanic glass. Smectite was formed in the 1–4 M NaOH solutions. An unidentified

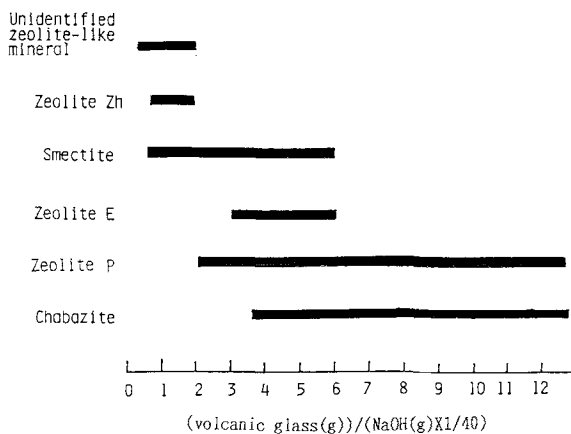


Figure 2. Formation ranges of smectite and zeolites.

Table 1. Chemical analyses of starting volcanic glass and synthesized sample.

	1	2	3
SiO ₂	73.94%	50.0%	71.40%
TiO ₂	0.35	3.2	0.25
Al ₂ O ₃	11.97	11.2	13.65
Fe ₂ O ₃	0.61	11.6*	0.76
FeO	0.85		1.55
MnO	0.05	0.8	0.04
MgO	0.13	4.1	0.48
CaO	1.09	n.d.	1.88
Na ₂ O	3.32	2.8	3.36
K ₂ O	3.52	0.2	2.70
H ₂ O(+)	3.53	16.1	3.40
H ₂ O(-)	0.48		0.62
P ₂ O ₅	0.02		0.05
Total	99.86%	100.0%	100.14%

¹ Volcanic glass in the Osumi pumice fall from Kanoya, Kagoshima Prefecture, Japan.

² Sample synthesized from the volcanic glass in the presence of 2 M NaOH at 90°C for 7 days, then treated with 1% CH₃COOH.

³ Pyroclastic flow deposit from Kagoshima City.

* Total iron determined as Fe₂O₃.

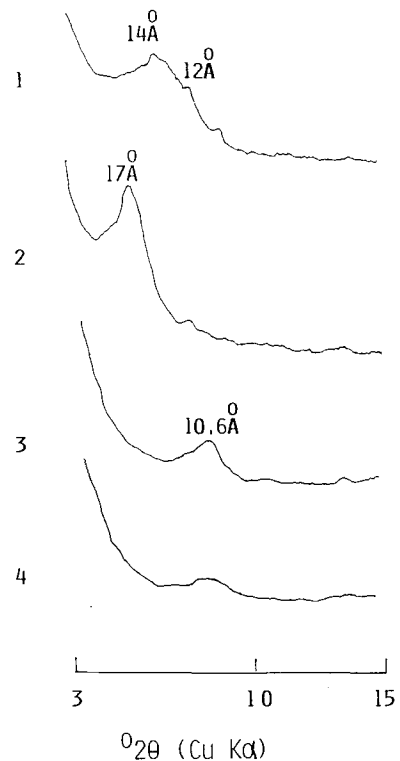


Figure 3. X-ray powder diffraction patterns of the smectite synthesized by reaction of 0.02 g of volcanic glass and 10 ml of 2 M NaOH solution at 90°C for 7 days after various treatments: 1) synthesized smectite, 2) treated with ethylene glycol, 3) heated to 500°C for 1 hr, and 4) heated to 700°C for 1 hr.

Table 2. Reaction products of volcanic glass and NaOH solution at 90°C.

Run no.	Volcanic glass (g)	NaOH solution		Reaction time (days)	Products
		Mol/liter	ml		
554	0.02	1	10	3	S
555	0.04	1	10	3	P, E, Ch, S
627	0.06	1	10	3	P, Ch, S
557	0.08	1	10	3	Ch, P
759	0.2	1	10	3	Ch

S = Smectite, P = Zeolite P, E = Zeolite E, Ch = Chabazite.

zeolite-like mineral was formed with higher concentrations of NaOH solution. Other experiments were carried out with 0.06 g of the volcanic glass. Reaction products of 0.06 g of the volcanic glass and various concentrations of NaOH solution after 3 days and 7 days are also listed in Table 3. Smectite was formed in the 1–10 M NaOH solutions after 3 days of reaction, and in the 1–6 M NaOH solution after 7 days. Formation ranges of smectite and zeolites are shown in Figure 2 using values of weight of volcanic glass(g)/(NaOH(g)/40) as an indicator.

Table 3. Reaction products of volcanic glass and NaOH solution.

Run no.	Volcanic glass (g)	NaOH solution		Reaction time (days)	Products	Remarks
		Mol/liter	ml			
483	0.02	0.1	10	3	–	
519	0.02	0.5	10	3	–	
520	0.02	1.0	10	3	Sm	
521	0.02	2.0	10	3	Sm	Sm = 12.5 Å
522	0.02	3.0	10	3	Un, (Sm)	
523	0.02	4.0	10	3	Un	
524	0.02	6.0	10	3	Un	
525	0.02	8.0	10	3	Un	
526	0.02	10.0	10	3	Un	
682	0.02	0.1	10	5	–	
540	0.02	0.5	10	5	P, Ch	
541	0.02	1.0	10	5	Sm	Sm = 13.4 Å
542	0.02	2.0	10	5	Sm	Sm = 13.0 Å
543	0.02	3.0	10	5	–	
544	0.02	4.0	10	5	Un	
545	0.02	6.0	10	5	Un	
546	0.02	8.0	10	5	–	
547	0.02	10.0	10	5	Un	
577	0.02	0.1	10	7	–	
569	0.02	0.5	10	7	P, Ch	
570	0.02	1.0	10	7	Sm	
571	0.02	2.0	10	7	Sm	Sm = 14 Å
572	0.02	3.0	10	7	Un, (Sm)	
573	0.02	4.0	10	7	Un, (Sm)	
574	0.02	6.0	10	7	Un	
575	0.02	8.0	10	7	Un	
576	0.02	10.0	10	7	Un	
625	0.06	0.1	10	3	–	
626	0.06	0.5	10	3	Ch, (P)	
627	0.06	1.0	10	3	Ch, P, (Sm)	
628	0.06	2.0	10	3	E, P, (Sm)	Sm = 13.6 Å
629	0.06	3.0	10	3	P, Zh	P = double
630	0.06	4.0	10	3	Zh, (P), (Sm)	
631	0.06	6.0	10	3	Sm, Zh	Sm = 13.8 Å
632	0.06	8.0	10	3	Zh, (Sm)	
633	0.06	10.0	10	3	Zh, Sm	
586	0.06	0.1	10	7	–	
578	0.06	0.5	10	7	Ch, P	
579	0.06	1.0	10	7	P, E, (Ch), (Sm)	
580	0.06	2.0	10	7	P, E, Sm	P = double
581	0.06	3.0	10	7	P, Zh, Sm	P = double
582	0.06	4.0	10	7	Zh, (P), (Sm)	
583	0.06	6.0	10	7	Zh, (Sm)	
584	0.06	8.0	10	7	Un	
585	0.06	10.0	10	7	Un	

Ch = chabazite, P = zeolite P, E = zeolite E, Zh = zeolite Zh, Sm = smectite, un = unidentified zeolite-like mineral, – = no products, () = poor yield.

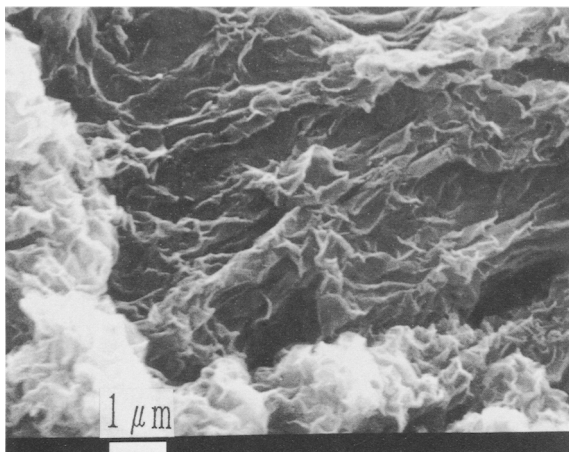


Figure 4. Scanning electron micrograph of the synthesized smectite.

Mineralogical properties of the synthesized smectite

A homogeneous smectite synthesized by reaction of 0.02 g of volcanic glass and 10 ml of 2 M NaOH solution at 90°C for 7 days was selected to investigate in detail its mineralogical properties.

X-ray analysis. X-ray diffraction patterns of the sample after various treatments are shown in Figure 3. The X-ray diffraction pattern of the smectite shows a 14 Å peak, which expanded to 17 Å by treatment with ethylene glycol. A small 12 Å peak still remained after treatment with ethylene glycol. After the sample was heated to 500°C for 1 hr, the major peak collapsed to

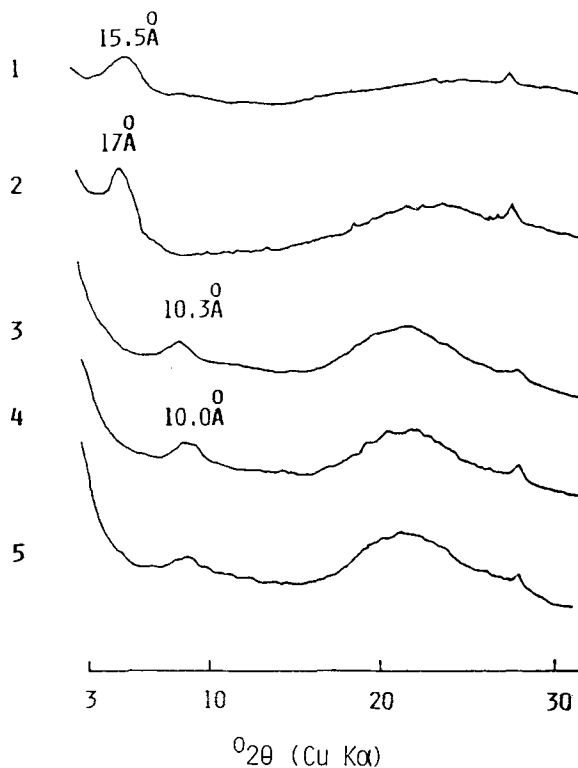


Figure 6. X-ray powder diffraction patterns of the smectite treated with acetic acid after various treatments: 1) smectite treated with 1% CH_3COOH , 2) treated with ethylene glycol, 3) heated to 300°C for 1 hr, 4) heated to 500°C for 1 hr, 5) heated to 700°C for 1 hr.

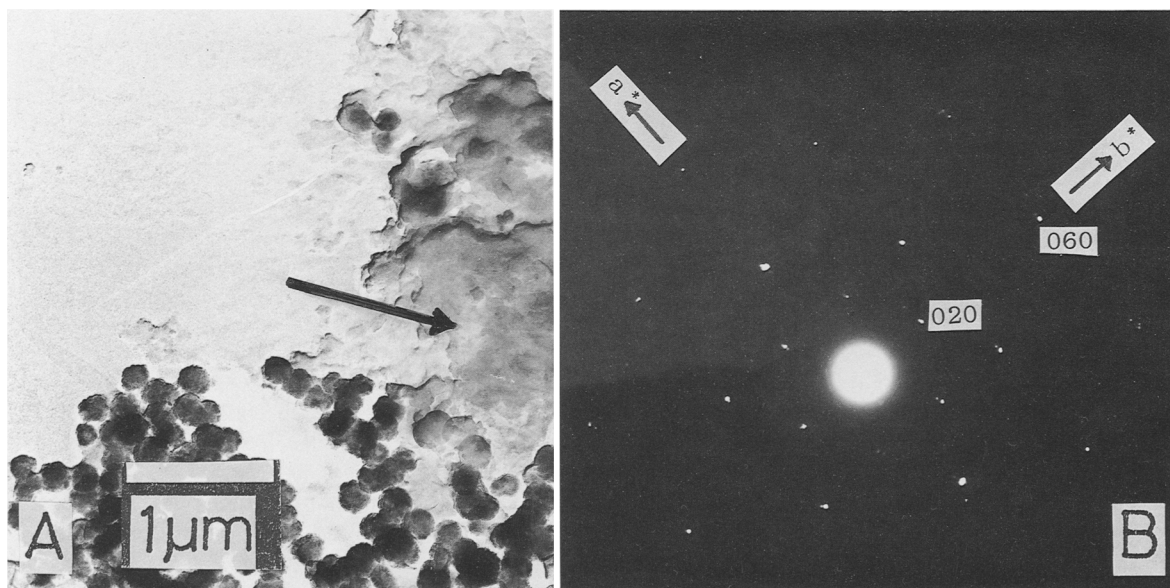


Figure 5. Transmission electron micrograph and electron diffraction pattern of the smectite: A) transmission electron micrograph and B) electron diffraction pattern.

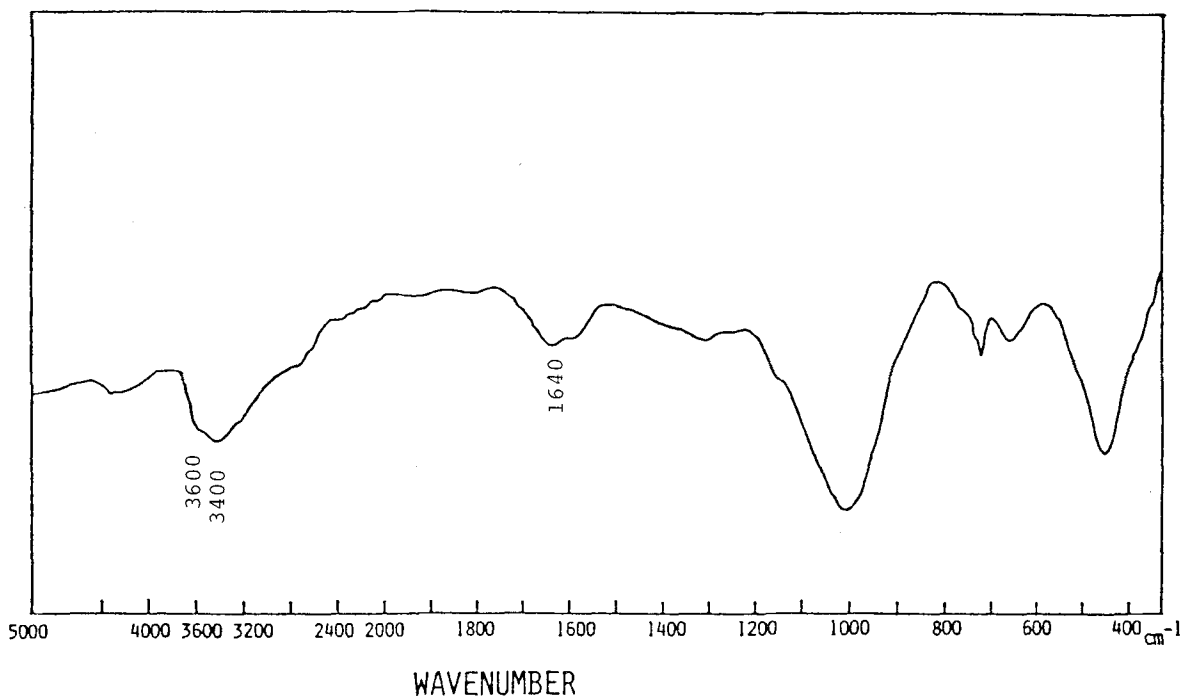


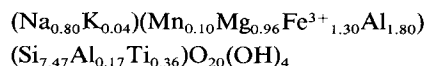
Figure 7. Infrared absorption spectra of the smectite.

10.6 Å and a very weak 10.5 Å peak remained after heating to 700°C for 1 hr. The persistence of a 10.5 Å spacing at 700°C is not consistent with nontronite. This specimen is considered to be an intermediate mineral between nontronite and montmorillonite.

Scanning electron microscopic observation and electron diffraction. A scanning electron micrograph of the specimen is shown in Figure 4. The morphology of the smectite is similar to that of natural smectite. Figure 5 shows a transmission electron micrograph of the specimen (Figure 5A) and an electron diffraction pattern of the smectite (Figure 5B). The electron diffraction pattern is that of an hk-ordered layer silicate species. The rings expected of a turbostratic smectite are not present. The presence of hk ordering is possible for nontronite. A value of $b = 9.2$ Å was derived from 0K0 reflections.

Chemical analysis by EPMA. The specimen was treated with acetic acid to remove calcite. After wetting the sample with 1% of CH_3COOH solution, the sample was washed with distilled water. The X-ray powder diffraction patterns of the acid treated sample after treatment with ethylene glycol and heat treatment are shown in Figure 6. The X-ray powder diffraction pattern of the acid-treated sample showed only the 15.5 Å (001) reflection and the 12 Å peak disappeared. The 15.5 Å peak shifted to 17 Å by treatment with ethylene glycol. The X ray powder diffraction patterns of the treated smectite after various treatments showed be-

haviors similar to those of natural smectites. The chemical composition of the acid-treated smectite obtained by EPMA is listed in Table 1. Assuming that Fe is in the ferric form, the structure formula of the smectite calculated from the chemical composition is as follows:



Infrared absorption spectra. An infrared absorption spectrum of the synthesized smectite is shown in Figure 7. The absorption band at about 3600 cm^{-1} due to OH stretching vibration is not well defined. The broad bands at 3400 cm^{-1} and 1640 cm^{-1} are attributable to inter-layer water and adsorbed water. Farmer and Russell (1964) reported that nontronite does not show clear absorption band of O-H stretching vibration.

DISCUSSION AND CONCLUSIONS

Smectite and various kinds of zeolites were formed as the products of the reaction between volcanic glass and NaOH solution at 90°C under atmospheric pressure. The ratio of volcanic glass to number of Na ions in the solution is important for the formation of smectite. Formation conditions were restricted by the ratio of the amount of volcanic glass (g) to $\text{NaOH(g)}/40$ in the solution as shown in Figure 2. Smectite was formed under the condition that the ratio is between 0.5 and 6, and formed fairly well when the ranges are between 1 and 2. In an experiment where a pumice of 1–2 mm

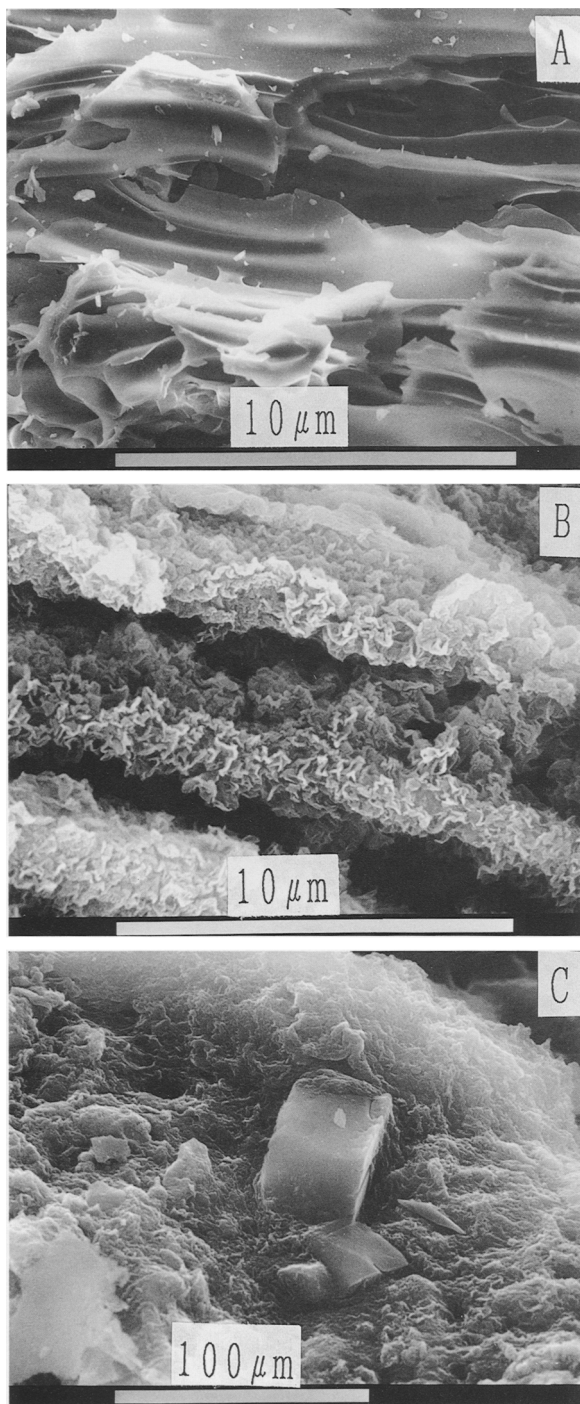


Figure 8. Scanning electron micrographs A) of a pumice, B) of smectite formed on the surface of a pumice, and C) of a zeolite formed in the pumice.

size was used as a starting sample, smectite was formed on the surface of the pumice as shown in Figure 8, and zeolites were formed in the vesicles in the pumice. It seems to be possible to explain the formation mech-

anism of smectite by growth- and dissolution-reaction kinetic model proposed by Dibble and Tiller (1981a, 1981b). But the formation mechanism of smectite and zeolites from volcanic glass is a problem to be solved in the future.

In the formation of smectite, the formation of the octahedral layer is considered to be important (Nemecz, 1981). Tomita (1970) synthesized smectite and vermiculite from sericite, pyrophyllite, and chemical reagents by adding small amount of magnesium carbonate under alkaline conditions usually forming zeolites. In Tomita's case Mg played an important role in forming octahedral layers. In nature, smectite is formed on the surface of pyroclastic materials in sediments, and zeolites are formed in the vesicles (Sheppard and Gude, 1968, 1969, 1973). Formation conditions of smectite and zeolites in this experiment are similar to those deposits of Lake Tecopa, California (Sheppard and Gude, 1968). The result of this study is useful to interpret the paragenesis of zeolites and smectite in tuffs formed by authigenesis or diagenesis.

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