

FORMATION OF ALLOPHANE AND BEIDELLITE DURING HYDROTHERMAL ALTERATION OF VOLCANIC GLASS BELOW 200°C

MOTOHARU KAWANO¹ AND KATSUTOSHI TOMITA²

¹ Department of Environmental Sciences and Technology, Faculty of Agriculture, Kagoshima University
1-21-24 Korimoto, Kagoshima 890, Japan

² Institute of Earth Sciences, Faculty of Science, Kagoshima University
1-21-35 Korimoto, Kagoshima 890, Japan

Abstract—Experimental alteration of volcanic glass has been carried out in distilled water at 200°C and 150°C. The formation and transformation processes of alteration products have been examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), infrared absorption analysis, and X-ray photoelectron spectroscopy. SEM and TEM clearly show that amorphous aluminum-silicate coatings with allophane particles precipitate on the surface of volcanic glass during the earliest alteration stage. Noncrystalline flaky and/or fibrous materials are formed from the allophane aggregates and from the amorphous coatings as new reaction products. The flaky and/or fibrous materials curl inward and transform into 100–500 nm circular smectite. The Al/Si atomic ratio of 1.09 for allophane decreases progressively to 0.65 for smectite through 0.86 for noncrystalline transitional material. The smectite has d(06) spacing of 1.497 Å and consists mainly of Si, Al, and small amounts of Fe, Ca, and Na.

Key Words—Allophane, Amorphous aluminum-silicate coating, Experimental alteration, Smectite, Transitional material, Volcanic glass.

INTRODUCTION

Hydrous silicates such as allophane, halloysite, or beidellite are clay minerals distributed widely on the earth's crust as weathering products of volcanic glasses and rock-forming minerals (Jackson *et al.*, 1952; Malcolm *et al.*, 1969; Parfitt *et al.*, 1983; Wada, 1989). On the basis of field observation, it has been considered that allophane is formed during the earliest weathering stage of volcanic glasses and transformed into beidellite as alteration proceeds (Reiche, 1950; Frederickson, 1951; Snetsinger, 1967; Guilbert and Sloane, 1968; Dudas and Harward, 1975a, 1975b).

Wada *et al.* (1988) reported the formation of allophane-like aluminosilicates in solutions containing Si and Al ions maintained at 95°–100°C and a pH range from 6.5 to 9.0. Farmer *et al.* (1991a, 1991b) found that saponite- and nontronite-like structures developed from aluminosilicate precipitates digested at 20°–89°C in solutions containing Mg and Fe ions, respectively. On the other hand, beidellite has been synthesized from aluminosilicate gel in NaOH solutions at 300°–340°C (Plee *et al.*, 1987; Schutz *et al.*, 1987). Klopogge *et al.* (1990) carried out hydrothermal synthesis of beidellite from aluminosilicate gel in NaOH solutions with a pH range from 7.5 to 13.5 at a temperature of 350°C. They reported that the most highly crystallized beidellite was obtained at 350°C, 1 kbar, 5 days of reaction, and a pH of 10 in the starting solution.

However, the transformation of allophane to beidellite has not been confirmed by experimental alteration of glasses. Recently, Murakami *et al.* (1989) and

Banba *et al.* (1990) examined the experimental alteration of synthetic borosilicate glass and observed both that an amorphous fibrous phase was initially produced within a “mottled phase” and that crystalline materials such as nontronite, chlorite, septechlorite, and/or stilpnomelane appeared to precipitate. Abrajano *et al.* (1990) also reported secondary phyllosilicates precipitated from the leachant solution during simulated weathering of nuclear waste glasses. Tazaki *et al.* (1989) observed the domain structure of crystalline regions within the noncrystalline volcanic glass matrix and the formation of clays with 14 and 16.7 Å spacings and suggested that the crystalline regions represented noncrystalline matrix directly transformed into clay minerals. These studies provided important information concerning the formation process of crystalline materials during the alteration process of glasses. However, the formation process of allophane and beidellite during weathering remains unclear. The present study investigated experimental alteration of volcanic glass under relatively low temperature hydrothermal conditions in order to elucidate the processes forming alteration products during weathering.

EXPERIMENTAL METHODS

The volcanic material used in this study was collected from a pyroclastic flow deposit in Makurazaki, Kagoshima Prefecture, Japan. Grains, 50 to 100 mesh in size, were selected by sieving, washed by ultrasonic treatment, then dried at 105°C. The starting material was mainly composed of volcanic glasses. Feldspar

Table 1. Chemical compositions of starting material.

	Gl	Fl	Opx	Bulk
SiO ₂	77.63	58.12	51.65	73.93
Al ₂ O ₃	12.26	27.95	0.61	13.57
TiO ₂	0.15	0.02	0.11	0.12
FeO ¹	1.24	0.22	32.17	1.92
MnO	0.05	0.04	1.46	0.09
MgO	0.15	0.05	15.23	0.35
CaO	1.15	10.36	0.70	0.91
Na ₂ O	2.84	5.74	0.03	3.02
K ₂ O	3.44	0.23	0.01	2.95
H ₂ O				2.68
Total (%)	98.91	102.73	101.94	99.54

The chemical compositions of (Gl) volcanic glass, (Fl) feldspar, and (Opx) orthopyroxene were measured by electron probe microanalysis. The chemical analysis of (Bulk) bulk material (50–100 mesh grains) was carried out by wet chemical analysis.

¹ Total iron as FeO.

(about 20 wt. %) and orthopyroxene (<5 wt. %) grains were also present. The volcanic glass grains exhibited planar surfaces with small vesicles. Weathering products such as allophane, halloysite, or smectite could not be seen on the surface of the grains. Microprobe analyses of the volcanic glass, feldspar, and orthopyroxene are presented in Table 1 together with the bulk chemical composition of the starting material.

In each experiment, 4.00 g of the starting material were placed in a Teflon bottle with 100 ml of distilled water. The individual bottles were placed in pressure vessels and kept at 150°C for 6 hr, 1, 3, 5, 10, and 30 days or 200°C for 6 hr, 1, 3, and 5 days. The pressure was the equilibrium water vapor pressure at the corresponding temperature. After hydrothermal treatment, the pressure vessels were quenched to room temperature.

The treated glasses were separated by hand-picking, and examined by scanning electron microscopy (SEM) using a JEOL JSM-25SII instrument operating at 25 kV. The alteration products collected by dispersion and sedimentation in distilled water were studied by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and infrared absorption analysis (IR). XRD patterns were obtained with a RIGAKU RU-200 diffractometer (30 kV, 100 mA, CuK α radiation) equipped with a graphite monochromator from oriented, powdered samples mounted on glass slides. TEM was performed with a Hitachi H-700H instrument operated at an accelerating voltage of 200 kV. XPS analyses were made with a Shimadzu ESCA-1000 instrument employing MgK α radiation as the X-ray source. IR spectra were recorded with a Nihonbunko A-302 instrument using the KBr disk technique. About 1.0 mg of the sample was mixed with 30 mg of KBr powder and pressed into a transparent disc while under vacuum.

Table 2. Experimental conditions and results of reaction products.

Run	Temp. (°C)	Duration	pH	Products
A-1	200	6 hr	7.3	As, Allophane, (Boehmite)
A-2	200	1 day	7.8	As, Allophane, Precursor
A-3	200	3 days	8.2	Precursor
A-4	200	5 days	8.6	Smectite
B-1	150	6 hr	6.6	As, Allophane
B-2	150	1 day	7.4	As, Allophane
B-3	150	3 days	8.1	As, Allophane
B-4	150	5 days	8.4	As, Allophane, Precursor
B-5	150	10 days	8.3	As, Allophane, Precursor
B-6	150	30 days	8.5	Precursor

() = trace product; As = amorphous aluminum-silicate coating; Precursor = noncrystalline transitional materials showing flaky and/or fibrous habits.

RESULTS

Alteration products of 200°C experiment

For the 200°C experiments, amorphous coatings, allophane, noncrystalline fibrous material, smectite, and very small amounts of boehmite were produced (Table 2). SEM clearly showed that thin coatings about 0.5 to 1.0 μm in thickness were produced on the surface of glasses after 6 hr (Figure 1a). The coatings were essentially flat with irregular cracks on which aggregates of allophane-like material were observed. TEM showed that the product was composed of an aggregate of fine particles (Figure 2a) that exhibits a morphology similar to natural allophane (Birrell and Fieldes, 1952; Watanabe and Sudo, 1969). The XRD pattern of the product (Figure 3a) showed a 39 Å reflection due to small-angle scattering of the allophane. The diameter of the allophane crystalline domains was estimated by the method of small-angle X-ray scattering for dense systems of identical spherical particles (Guinier, 1963). The estimated value of 43–47 Å agrees well with reported values for natural allophane (Henmi and Wada, 1976). The IR spectrum (Figure 4a) exhibited absorption bands of H₂O at 3430 and 1635 cm⁻¹, Si-O at 1035 cm⁻¹, Al^{VI}-O at 575 cm⁻¹ (Farmer, 1974), and Si-O-Al^{VI} at 468 cm⁻¹. The spectrum was very similar to that of Si-rich natural allophane described by Parfitt *et al.* (1980). However, the absorption bands at 468, 575, and 1035 cm⁻¹ appeared at considerably higher frequencies than those of the natural allophanes. This is probably caused by higher Si content of this product (Henmi and Wada, 1976). Similar products were synthesized by Wada *et al.* (1988) and Farmer *et al.* (1991a, 1991b) as precipitates from solutions containing Si and Al by digesting at 95°C to 100°C and 80°C, respectively.

With increasing reaction duration, the allophane precipitate on the coating surface changed the morphology into a more flaky habit after 1 day (Figure 1b). In the TEM of the product (Figure 2b), development of a very

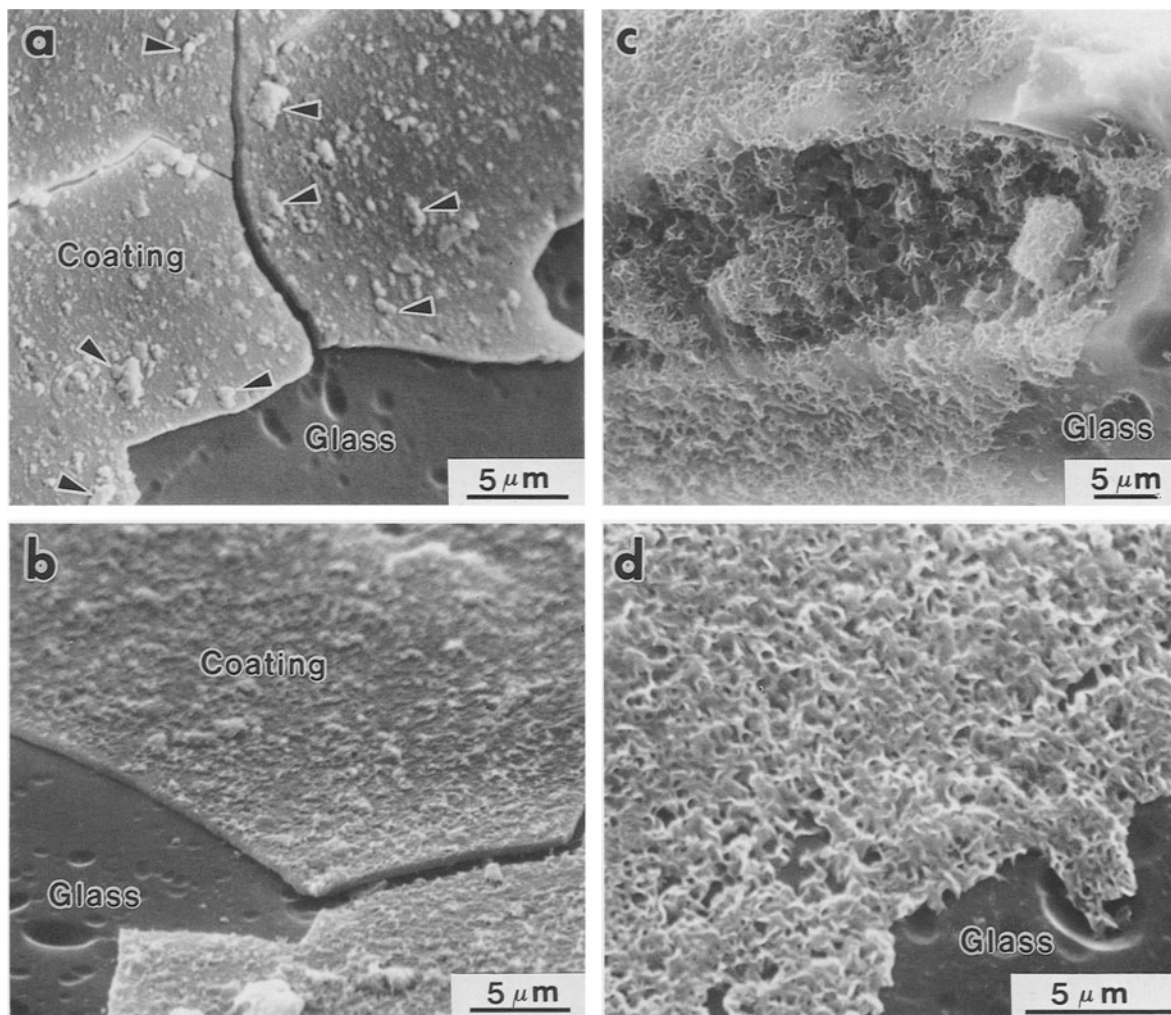


Figure 1. Scanning electron micrographs of reaction products formed on the surface of volcanic glasses by 200°C experiments for (a) 6 hr, (b) 1 day, (c) 3 days, and (d) 5 days. Amorphous coatings with allophane particles appear on the volcanic glass surface after 6 hr reaction. Small amounts of flaky transitional materials are observed on the surface of amorphous coatings of 1-day reaction product. Flaky transitional material and smectite appear after 3 and 5 days of reaction, respectively.

thin fibrous material was observed in the aggregates of allophane particles. These fibers gave diffuse electron diffraction halos suggesting noncrystalline material. The coatings appearing after 6 hr and 1 day of reaction transformed completely into aggregates of flaky and/or crinkled thin films with further reaction (Figures 1c and 1d). They exhibit the characteristic morphology of smectites. The allophane transformed completely into flaky material after 3 days of reaction (Figure 2c), and the product gave very weak and diffuse electron diffraction rings at 4.51 and 2.61 Å suggesting poorly ordered structure. The XRD patterns of 1- and 3-day reaction products (Figures 3b and 3c) contained no diffraction peaks suggesting noncrystalline material. The IR spectrum of 1-day reaction product showed similar patterns to that of allophane (Figure 4b); whereas, that

of 3-day reaction product exhibited smectite-like absorptions (Figure 4c). The morphology and IR absorption features of the 3-day reaction product were similar to those of smectite and also gave electron diffraction rings. However, XRD confirmed that the material was structurally amorphous. Consequently, the product must be a transitional phase having partly ordered structure.

For the 5-day reaction product, the flakes curled inward and the bundles curved to circular forms with 100–500 nm diameters and gave diffraction rings at 4.51 and 2.61 Å (Figure 5). The XRD patterns of the product showed a 15.0 Å reflection, which shifted to 17.0 and 10.1 Å after ethylene glycol solvation and heating at 400°C for 1 hr (Figure 3d–f). The $d(06)$ value obtained from randomly oriented material was 1.497

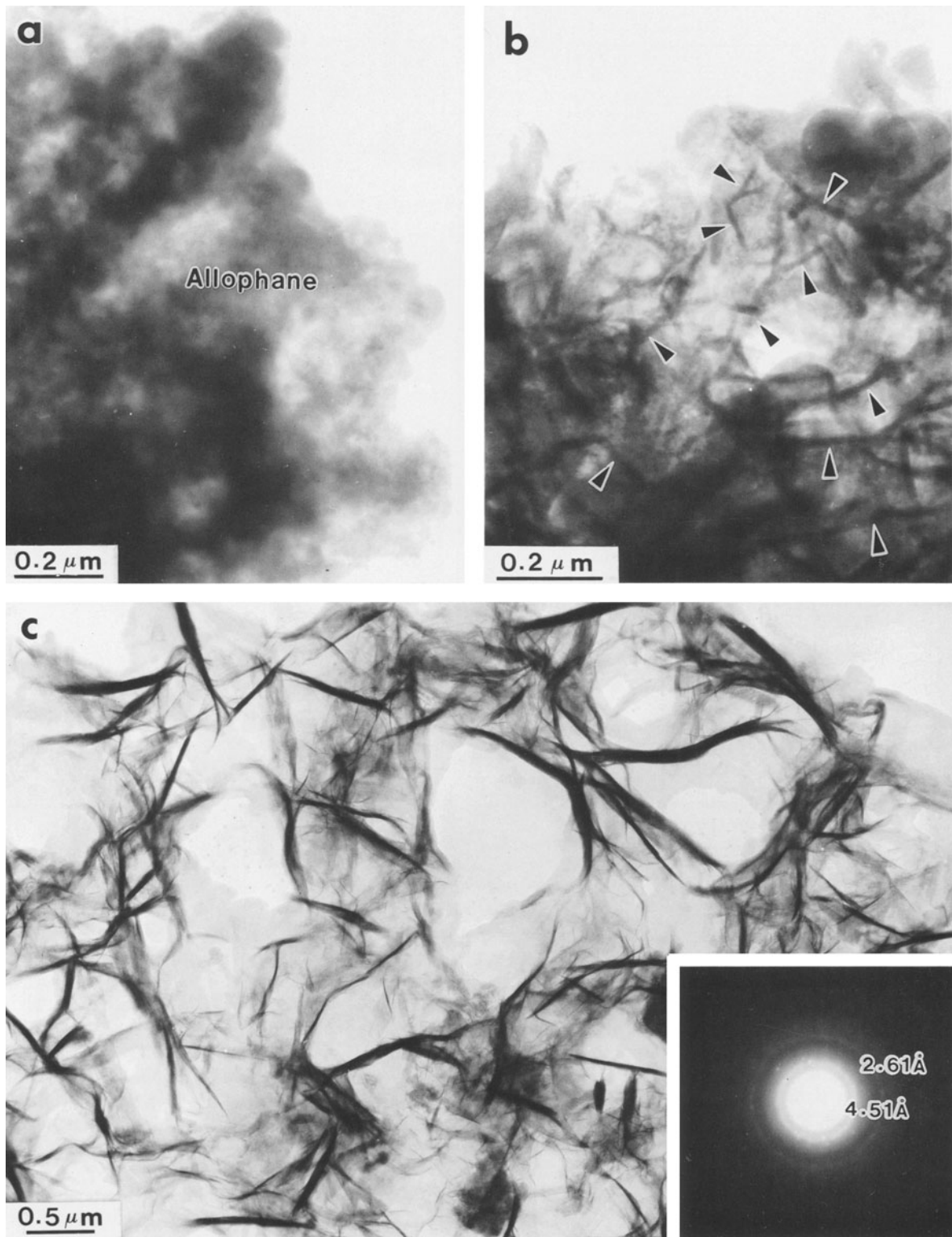


Figure 2. Transmission electron micrographs of (a) allophane, (b) noncrystalline fibrous material formed in aggregates of allophane particles, and (c) noncrystalline transitional material from allophane to smectite. These materials were produced by 200°C experiments for 6 hr, 1 and 3 days, respectively. Arrows indicate noncrystalline fibrous materials.

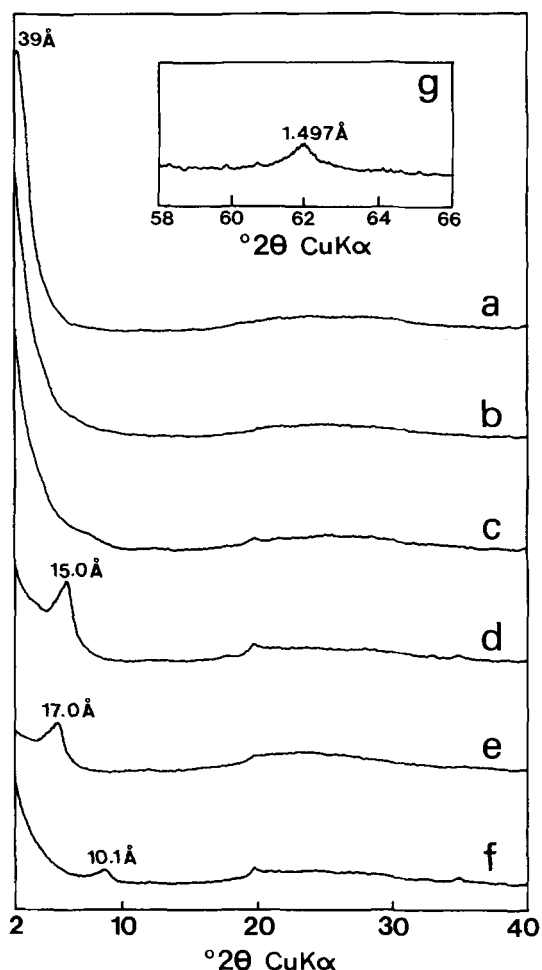


Figure 3. X-ray powder diffraction patterns for (a) 6 hr, (b) 1-day, (c) 3-day, and (d) 5-day reaction products from 200°C experiments. (e) and (f) represent X-ray powder diffraction patterns for the 5-day reaction product after ethylene glycol solvation and heating at 400°C for 1 hr, respectively. (g) Signifies (06) refraction of the 5-day reaction product.

Å (Figure 4g), indicating a dioctahedral structure. The IR spectrum of the 5-day reaction product exhibited absorption bands of OH at 3630 cm⁻¹; H₂O at 3430 and 1635 cm⁻¹; SiO at 1035 cm⁻¹; and SiOAl^{VI} at 535 and 475 cm⁻¹ (Figure 4d). All of these are characteristic absorptions of dioctahedral smectite (Stubičan and Roy, 1961; Farmer, 1974). A synthetic beidellite produced from aluminosilicate gel at 350°C also displayed a similar spectrum (Klopprogge *et al.*, 1990).

Figure 6 shows the XPS spectrum of the 200°C/5-day reaction product. The electron lines from individual elements in the product are: Fe_{2p3/2}, O_{1s}, Ca_{2p}, C_{1s}, Si_{2s}, Al_{2s}, Si_{2p}, Al_{2p}, and O_{2s}. The C_{1s} line at 284.6 eV is due to carbon in the background spectrum and is used for calibration of the binding energy. Strong Auger lines of O at 745 and 767 eV and Na at 264 eV were also observed. Small peaks at the right of the O_{1s} and

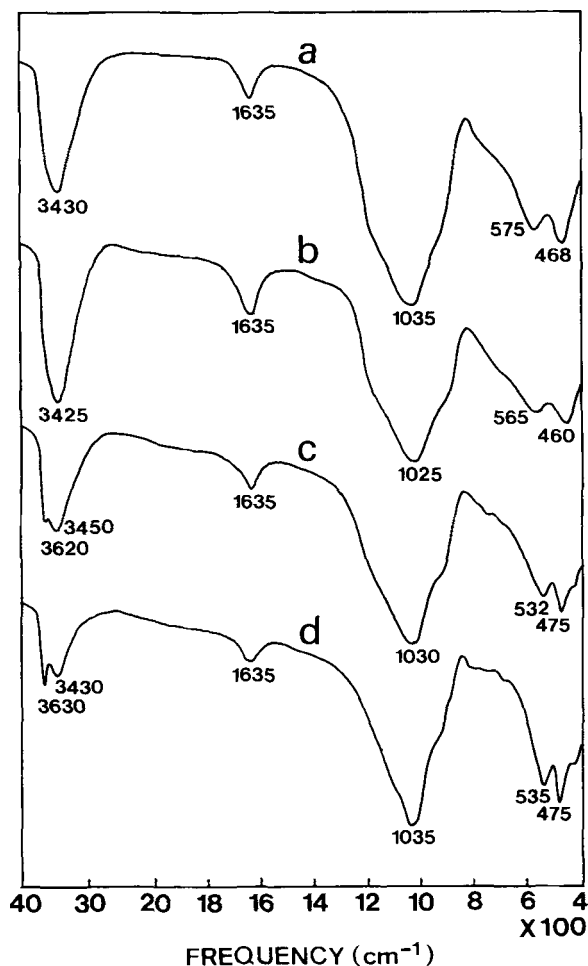


Figure 4. Infrared absorption spectra for (a) 6 hr, (b) 1-day, (c) 3-day, and (d) 5-day reaction products from 200°C experiments.

Si_{2p} are satellite lines, probably arising from MgKα_{3,4} in the X-ray source. Thus, the spectrum indicated that the materials consisted mainly of Si, Al, and small amounts of Fe, Ca, and Na, and that the material should be classified as beidellite.

Figure 7 shows the linear relationship between Al_{2p}/Si_{2p} intensity ratios and Al/Si atomic ratios of some phyllosilicates reported in the literature. The Al/Si atomic ratios of the reaction products were estimated by using this figure. Table 3 shows binding energies of Si_{2p} and Al_{2p}, Al_{2p}/Si_{2p} intensity ratios, and estimated Al/Si atomic ratios. The binding energies of Si_{2p} and Al_{2p} did not show significant differences among these products. The Al_{2p}/Si_{2p} intensity ratio, however, decreased with increasing reaction time. The estimated Al/Si atomic ratio of allophane was 1.09. This value is relatively lower than those of natural allophanes, which have the ratios between 1.1 and 2.9 (Parfitt *et al.*, 1980; Parfitt and Kimble, 1989). The Al/Si ratio

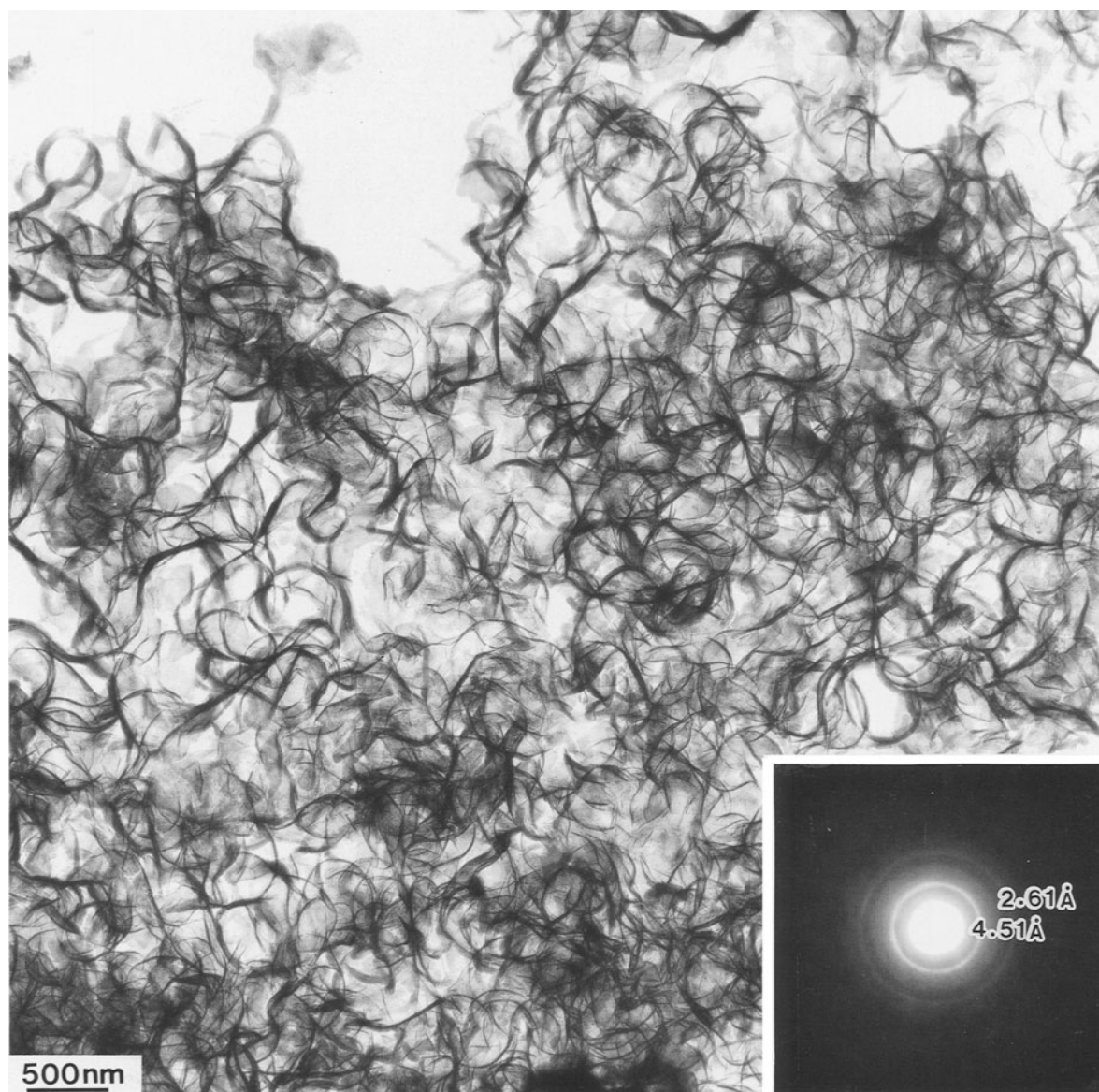


Figure 5. Transmission electron micrograph of circular smectite transformed from noncrystalline transitional material by 200°C/5-day experiment.

of smectite was 0.65, which agrees well with theoretical beidellite composition (Newman and Brown, 1987).

Alteration products of 150°C experiment

Amorphous aluminum-silicate coatings, allophane, and noncrystalline flaky material were produced by the experimental alteration at 150°C (Table 2). SEM of the 6 hr, 3-day, and 5-day reaction products showed that thin amorphous coatings less than 1 μm in thickness were produced on the surface of the altered volcanic glasses after 6 hr, 1 day, and 3 days. Small amounts of flaky materials, with habits similar to those of 200°C, 1-day product (Figure 3b), appeared after 5 days of

reaction and increased in abundance with increasing reaction time. TEM showed aggregates of fine allophane particles. Noncrystalline fibrous material appeared within the allophane aggregates after 3 days of reaction (Figure 8a). The allophane particles decreased and fibrous materials increased with increasing reaction time (Figure 8b). The fibrous materials gave diffuse electron diffraction halos and XRD showed them to be noncrystalline.

DISCUSSION AND CONCLUSIONS

Experimental alteration of volcanic glass has been performed in distilled water at 200°C and 150°C with-

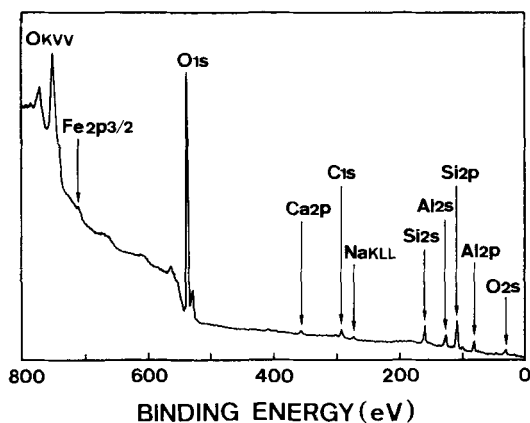


Figure 6. XPS wide-scan spectrum for smectite produced by 200°C/5-day experiment. MgK α radiation was used for X-ray source.

out the addition of any chemical reagent. SEM, TEM, and XRD studies have revealed formation and transformation processes of alteration products as follows:

1. Amorphous coatings with allophane particles precipitated on the glass surfaces.
2. Noncrystalline fibers were produced within the aggregates of allophane particles.
3. Allophane particles and amorphous coatings transformed completely into noncrystalline flaky or fibrous materials.
4. Flakes curled inward and transformed into 100–500 nm diameter beidellite with $d(06)$ equal to 1.497 Å.

The Al/Si atomic ratio of products obtained by 200°C experiments decreased as the length of the reaction increased. The Al/Si atomic ratio of 1.09 for allophane decreased progressively to 0.65 for beidellite from 0.86 for noncrystalline fibrous transitional material. In further reaction at 200°C over 30 days, circular beidellite was produced well, suggesting that the beidellite must be equilibrium phase.

The allophane formed by the 200°C, 6 hr experiment showed an IR spectrum similar to that of “embryonic halloysite” (Wada and Kakuto, 1985; Wada *et al.*, 1985) or “proto-halloysite allophane” (Farmer *et al.*, 1991a) and was characterized by low Al and high Si contents.

Table 3. XPS binding energies, Al_{2p}/Si_{2p} intensity ratios, and estimated Al/Si atomic ratios of reaction products at 200°C.

Duration	Binding energy (eV)		Intensity ratio Al _{2p} /Si _{2p}	Atomic ratio ¹ Al/Si
	Si _{2p}	Al _{2p}		
6 hr	102.1	74.1	0.553	1.09
1 day	102.1	73.8	0.496	0.96
3 days	102.4	74.2	0.455	0.86
5 days	101.7	73.7	0.366	0.65

¹ From Figure 7.

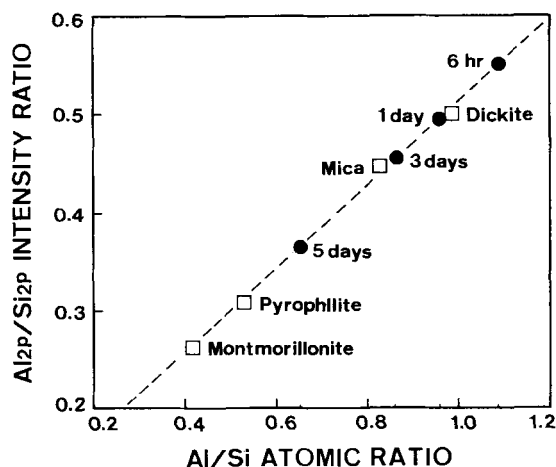


Figure 7. Relationship between Al_{2p}/Si_{2p} intensity ratios and Al/Si atomic ratios of (□) some phyllosilicates, and (●) plots of reaction products produced by 200°C experiments. 6 hr to 5 days represent 6 hr, 1-day, 3-day, and 5-day reaction products from 200°C experiments. The chemical analysis data of montmorillonite used for Uno *et al.* (1986) and those of pyrophyllite, mica, and dickite for Kawano and Tomita (1991).

The synthetic “proto-halloysite allophane” formed in aluminosilicate precipitates digested at 89°C also showed low Al/Si ratio of 1.06 (Farmer *et al.*, 1991b). The noncrystalline fibrous materials, appearing as a transitional phase between allophane and beidellite, exhibited no crystalline peak by XRD, but gave electron diffraction rings and an IR spectrum similar to that of beidellite. Furthermore, the Al/Si ratio was compatible with intermediate value between those of allophane and beidellite. The materials are essentially smectite-like in structure; however, the framework of allophane may be retained for the fibrous material. According to Parfitt and Henmi (1980) and Parfitt *et al.* (1980), the proto-halloysite allophane is made up of a silicate sheet having defect sites at the outer surface and a framework of an octahedral sheet at the inner surface. Such tetrahedral defects may be preserved in the fibrous material, which probably leads to disorder of *c*-axis. The transitional material from allophane to smectite has not been reported in nature; however, the natural smectites formed from volcanic glasses have been possibly developed from the glasses through noncrystalline transitional phase rather than direct formation. The immediate precursors of halloysite exhibiting noncrystalline hollow-packed spheres (Eggleton, 1980; Eggleton and Keller, 1982; Tazaki, 1986; Tazaki and Fyfe, 1985, 1987a, 1987b; Eggleton, 1987; Tazaki *et al.*, 1989) have a close relation with the transitional materials in their formation processes.

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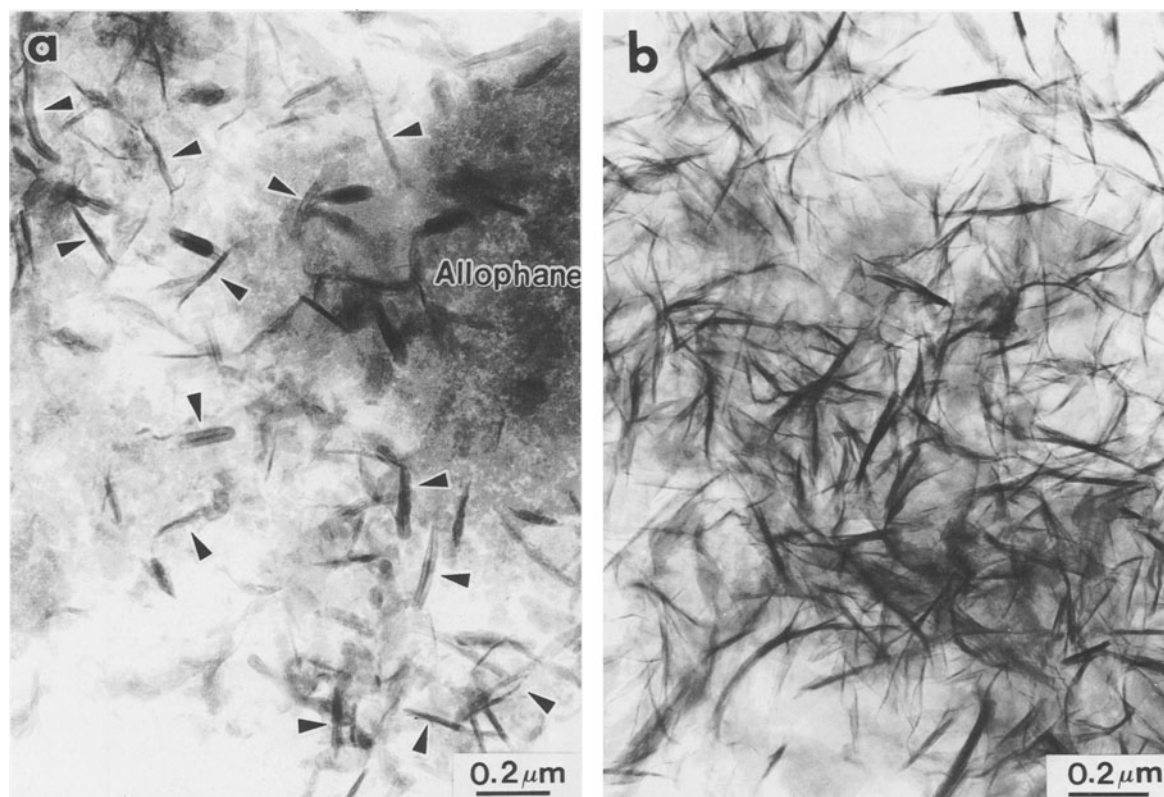


Figure 8. Transmission electron micrographs of reaction products formed by 150°C experiments for (a) 5 days and (b) 10 days. Arrows indicate noncrystalline fibrous materials.

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