

## EXPERIMENTAL STUDY ON THE FORMATION OF CLAY MINERALS FROM OBSIDIAN BY INTERACTION WITH ACID SOLUTION AT 150° AND 200°C

MOTOHARU KAWANO<sup>1</sup> AND KATSUTOSHI TOMITA<sup>2</sup>

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

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

**Abstract**—Experimental alteration of obsidian with HCl solution was performed to elucidate dissolution mechanism and formation process of clay minerals in acid solution. Reactions were carried out using 0.1, 0.5, and 4.0 g of obsidian to 100 ml of 0.01 N HCl solution at 150° and 200°C for 1 to 60 days. The reaction products were examined by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy (TEM), and energy dispersive X-ray analysis. The surface composition of obsidian before and after alteration was investigated by X-ray photoelectron spectroscopy (XPS). TEM showed that boehmite precipitated at early stage and spherical kaolinite appeared subsequently by 200°C reactions. However, spherical halloysite occurred predominantly with small amounts of allophane, boehmite, and kaolinite by 150°C reaction in which formation process of the halloysite from allophane passing through an intermediate phase of small size rounded aggregate that consists of fine particles of allophane was observed. A boehmite exhibiting hexagonal platy habit with higher degree of crystallinity was formed by 200°C reaction as a stable phase in solution containing lower Si concentration at which the solution composition coincides with the stability field of boehmite on activity diagram for the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. The fibrous boehmite having lower crystallinity appeared with increasing Si concentration, considered as a metastable phase in the stability field of kaolinite. XPS indicated that dissolution of obsidian in acid solution proceeded initially by cation exchange between Na ions and hydronium ions in solution and subsequently by preferential release of Al ions relative to Si from the Na depleted surface.

**Key Words**—Acid solution, Allophane, Boehmite, Experimental alteration, Halloysite, Obsidian, Spherical kaolinite.

### INTRODUCTION

Clay minerals are widely occurred by interface reaction between the earth's surface constituents and aqueous solution in which the minerals tend to transform very slowly into more stable secondary minerals. Allophane, halloysite, and kaolinite are common clay minerals distributed extensively on the earth's surface, and it has been presumed that allophane is formed at first and transformed subsequently into halloysite and then finally into kaolinite (Tamura and Jackson 1953, Sudo and Takahashi 1956, Siefferann and Millot 1969, Sudo and Takahashi 1971, Thomas 1971, La Iglesia and Galan 1975, Nagasawa 1978a, 1978b). The formation conditions of these materials have been extensively discussed from the view point of equilibrium relations on activity diagram and synthesis of these materials has been conducted using the equilibrium relations (Robbie and Waldbaum 1968, Helgeson *et al* 1969, Kittrick 1970, Helgeson 1971, Huang and Keller 1973, La Iglesia *et al* 1976, La Iglesia and Van Oosterwyck-Gastuche 1978, Tsuzuki and Suzuki 1980, Tsuzuki and Kawabe 1983).

On the other hand, various clay minerals including kaolinite and halloysite have been also synthesized from a view point of alteration of starting materials. Gruner

(1944), in his experimental work on feldspar alteration, found that kaolinite and pyrophyllite were formed from albite in HCl solution at 300°C. Morey and Chen (1955) performed experimental alteration of albite in water, and reported that albite was altered to boehmite and kaolinite at 200°C, and analcime, boehmite, K-mica, and paragonite at 300°C. Similarly, Brindley and Radoslovich (1956) reported that boehmite and kaolinite appeared as main alteration products of albite in 0.1 N HCl solutions at 285° to 435°C. Morey and Fournier (1961) identified boehmite, paragonite, and amorphous material at 295°C. Parham (1969) likewise obtained halloysite and boehmite from K-feldspar and plagioclase, respectively, by reaction with water at 77–78°C for 140 days. Tsuzuki and Suzuki (1980) carried out experimental alteration of labradorite in HCl solution at 230°C, and reported that amorphous silica and boehmite were initially formed and later kaolinite appeared. At room temperature condition, Busenberg (1978) obtained gibbsite and microcrystalline halloysite as alteration products of albite in aqueous solution. However, dissolution process of volcanic glass in acid solutions has not been well understood and formation process of the reaction products has not been sufficiently investigated.

The present study performed experimental alter-

ation of obsidian with HCl solution in closed system at 150° and 200°C, and dissolution process of the obsidian in acid solution and formation of reaction products were examined.

## MATERIAL AND EXPERIMENTAL METHODS

An obsidian collected from Mifune, Kagoshima Prefecture, Japan is the material used in this study. Samples were crushed, then particles of obsidian between 50 to 100 mesh size were selected and cleaned ultrasonically in acetone to remove adhering fine particles, and were used as a starting material. The chemical composition of obsidian was first determined by electron probe microanalyzer as: 80.04% SiO<sub>2</sub>, 12.27% Al<sub>2</sub>O<sub>3</sub>, 0.16% TiO<sub>2</sub>, 0.84% FeO, 0.18% MgO, 1.10% CaO, 3.14% Na<sub>2</sub>O, and 3.04% K<sub>2</sub>O. The experiments were performed at 150° and 200°C for 1 to 60 days using a Teflon bottle in which various amounts of starting material and 100 ml of 0.01 N HCl solution were placed. The amounts of starting material used were 0.1, 0.5, and 4.0 g for 200°C experiments, and 0.5 and 4.0 g for 150°C. The pressure was held at its equilibrium vapor pressure at each temperature. After different reaction times, the Teflon bottle was quenched and the reaction products, residual starting materials, and solutions were separated. The reaction products were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). The residual starting materials were investigated by SEM and X-ray photoelectron spectroscopy (XPS). The concentrations of dissolved elements and pH values of the solutions were measured. Details of the analytical techniques have been described by Kawano and Tomita (1992) and Kawano *et al* (1993).

## RESULTS

### Products of 200°C experiments

The experimental conditions, pH values of final solutions, and reaction products identified by XRD and TEM are summarized in Table 1. XRD profiles of the products formed by 200°C reactions indicated that boehmite appeared at early reaction stage and kaolinite was formed subsequently (Figure 1). For the reactions using 4.0 g of starting material, broad peaks corresponding to 020 ( $d = 6.15 \text{ \AA}$ ) and 120 ( $d = 3.18 \text{ \AA}$ ) reflections of boehmite were detected by XRD in 1-day product. Small peaks due to basal reflections of kaolinite appeared by 5-day reaction, which continuously increased in intensity with time. The XRD profile of kaolinite in 60-day product exhibited sharp basal reflections at 7.19 and 3.58 Å with poorly separated 11 $\bar{1}$  and 1 $\bar{1}$ 0 reflections, suggesting highly disordered structure (Hinckley 1963). For the reactions using 0.5 g of starting material, sharp 020 ( $d = 6.13 \text{ \AA}$ ), 120 ( $d = 3.17 \text{ \AA}$ ), and 031 ( $d = 2.352 \text{ \AA}$ ) reflections of boehmite

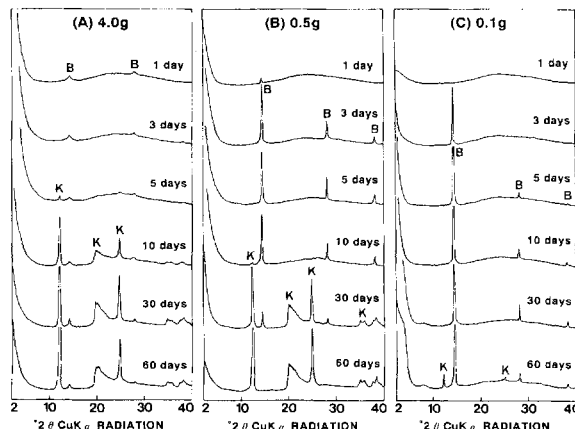


Figure 1. X-ray powder diffraction profiles of reaction products formed by 200°C reactions using (a) 4.0, (b) 0.5, and (c) 0.1 g of starting material. The labels B and K represent diffraction peaks of boehmite and kaolinite, respectively. The labels 1 to 60 days signify reaction time.

were clearly observed in 3-day product, and the intensity gradually decreased with time. A small peak of 001 reflection of kaolinite appeared by 10-day reaction and then the basal reflections and broad non-basal reflections increased in intensity with time. No significant diffraction peak could be detected in 1-day product produced by reaction using 0.1 g of starting material. A sharp 020 ( $d = 6.12 \text{ \AA}$ ) reflection of boehmite however appeared after 3 days and small peaks of basal reflections of kaolinite were found in 60-day product. Consequently, kaolinite tended to appear at early stage with large volume as amount of starting material were increased.

SEM of the reaction products of 4.0 g of starting material showed that the boehmite of 1-day reaction exhibited aggregated texture of flakes (Figure 2a). EDX indicated that the boehmite consisted mainly of Al and a small amount of Si (Figure 2d). TEM confirmed that the flakes were composed of aggregates of thin fibers elongated in various direction and of bundles of fibers (not shown). Boehmites exhibiting similar habit have been reported by Tchoubar (1965) and Kawano and Tomita (1993). SEM of 5-day product showed that thin coating less than 0.1 μm thickness was precipitated on the obsidian surface on which very small spherical kaolinite less than 0.1 μm in diameter and flaky boehmite were likewise observed (Figure 2b). EDX of the coating adhering very small amounts of both kaolinite and boehmite particles displayed strong peak of Al and relatively small peak of Si (Figure 2e), indicating that the coating consisted of aluminosilicate of which chemical composition was rich in Al rather than Si. The coating disappeared as reaction proceeded and size of the spherical kaolinite increased with time (Figure 2c); average values of the diameter are: 0.09, 0.13, 0.17, 0.24, 0.33, and 0.38 μm for 1- to 60-day products.

Table 1. Experimental conditions and reaction products from obsidian by interaction with HCl solution.

Run	Temp. (°C)	Obsidian (g)	Duration (day)	pH <sup>1</sup>	Reaction products <sup>2</sup>
A1-1	200	4.0	1	2.15	Boehmite(f), Allophane
A1-2	200	4.0	3	2.24	Boehmite(f), Allophane, (Kaolinite)
A1-3	200	4.0	5	2.29	Kaolinite, Boehmite(f), Allophane
A1-4	200	4.0	10	2.73	Kaolinite, Boehmite(f), Allophane
A1-5	200	4.0	30	3.42	Kaolinite, Boehmite(f), Allophane
A1-6	200	4.0	60	4.57	Kaolinite, Boehmite(f), Allophane
A2-1	200	0.5	1	2.12	Boehmite(l), (Disk), (Allophane)
A2-2	200	0.5	3	2.18	Boehmite(l), (Kaolinite), (Disk), (Allophane)
A2-3	200	0.5	5	2.23	Boehmite(l, f), (Kaolinite), (Disk), (Allophane)
A2-4	200	0.5	10	2.23	Boehmite(f), Kaolinite, (Disk), (Allophane)
A2-5	200	0.5	30	2.24	Boehmite(f), Kaolinite, (Disk), (Allophane)
A2-6	200	0.5	60	2.25	Boehmite(f), Kaolinite, (Disk), (Allophane)
A3-1	200	0.1	1	2.12	Boehmite(p), (Disk), (Allophane)
A3-2	200	0.1	3	2.17	Boehmite(p), (Disk), (Kaolinite), (Allophane)
A3-3	200	0.1	5	2.23	Boehmite(p), (Disk), (Kaolinite), (Allophane)
A3-4	200	0.1	10	2.23	Boehmite(p), (Disk), (Kaolinite), (Allophane)
A3-5	200	0.1	30	2.24	Boehmite(p, f), (Kaolinite), (Disk), (Allophane)
A3-6	200	0.1	60	2.25	Boehmite(p, f), Kaolinite, (Disk), (Allophane)
B1-1	150	4.0	1	1.96	(Boehmite(f)), (Halloysite), (Allophane)
B1-2	150	4.0	3	2.02	(Boehmite(f)), (Halloysite), (Allophane)
B1-3	150	4.0	5	2.12	(Boehmite(f)), (Halloysite), (Allophane), (Kaolinite)
B1-4	150	4.0	10	2.17	(Boehmite(f)), (Halloysite), (Allophane), (Kaolinite)
B1-5	150	4.0	30	2.28	(Boehmite(f)), (Halloysite), (Allophane), (Kaolinite)
B1-6	150	4.0	60	2.41	(Boehmite(f)), (Halloysite), (Allophane), (Kaolinite)
B2-1	150	0.5	1	2.09	(Boehmite(l)), (Disk), (Allophane)
B2-2	150	0.5	3	2.11	(Boehmite(l)), (Disk), (Allophane)
B2-3	150	0.5	5	2.14	(Boehmite(l)), (Disk), (Allophane)
B2-4	150	0.5	10	2.15	(Boehmite(l, f)), (Disk), (Allophane)
B2-5	150	0.5	30	2.18	(Boehmite(l, f)), (Disk), (Allophane)
B2-6	150	0.5	60	2.21	(Boehmite(l, f)), (Disk), (Allophane)

Boehmite(p) = hexagonal platy boehmite, Boehmite(l) = lath-shaped boehmite, Boehmite(f) = fibrous boehmite, Disk = rounded platy material exhibiting disk-like habit. ( ) = trace products detected by transmission electron microscopy.

<sup>1</sup> pH-values of final solutions measured at room temperature.

<sup>2</sup> The reaction products were identified by X-ray powder diffraction and transmission electron microscopy.

EDX (Figure 2f) confirmed that Al/Si ratio of the spheres is close to theoretical value of kaolinite (Al/Si = 1.0).

Using 0.5 g of starting material, the reaction at early stage produced boehmite that exhibits lath-like habit with hexagonal edge (Figure 3a). This however began to dissolve and new reaction phases of fibrous boehmite and spherical kaolinite appeared subsequently for longer duration at a later stage. In 1- and 3-day products, small amount of rounded platy material exhibiting disk-like habit with 0.5 to 1.5  $\mu\text{m}$  in diameter was observed (Figure 3b). A clear rounded outline of the material was displayed but it later changed to dissolved habit with irregular and vague outline suggesting that the material tended to decompose as reaction proceeded. Kawano and Tomita (1993) synthesized a similar rounded material by hydrothermal reaction between obsidian and  $\text{AlCl}_3$  solution at 200°C but the material was not characterized sufficiently and also remained unidentified. EDX spectrum of the rounded material showed strong X-ray peak of Al and small peak of Si indicating that the material consisted mainly of Al (Figure 3c). The electron diffraction in the direc-

tion normal to the surface of the rounded platy crystal showed a two-dimensional hexagonal net pattern (Figure 3D). The reciprocal cell axes were assumed to be  $a^*$  and  $c^*$  as directions labeled on Figure 3D. Cell dimensions determined from the diffraction data calibrated by ring diffraction of gold are approximately  $a = 4.5$  and  $c = 2.7$  Å. The values are close to the cell dimensions of diasporite ( $a = 4.396$  and  $c = 2.844$  Å; Brown 1980) rather than those of boehmite ( $a = 3.6936$  and  $c = 2.8679$  Å; Christoph *et al* 1979). It is also well known that aluminum hydroxides occurring in the order as increasing the temperature are as follows: gibbsite ( $\gamma\text{-Al}(\text{OH})_3$ )  $\rightarrow$  boehmite ( $\gamma\text{-AlOOH}$ )  $\rightarrow$  diasporite ( $\alpha\text{-AlOOH}$ ). Roy and Osborn (1954) reported that boehmite-diasporite transformation temperature is 275°C, indicating that formation temperature of diasporite is considerably higher than that of present study (200°C). However, we conclude that the rounded platy material may probably be diasporite on the basis of the EDX and electron diffraction data.

For the reaction using 0.1 g of starting material, hexagonal platy boehmite ranging in size from about 0.5



to 5.0  $\mu\text{m}$  was mainly formed at early stage in about 3 days. Small amounts of rounded plates less than 1.5  $\mu\text{m}$  in diameter (Figure 4a) were also formed at this stage. It can be noted that aluminosilicate coating that precipitated on the obsidian surface at reaction using 4.0 g of starting material could not be observed in this 0.1 g reaction. Both boehmite and rounded material exhibited clear outline which apparently began to dissolve at early stage reaction and new phases of fibrous boehmite and spherical kaolinite appeared as reaction proceeded (Figure 4B). The hexagonal boehmite gave characteristically very well shaped XRD reflections as shown in Figure 1, and the d-values tended to decrease slightly as the morphology changed from fibrous to lath-shaped and to hexagonal habits.

#### Products of 150°C experiments

XRD profiles of the reaction products at 150°C gave no significant diffraction peak except for small angle scattering. However, small amounts of products as summarized in Table 1 were clearly observed by TEM. The reaction products using 4.0 g of starting material were predominated by boehmite and halloysite with small amounts of allophane and spherical kaolinite. The boehmite exhibited aggregated texture of circled or straight fibers less than about 2.0  $\mu\text{m}$  in length similarly to the material as shown in Figure 2a. Some straight fibers were arranged in parallel orientation in bundles. The allophane appeared as two distinct textures exhibiting homogeneous and heterogeneous aggregates, respectively (Figures 5a and 5b). The homogeneous aggregate is the predominant form occurring in this system, which is composed of small particles of allophane gathered homogeneously (Figure 5a). Such homogeneous aggregate is also a characteristic texture of natural allophane occurring in weathering environment (Wada 1989). The heterogeneous aggregate is formed by aggregation of small rounded grains less than 0.2  $\mu\text{m}$  in diameter, which is possibly composed of allophane particles or intermediate phase between allophane and spherical halloysite (Figure 5b). The halloysite mainly occurred in spherical form less than about 0.2  $\mu\text{m}$  in diameter together with small amount of tubular habit (Figure 5c). These materials were produced by 1-day reaction and preserved well up to 60 days. A very small amount of spherical kaolinite also appeared as a new reaction phase after five days and increased in size with time.

In the reaction products using 0.5 g of starting material, lath-shaped boehmite, rounded platy diaspor, and a small amount of allophane were produced at early reaction stage. Fibrous boehmite however appeared after 10 days.

#### Surface alteration in acid solution

In the course of dissolution, small rounded and tiny elongated etch pits appeared on the obsidian surface

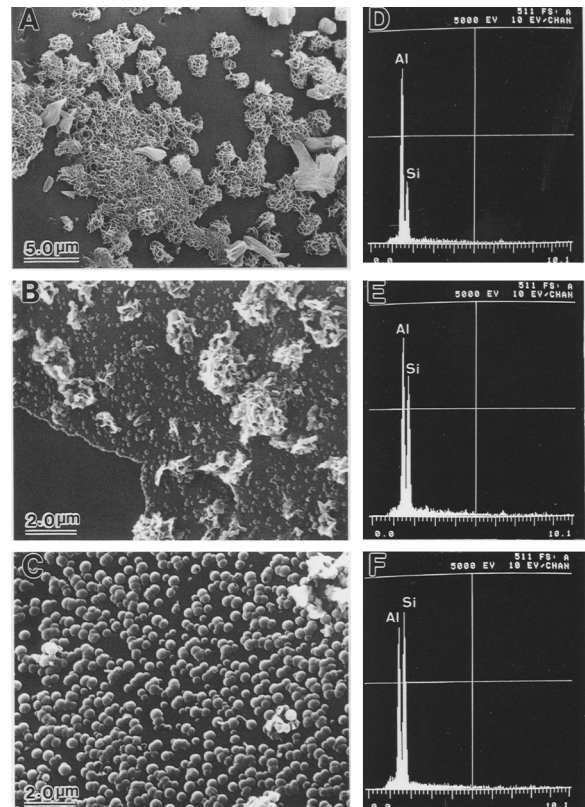


Figure 2. Scanning electron micrographs of reaction products formed by 200°C reactions using 4.0 g of starting material for (a) 1 day, (b) 3 days, and (c) 10 days. Also, energy dispersive X-ray spectra (d, e, and f) obtained from the products of a, b, and c, respectively. The reaction products observed in these photographs are (a) fibrous boehmite, (b) fibrous boehmite and very small spherical kaolinite adhered to non-crystalline aluminosilicate coating precipitated on the obsidian surface, and (c) spherical kaolinite.

during reaction within 1 day and tended to develop in size and depth with time. The formation of etch pits indicates selective dissolution at specific sites of excess energy, such as dislocations, defects, and microcracks produced by sample preparation. Moreover, TEM showed thin leached layer less than 0.1  $\mu\text{m}$  in thickness on the obsidian surface and the layer was noncrystalline for electron diffraction. The leached layer was composed of two distinct inner and outer layers less than about 0.08 and 0.03  $\mu\text{m}$  in thickness, respectively, and they were parallel to the obsidian surface with a sharp boundary and partly peeled off the surface.

The surface compositions of obsidian before and after alteration at 150°C were examined by XPS. The obsidian samples after alteration at 200°C were not used for XPS analysis because large amounts of adhering kaolinite crystals remained on the obsidian surface even after ultrasonic cleaning. Figures 6a and 6b respectively show variations with  $\text{Na}_{\text{KLL}}/\text{Si}_{2\text{p}}$  and  $\text{Al}_{2\text{p}}/\text{Si}_{2\text{p}}$  intensity ratios of obsidians altered by 150°C re-

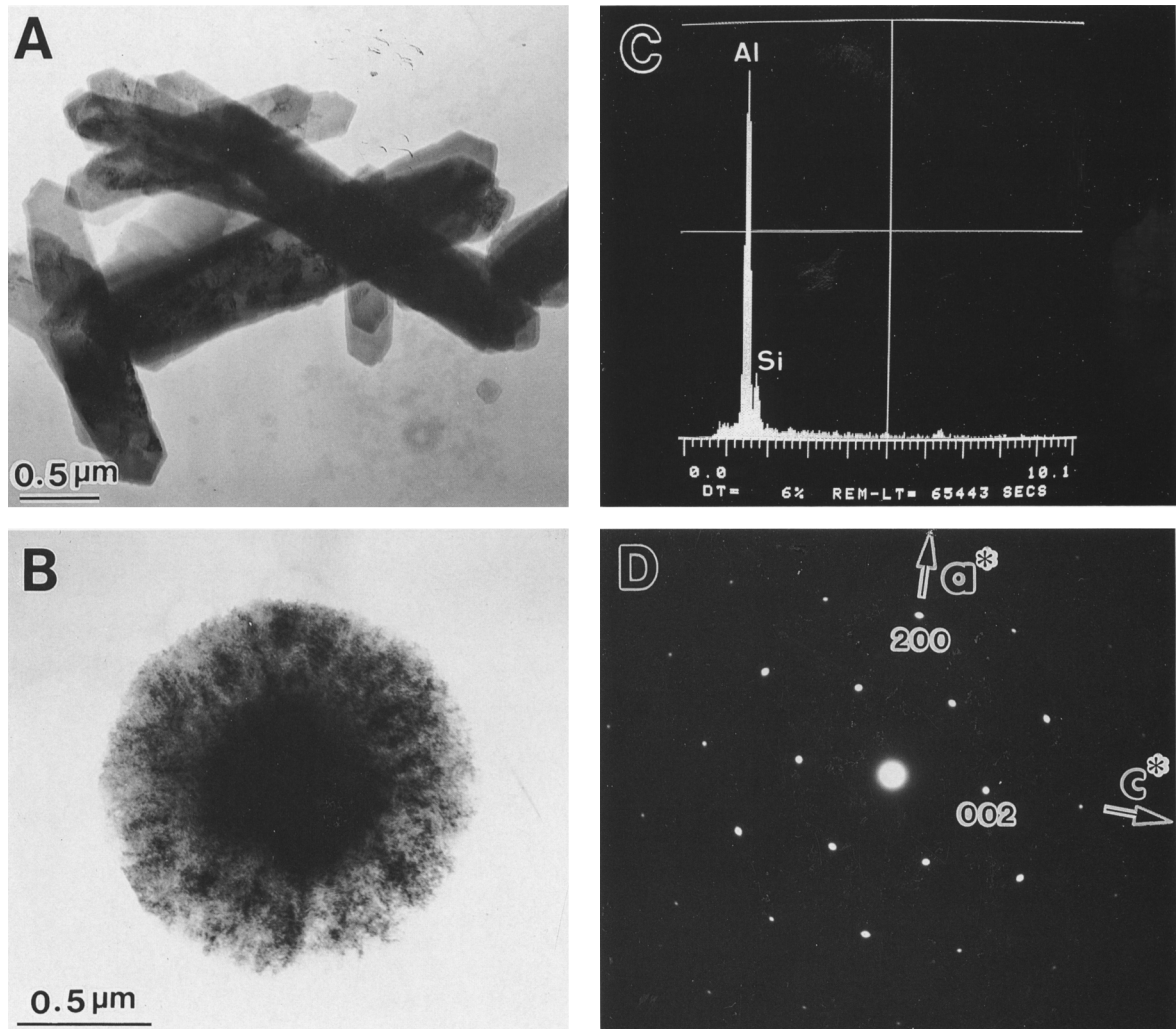


Figure 3. Transmission electron micrographs of reaction products formed by 200°C reactions using 0.5 g of starting material. (a) lath-shaped boehmite formed by 1-day reaction, (b) rounded material showing disk-like habit formed by 5-day reaction, (c) EDX spectrum of the rounded material, (d) electron diffraction of the rounded material b.

actions as a function of square root of time. The  $\text{Na}_{\text{KLL}}/\text{Si}_{2\text{p}}$  ratio of the original obsidian was 0.785 which decreased rapidly at the early reaction stage and still remained constant after. Similarly, the  $\text{Al}_{2\text{p}}/\text{Si}_{2\text{p}}$  ratio of the original obsidian was 0.153 which decreased gradually as reaction proceeded. These observations suggest that initially Na ions were released from the obsidian surface probably by cation exchange reaction, and subsequently Al ions were preferentially released relative to Si from the surface.

#### Chemistry of solutions

Figure 8 shows concentrations of dissolved Si, Al, and Na in solutions during dissolution process of obsidian. The concentrations of Na increased rapidly at early reaction stage and the increasing rates decreased

successively in each experiment. The leaching behaviors of elements during dissolution process of glass and silicate minerals are well known as a parabolic leaching kinetic which is due to the formation of a protective layer on the surface (Chou and Wollast 1984) or to the preferential dissolution of fine particles and of sites with excess energy (Holdren and Berner 1979). The concentrations of Si and Al as well as Na increased at early stage. However, the values varied depending on amount of starting material and on temperature after about 10 days. As shown in Table 1, reaction products consisting of Si and Al were produced in all experiments. Thus, the released Si and Al were consumed as components of the products so the concentrations of Si and Al were affected by amounts of the products. Other elements such as K, Ca, and Mg exhibited the



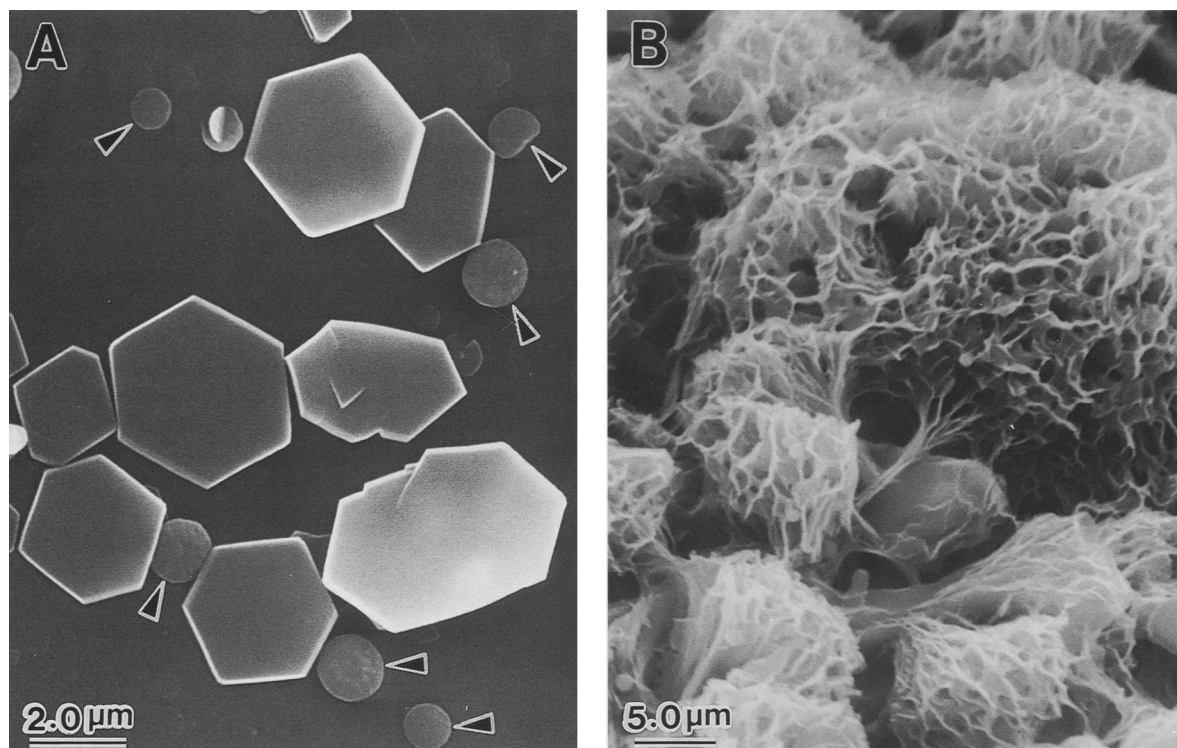


Figure 4. Scanning electron micrographs of products formed by 200°C reactions using 0.1 g of starting material. (a) hexagonal boehmite crystals and rounded materials formed by 1-day reaction, (b) fibrous boehmite formed by 30-day reaction. Arrows on Figure a indicate rounded materials.

same leaching behaviors as that of Na. However the values of concentrations appeared to be below at 50 ppm for K, 30 ppm for Ca, and 3 ppm for Mg throughout the 200°C reaction, and at 12 ppm for K, 10 ppm for Ca, and 0.5 ppm for Mg throughout the 150°C reaction.

#### DISCUSSION

In the reaction processes of obsidian with 0.01 N HCl solution, boehmite precipitated at first and kaolinite formed later at 200°C reactions, and halloysite appeared instead of kaolinite at 150°C reactions. The elements composed of obsidian structure are simultaneously released into the solution following the diffusion control process, and reaction products would precipitate from the solution when its compositions correspond to their stability fields. The solution compositions during the reactions at 200° and 150°C are plotted on activity diagrams for the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  as shown in Figures 8A and 8B, respectively. For the 200°C reactions using 4.0 g of starting material, the solution compositions fall into the stability field of kaolinite throughout the reactions. Then, kaolinite begins to precipitate in equilibrium with the solution as a stable phase and grows progressively during the reaction. However, a small amount of fibrous

boehmite appeared at early reaction stage, which suggests that the boehmite is formed as a metastable phase. The solution compositions of reactions using 0.5 and 0.1 g of starting materials correspond to stability field of boehmite at first and move to kaolinite field as reaction proceeds. The paths are consistent with the appearance of boehmite and kaolinite during the reaction as summarized in Table 1.

The solution compositions of 150°C reactions using 4.0 g of starting material fall into the stability field of kaolinite, and those using 0.5 g of starting material move from the stability field of boehmite to that of kaolinite during the reactions (Figure 8b). As shown in Table 1, boehmite appeared as a most abundant product during both the series of reactions, however halloysite occurred predominantly rather than kaolinite throughout the reactions using 4.0 g of starting material. Either kaolinite or halloysite could not be observed in products of the reactions using 0.5 g of starting material.

A small amount of allophane was found in products of all experiments independent of the solution compositions, suggesting that the material occurred as a metastable phase. Allophane was defined as a group name of naturally occurring hydrous aluminosilicates having short-range ordered structure (van Olphen

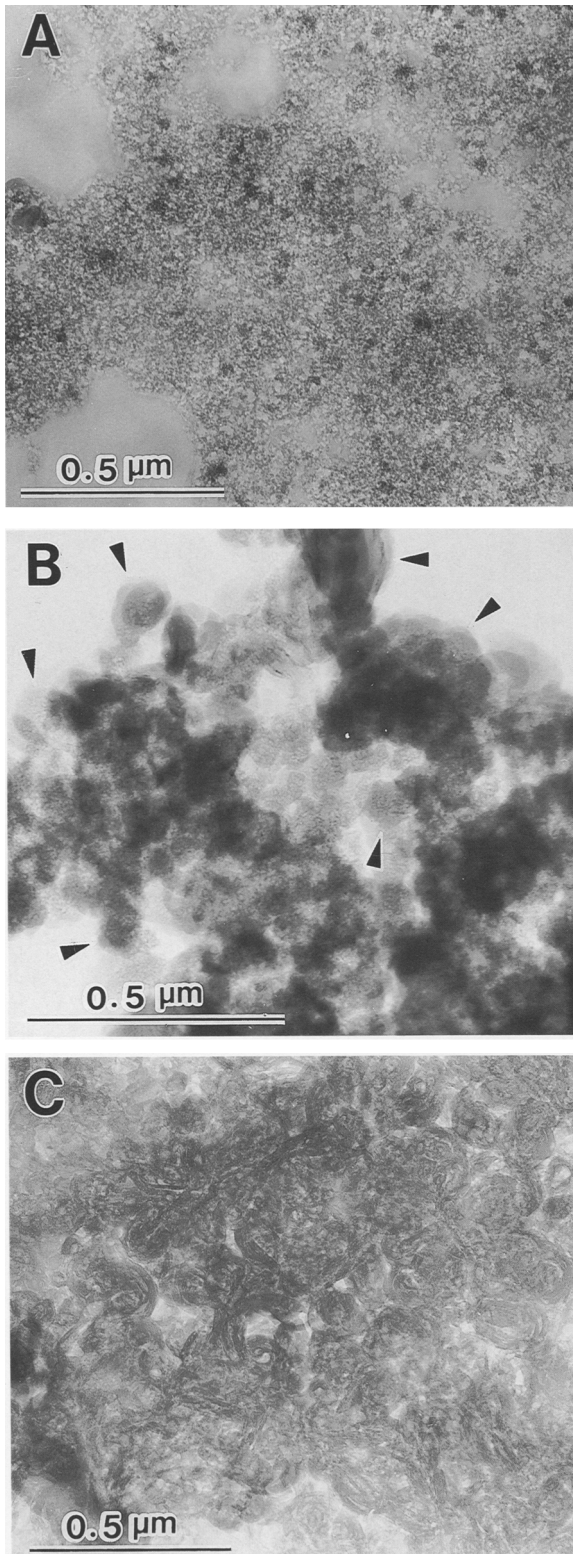


Figure 5. Transmission electron micrographs of reaction products formed by 150°C reactions using 4.0 g of starting material. (a) homogeneous aggregate of allophane particles

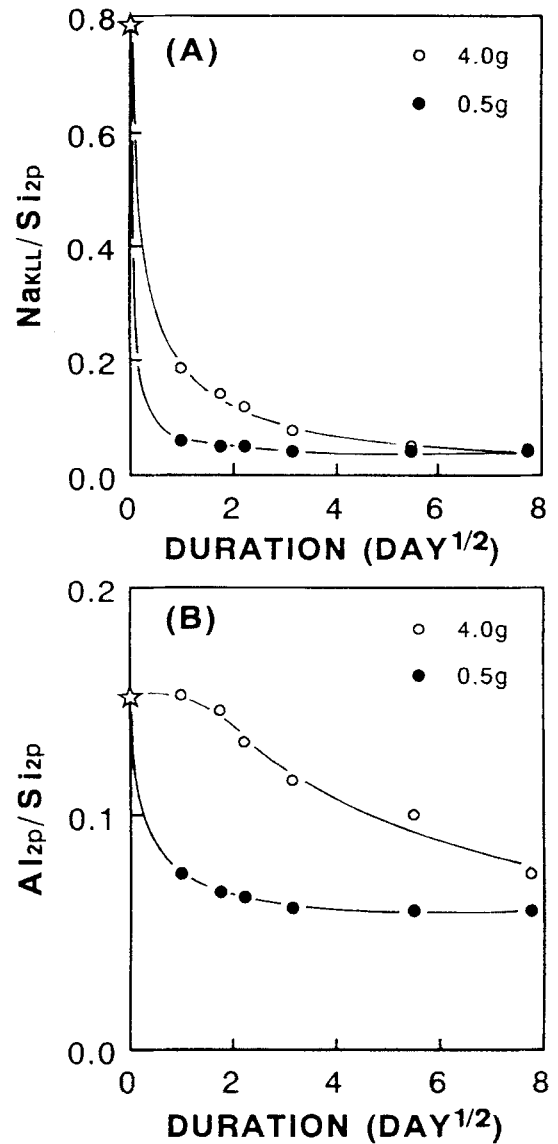


Figure 6. Variations of A) Na<sub>KLL</sub>/Si<sub>2p</sub> and B) Al<sub>2p</sub>/Si<sub>2p</sub> intensity ratios of X-ray photoelectron spectra of obsidian before and after alteration at 150°C as a function of square root of time. Stars indicate the values of original obsidian.

1971). The material consists of identical spherical particles as small as about 50 Å in diameter (Watanabe and Sudo 1969, Hall *et al* 1985), and the Si/Al ratios vary widely from 0.5 to 1.0 (Wada 1989). In nature,

← appeared by 10-day reaction, (b) heterogeneous aggregate of allophane particles that appeared in 10-day reaction, (c) spherical halloysite formed by 5-day reaction. Arrows on Figure b indicate some of rounded grains composed of allophane particles, which are intermediate transitional forms from allophane to spherical halloysite.

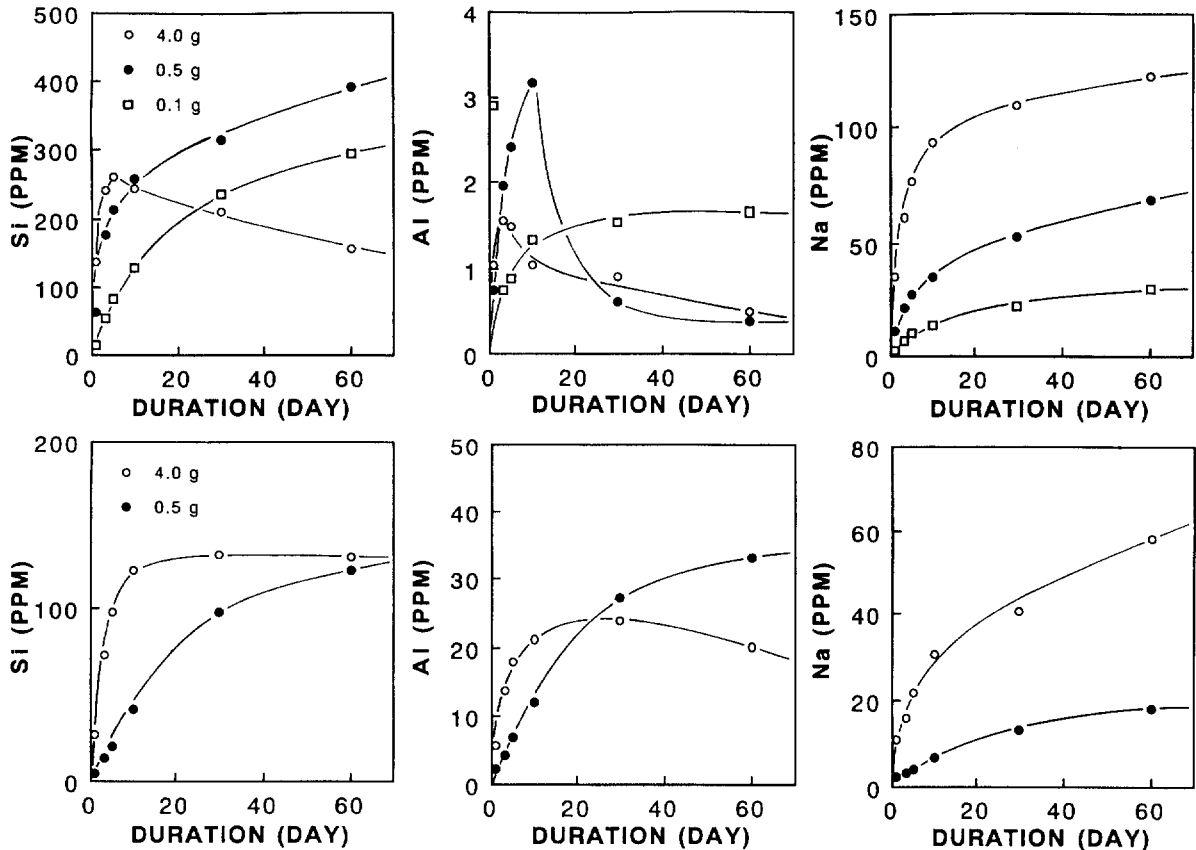


Figure 7. Concentrations of dissolved Si, Al, and Na in solutions during dissolution process of obsidian. Upper = reaction at 200°C, Lower = reaction at 150°C.

allophane is extensively formed under various environments on the earth's surface, for example, by weathering from volcanic glass (Allen and Hajek 1989, Parfitt and Kimble 1989, Wada 1989) and feldspar (Tazaki 1978), and by direct precipitation in river stream (Wells *et al* 1977). For syntheses, allophane is readily produced in acid solutions containing various proportions of Al and Si ions by heating at 95° to 100°C for 113 h (Wada *et al* 1979), and by acidifying the alkaline solutions containing the same cations (Farmer *et al* 1979, Wada and Wada 1981). These facts suggest that allophane is easily and rapidly formed in solutions having wide range of both Al/Si ratio and pH. Generally, materials having higher rate of precipitation tend to be produced as a metastable phase in a supersaturated solution in which the rate of dissolution competes with that of precipitation. Therefore, allophane that appeared in the products of these reactions may be formed as a metastable phase.

Boehmite appeared all throughout the experiments. It exhibited hexagonal platy, lath-shaped, and fibrous habits depending on the reaction conditions. The hexagonal platy boehmite was formed by 200°C reaction

as a stable phase in solution containing lower Si concentration which coincides with the stability field on activity diagram for the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (Figure 8). The lath-shaped and fibrous habits appeared successively as a metastable phase with increasing Si concentration which corresponds with stability field of kaolinite. For the 150°C reaction, lath-shaped boehmite was produced in solution corresponding with stability field of boehmite but fibrous boehmite appeared as a metastable phase in the stability field of kaolinite. The relationship between morphology of boehmite and formation conditions are schematically represented in Figure 9. It is well known that boehmite exhibits various degrees of structural disorder (Papée *et al* 1958). The platy boehmites gave symmetrical shape reflections of XRD profiles indicating higher crystallinity, whereas that of the fibrous boehmite was uniformly broad which suggests that the fibrous boehmite has highly disordered structure (Figure 1). Furthermore, the d-values of reflections tended to increase with increasing structural disorder. Calvet *et al* (1953) used the term *pseudoboehmite* for such a disordered boehmite. Later, Tettenhorst and Hofmann (1980) studied



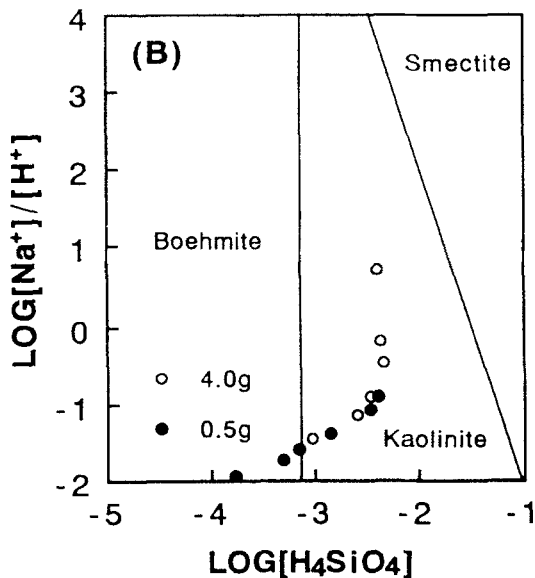
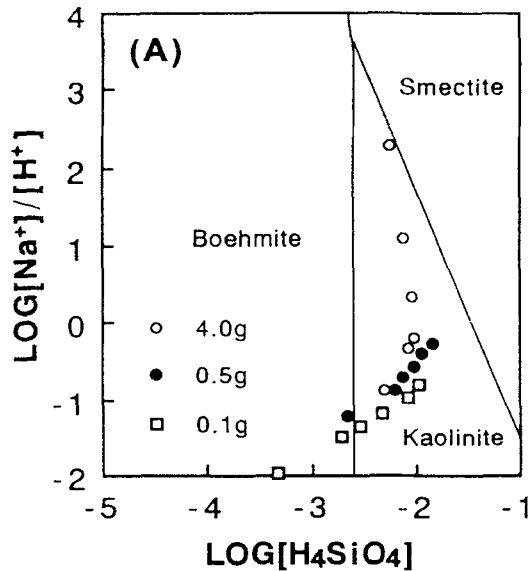


Figure 8. Plots of solution compositions on the activity diagrams for the system of  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  at (a) 200° and (b) 150°C. The positions of stability field boundaries were derived from Helgeson (1971).

crystal chemistry of boehmites having various degrees of disorder, and pointed out that pseudoboehmite is essentially finely crystalline boehmite containing more sorbed water intercalated randomly between octahedral layers.

Kaolinite was mainly formed by 200°C reactions but halloysite appeared predominantly by 150°C reaction with trace amount of kaolinite. The kaolinite exhibited characteristic spherical form similarly to that synthesized by Tomura *et al* (1983, 1985), and no platy form

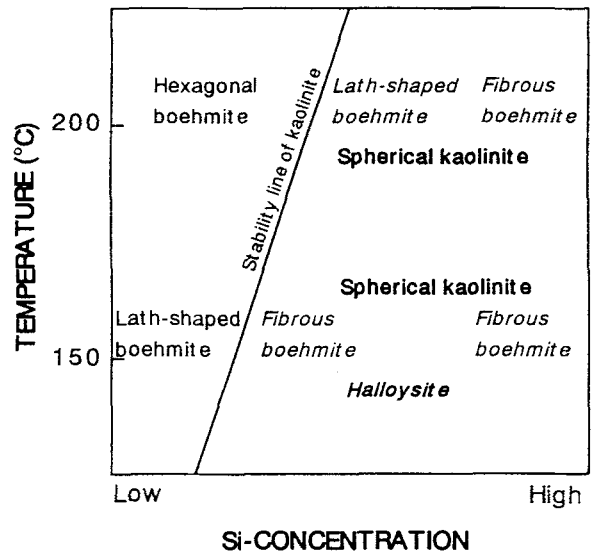


Figure 9. Schematic diagram showing relationship between formation condition and corresponding minerals. *Italic characters indicate metastable phases.*

could be observed in any products. The spheres initially occurred at the surface of obsidian in very small size (mean diameter of 1-day product was 0.09  $\mu\text{m}$ ) and increased progressively in size with time, suggesting that the kaolinite was formed as a thermodynamically stable phase by a process of heterogeneous nucleation on the obsidian surface and successive crystal growth in supersaturated solution.

Halloysite appeared together with fibrous boehmite and trace amounts of allophane and spherical kaolinite in the products of only 150°C reaction using 4.0 g of starting material (Table 1). This probably suggests that relatively low temperature and high Si-activity may be required for its formation. The halloysite was rapidly formed by 1-day reaction but no significant changes in both particle size and abundance could be recognized throughout the reaction up to 60 days. The amounts of fibrous boehmite and allophane also remained unchanged as well as halloysite, whereas the spherical kaolinite increased slightly in abundance with time. Thus, it is undoubtful that the halloysite occurred as a metastable phase in this system. The formation mechanism of halloysite remains uncertain in spite of one of the most abundant clay minerals occurring in the earth's surface (Minato and Utada 1969, Nagasawa 1978a, 1978b, Tazaki 1982, Velde 1985, Murray 1988, Dixon 1989). Parham (1969) and Busenberg (1979) have synthesized halloysite from feldspar by experimental alteration in aqueous solutions, and it was presumed that the halloysite was transformed from feldspar through a transitional phase of allophane. Sudo and Takahashi (1956) carried out electron microscopic study of some halloysites altered from volcanic glass

and postulated the transformation sequence as follows: volcanic glass → allophane → halloysite. They also stated that extremely fine particles of allophane will coagulate into rounded grains at initial stage and will change subsequently into an aggregate of hydrated halloysite with a low degree of crystallinity having shapes like twisted fibers or curled hairs. Unfortunately, a transitional phase of allophane to halloysite in this sequence has not been clearly observed, so it is unclear whether halloysite forms by precipitation due to dissolution of allophane or by solid state transition from allophane. According to the present study, two distinct types of homogeneous and heterogeneous aggregates of allophane were clearly observed by TEM in the products of 150°C reaction (Figures 5a and 5b). The former is a characteristic texture of natural allophane (Wada 1989), whereas the later is an unusual form exhibiting aggregated texture of rounded grains composed of fine particles of allophane. Thus, the rounded grains may be a transitional phase from allophane to halloysite and an individual rounded grain may develop progressively to a spherical halloysite by solid state transition mechanism as the reaction proceeds.

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