

GROWTH OF SMECTITE FROM LEACHED LAYER DURING EXPERIMENTAL ALTERATION OF ALBITE

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Abstract—Experimental alteration of albite in deionized-distilled water at 150° to 225°C for various times up to 30 days was performed to elucidate formation processes for alteration products of albite in aqueous solution. The alteration products were examined by X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). The surface compositions of albite before and after alteration were investigated by X-ray photoelectron spectroscopy (XPS). TEM clearly showed that an amorphous leached layer was produced on the albite surface at the earliest alteration stage together with small amounts of allophane. The leached layer increased successively in thickness and tended to be detached from the albite surface as alteration proceeded. Noncrystalline fibers less than 0.5 μm in length appeared within the leached layer matrix and transformed into thin flaky smectite and small amounts of K-mica. The leached layer gave electron diffraction patterns with a diffuse halo, whereas the flaky smectite displayed rings at 4.51, 2.61, and 1.54 Å. EDX confirmed that the flaky smectite consisted mainly of Si and Al, and small amounts of Na. The smectite was formed in the stability field of Na-smectite for the system of Na₂O–Al₂O₃–SiO₂–H₂O.

Key Words—Albite, Amorphous leached layer, Flaky smectite, Noncrystalline fiber, Transmission electron microscopy.

INTRODUCTION

Feldspars are the most abundant rock-forming minerals of the earth's crust. The minerals transform commonly into hydrous silicates in nature by weathering, hydrothermal alteration, or early diagenetic reactions. Such mineralogical changes result from the interaction of the minerals with an aqueous solution or fluid, which is an important geochemical process on the earth's surface. This paper studies the experimental alteration of albite in aqueous solution. The alteration products and dissolution processes of the reactant solid were investigated to provide information on the formation and transformation of hydrous silicates.

A large number of the papers dealing with feldspar dissolution in aqueous solution have elucidated the dissolution mechanism (e.g., Tamm, 1930; Correns and von Engelhardt, 1938; Lagache, 1965, 1976; Wollast, 1967; Busenberg and Clemency, 1976; Holdren and Berner, 1979; Chou and Wollast, 1984). Most of the work has shown parabolic and incongruent dissolutions, and two types of diffusion-controlled mechanisms have been considered to explain such parabolic dissolution behaviors: 1) formation of a nonstoichiometric leached layer at the feldspar surface (Luce *et al.*, 1972; Pačes, 1973; Busenberg and Clemency, 1976; Chou and Wollast, 1984); and 2) formation of a protective layer composed of amorphous or crystalline precipitate (Correns and von Engelhardt, 1938; Correns, 1940, 1961, 1963; Wollast, 1967; Helgeson, 1971, 1972). The nonstoichiometry of released elements in

the leachant solution has been attributed to precipitation of secondary products composed of aluminum hydroxide or aluminum silicates distinct from the feldspar surface (Lagache, 1965; Petrović, 1976; Busenberg, 1978; Holdren and Adams, 1982). On the other hand, another line of thought on feldspar dissolution has posited it as a surface-reaction mechanism (Lagache *et al.*, 1961; Lagache, 1965; Petrović, 1976; Petrović *et al.*, 1976; Berner and Holdren, 1977; Berner, 1978, 1981; Holdren and Berner, 1979; Dibble and Tiller, 1981; Aagaard and Helgeson, 1982). This concept can be simply defined by detachment of ions from the feldspar surface by crystal-solution interface reaction (Berner, 1978). However, incongruent dissolution appears due to preferential dissolution of dislocation, defect, or similar sites of excess energy on the feldspar surface (Holdren and Berner, 1979).

Recently, various spectroscopic techniques such as secondary ion mass spectrometry (Nesbitt *et al.*, 1991; Muir and Nesbitt, 1991), Rutherford backscattering (Casey *et al.*, 1988, 1989a), and X-ray photoelectron spectroscopy (Muir *et al.*, 1989, 1990; Hellmann *et al.*, 1990) have been applied to investigate the surface composition and its depth profiles. These studies indicated formation of a dealcalized-leached layer as deep as 1000 Å, which was enriched in Si or Al depending on the pH of the solution during the early dissolution stage (Schott and Petit, 1987; Casey and Bunker, 1990). The leached layer increases in thickness with decreasing pH and tends to be enriched in Si and depleted in Al, Na,

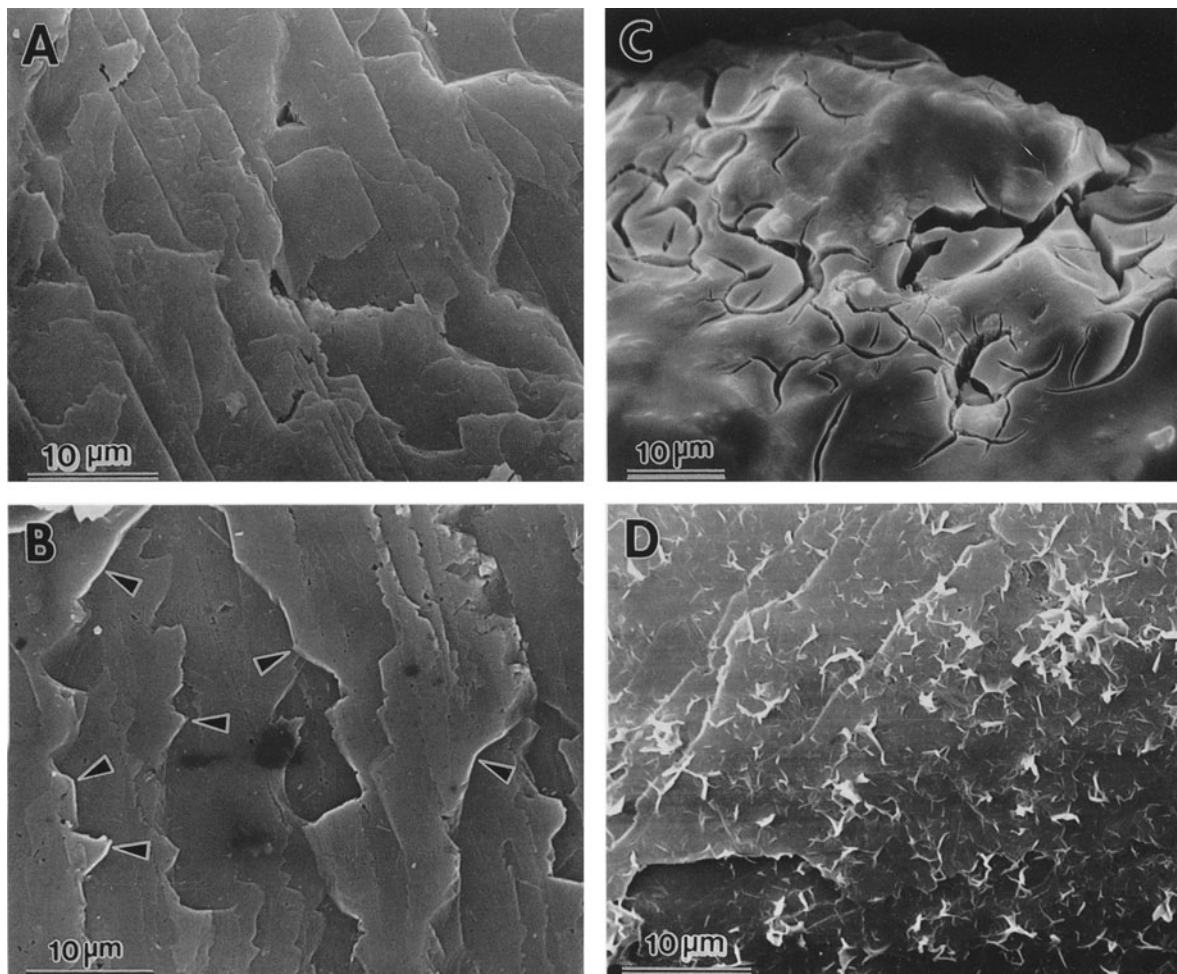


Figure 1. Scanning electron micrographs of albite surface after alteration at 225°C for A) 1 day, B, C) 3 days, and D) 30 days. Arrows on B indicate smectite formed at the edge of {001} cleavage plane.

and Ca during reaction with an acidic solution (Casey *et al.*, 1988, 1989b; Althaus and Tirtadinata, 1989; Goossens *et al.*, 1989; Muir *et al.*, 1989, 1990; Hellmann *et al.*, 1990; Nesbitt *et al.*, 1991); however, such preferential dissolution cannot be recognized in near-neutral and alkaline solutions (Casey *et al.*, 1989a). On the other hand, Nesbitt and Muir (1988) reported formation of an Al-enriched layer on the naturally weathered feldspar surface, and they concluded that these differences may reflect compositional differences in the weathering solutions. For the dissolution rate, it is known that the feldspar composition (Petit *et al.*, 1989; Casey *et al.*, 1991), cation concentration of the leachant (Muir and Nesbitt, 1991), and pH of the solution (Knauss and Wolery, 1986; Blum and Lasaga, 1988, 1991) are very sensitive to the dissolution rate.

EXPERIMENTAL METHODS

Albite crystals from Niigata Prefecture, Japan, were crushed in an agate mortar and grains of 50 to 100

mesh size were separated by sieving. The selected grains were cleaned ultrasonically in acetone more than five times to remove adhering ultrafine particles produced by crushing, and were used as starting material. No weathering products such as smectite, halloysite, or allophane could be detected by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM). Scanning electron microscopy showed the development of the {001} cleavage and no remaining ultrafine particles. The structural formula calculated from chemical analysis obtained by electron probe microanalysis is: $(\text{Na}_{0.96}\text{K}_{0.01}\text{Ca}_{0.02})[\text{Al}_{1.01}\text{Si}_{2.99}]\text{O}_8$.

All experiments were performed using Teflon bottles containing 4.0 g of starting material and 100 ml of distilled-deionized water. The pH of the water before reaction was determined to be approximately 6.8. The alteration was conducted at 150°, 175°, 200°, and 225°C for 6 hr and 1, 3, 5, 10, and 30 days in a pressure vessel. The pressure was maintained at the equilibrium vapor pressure for the corresponding temperature. After

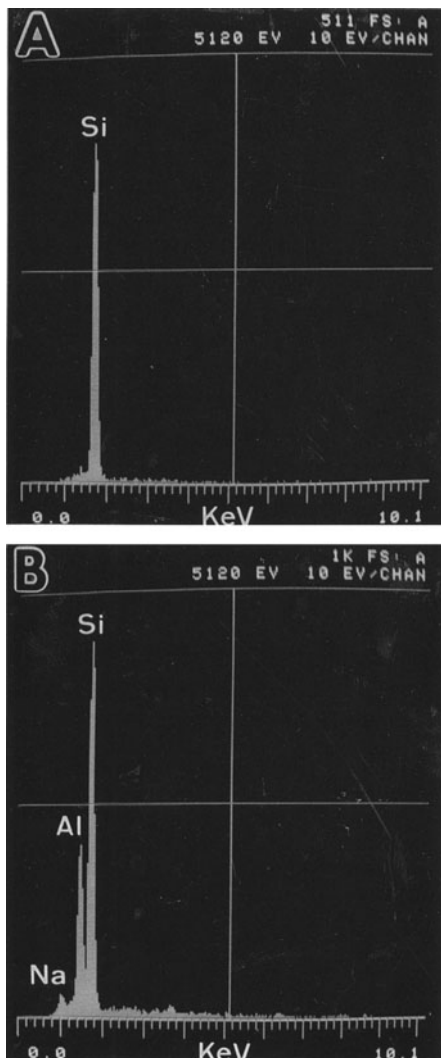


Figure 2. Energy dispersive X-ray analysis spectra of A) amorphous silica precipitate formed at 225°C for 3 days and B) smectite formed at 225°C for 30 days.

varying periods of reaction, the vessel was quenched in water, and solids and solutions were separated by centrifuge. Small amounts of solids (approximately 0.1 g) were used for scanning electron microscopy (SEM). The remainder was cleaned ultrasonically in acetone to remove adhering alteration products and was used for X-ray photoelectron spectroscopy (XPS). The alteration products were collected by centrifugation and were washed with distilled-deionized water. The samples were used for XRD, TEM, and energy dispersive X-ray analysis (EDX). For the solutions, concentrations of released elements were measured by colorimetry for Si as described in Grasshoff *et al.* (1983) and by atomic absorption spectroscopy for Al, Na, and K. The activity of the hydrogen ion was measured with a TOA HM-20S digital pH meter using a glass electrode. Details of the analytical techniques have been

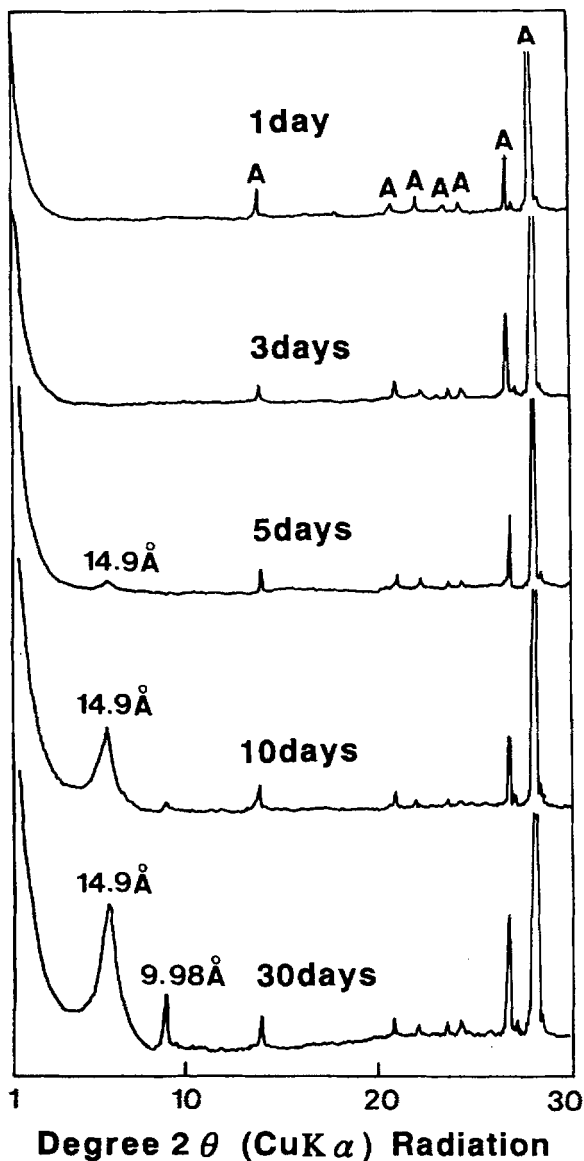


Figure 3. X-ray powder diffraction patterns of alteration products at 225°C for 1 to 30 days. Labels A indicate reflections of albite used as starting material. The 14.9 and 9.98 Å peaks represent (001) reflection of smectite and K-mica, respectively.

described by Kawano and Tomita (1992) and Kawano *et al.* (1993). The experimental conditions and reaction products are given in Table 1.

RESULTS

Alteration products

Figure 1 shows SEM views of the albite surface after experimental alteration at 225°C. The surface morphology of albite did not change significantly after 1 day of reaction (Figure 1A). Smectite-like flaky materials appeared initially at the edge of {001} cleavage

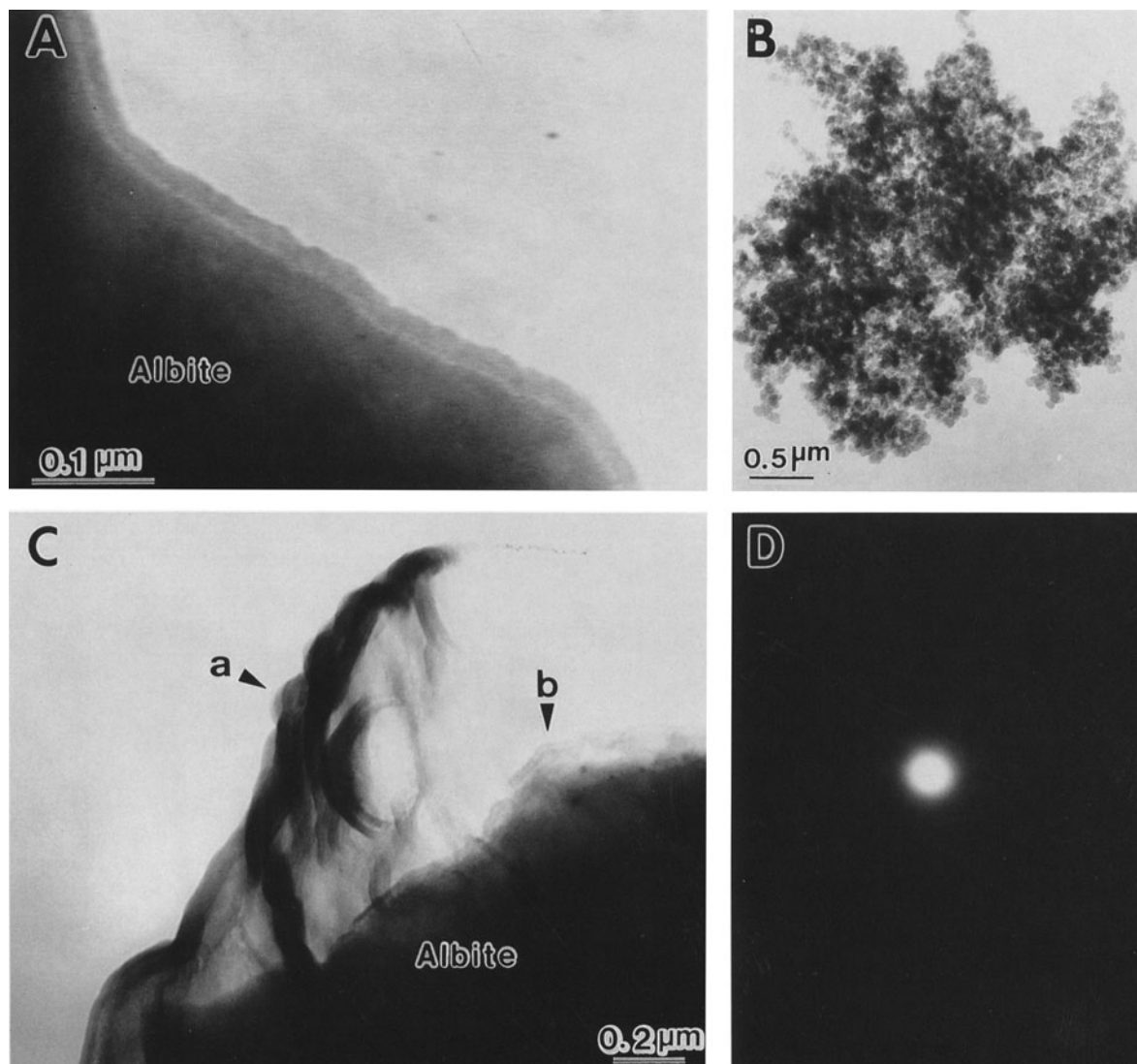


Figure 4. Transmission electron micrographs of leached layers produced at 225°C for A) 1 day and C) 3 days, and B) allophane formed at 225°C for 1 day. D) is an electron diffraction pattern of the leached layer C. Arrows (a) and (b) on C indicate a leached layer detached from the albite surface and a new leached layer formed on the surface after the detachment, respectively.

plane (Figure 1B), and amorphous silica precipitates with 0.5–2.0 μm in thickness exhibiting planar surface with irregular microcrack were deposited on the albite surface (Figure 1C) after 3 days of reaction. EDX indicated that the precipitates consisted only of Si (Figure 2A). The flaky materials increased with time and covered the whole surface of albite after 30 days of reaction (Figure 1D). XRD patterns showed a weak 14.9 \AA reflection at 50% relative humidity in the 5-day product (Figure 3). With increasing reaction time, the 14.9 \AA reflection was enhanced and an additional small peak at 9.98 \AA appeared. The 14.9 \AA peak shifted to 16.9 and 9.9 \AA after ethylene glycol solvation and heating at 400°C for 1 hr, respectively, whereas the 9.98 \AA

reflection did not move significantly by these treatments. Therefore, the 14.9 and 9.98 \AA peaks were assigned to the (001) reflections of smectite and mica, respectively. EDX confirmed that the smectite consisted mainly of Si, Al, and small amounts of Na (Figure 2B), indicating that the smectite was further classified as beidellite. Thus, the flaky material should be identified as beidellite, and small amounts of mica were also contained in these products.

TEM clearly showed the formation of a leached layer less than 0.03 μm thick on the albite surface after 1 day of reaction (Figure 4A). Mottled materials, which were probably precipitated from leachant, were present in the product (Figure 4B). The materials gave electron

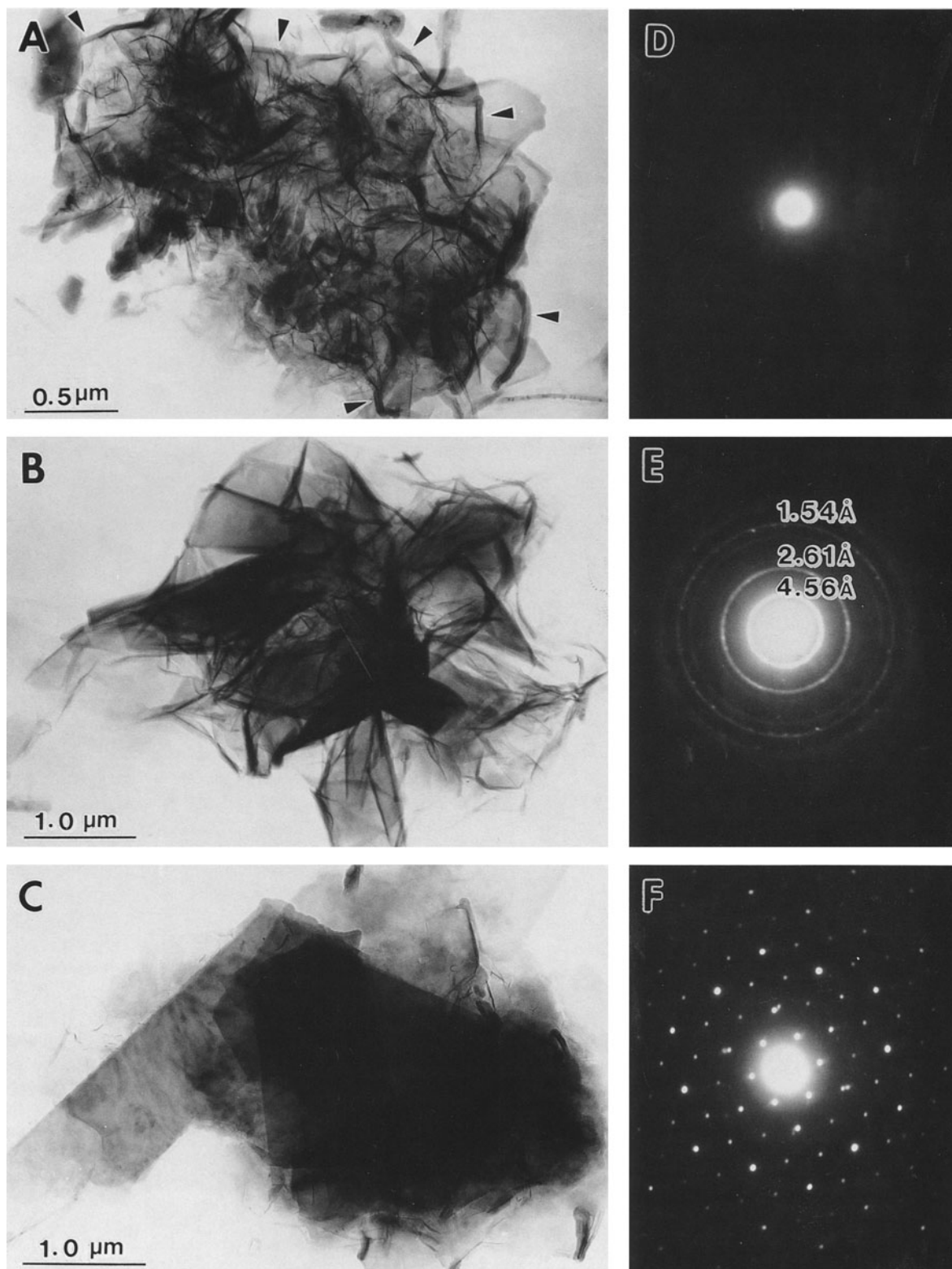


Figure 5. Transmission electron micrographs of alteration products at 225°C for A) 5 days and B, C) 10 days. D, E, and F are electron diffraction patterns of the products A, B, and C, respectively. Arrows on A indicate fibers.

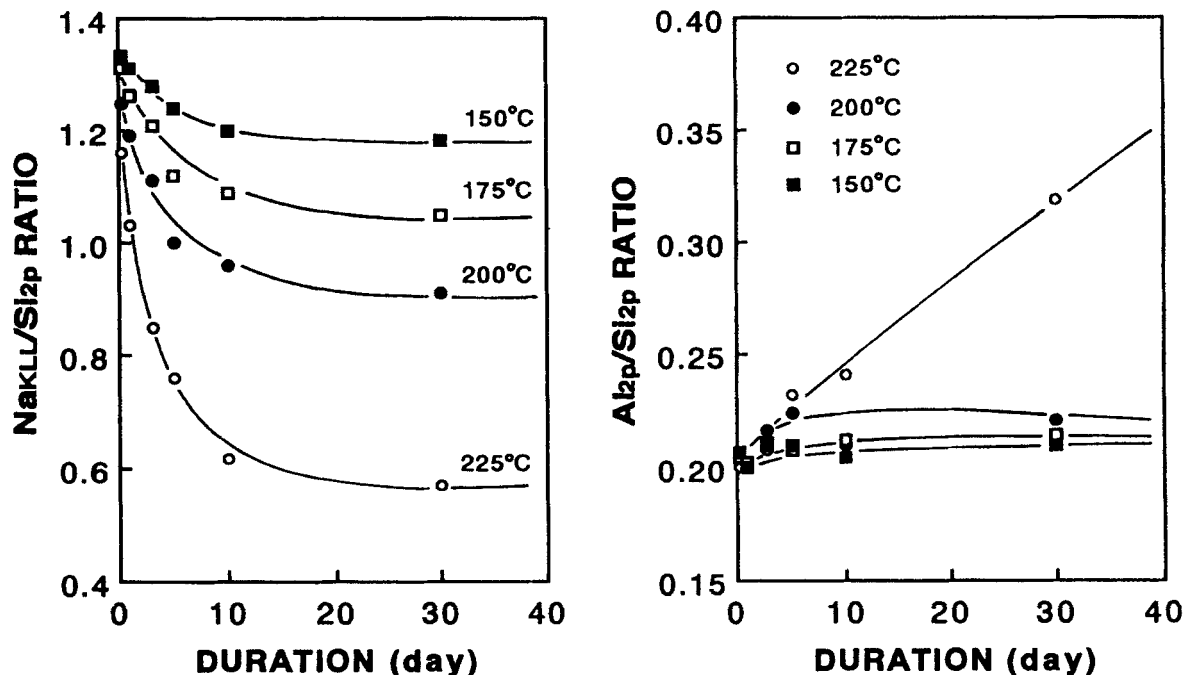


Figure 6. Variations of $\text{Na}_{\text{KLL}}/\text{Si}_{2\text{p}}$ and $\text{Al}_{2\text{p}}/\text{Si}_{2\text{p}}$ intensity ratios of XPS spectra for albite after experimental alterations. The $\text{Na}_{\text{KLL}}/\text{Si}_{2\text{p}}$ and $\text{Al}_{2\text{p}}/\text{Si}_{2\text{p}}$ intensity ratios of original albite are 1.351 and 0.203, respectively.

Table 1. Experimental conditions and alteration products.

Temp. (°C)	Duration	Alteration products
225	6 hr	Allophane
225	1 day	Allophane
225	3 days	Allophane, Fiber (As)
225	5 days	Fiber (Smectite) (As)
225	10 days	Smectite, (Mica) (As)
225	30 days	Smectite, Mica (As)
200	6 hr	Allophane
200	1 day	Allophane
200	3 days	Allophane
200	5 days	Fiber
200	10 days	Smectite (As)
200	30 days	Smectite (Mica) (As)
175	6 hr	Allophane
175	1 day	Allophane
175	3 days	Allophane
175	5 days	Allophane
175	10 days	Fiber
175	30 days	Smectite (Mica)
150	6 hr	Allophane
150	1 day	Allophane
150	3 days	Allophane
150	5 days	Allophane
150	10 days	Allophane (Fiber)
150	30 days	Fiber

Fiber = noncrystalline transitional material from amorphous leached layer to smectite, showing fibrous habit; As = amorphous silica precipitate; () = trace product. An amorphous leached layer formed on the albite surface was observed through all experimental runs by transmission electron microscopy.

diffraction patterns with a diffuse halo, but small angle scattering at 35–40 Å was observed by XRD. These observations indicated that the materials were essentially noncrystalline but contained structures with short-range order. Such structural characteristics are consistent with the definition of usage of the group name allophane (van Olphen, 1971). The thickness of the leached layer increased successively as the reaction proceeded. Finally, the layer was detached from the albite surface, and a new leached layer began to form on the albite surface exposed after the detachment (Figure 4C). Electron diffraction of these leached layers displayed no significant pattern, indicating noncrystalline structure (Figure 4D). After 5 days of reaction, noncrystalline fibrous materials less than 0.1 μm in width appeared within the leached layer matrix (Figure 5A), and the fibers grew to flaky smectite after 10 days (Figure 5B). The fibers gave electron diffraction patterns with diffuse haloes (Figure 5D), whereas the smectite exhibited diffraction rings at 4.51, 2.61, and 1.54 Å (Figure 5E). Small amounts of thin plates, laths, or mutual orientation of the particles having partly hexagonal edges appeared in the 10-day product (Figure 5C) and increased in abundance as the reaction progressed. Electron diffraction patterns of the particles displayed spots with approximately hexagonal symmetry (Figure 5F). XRD of the 10- and 30-day products showed weak reflection at 9.98 Å, which did not shift by ethylene glycol solvation or heating as mentioned

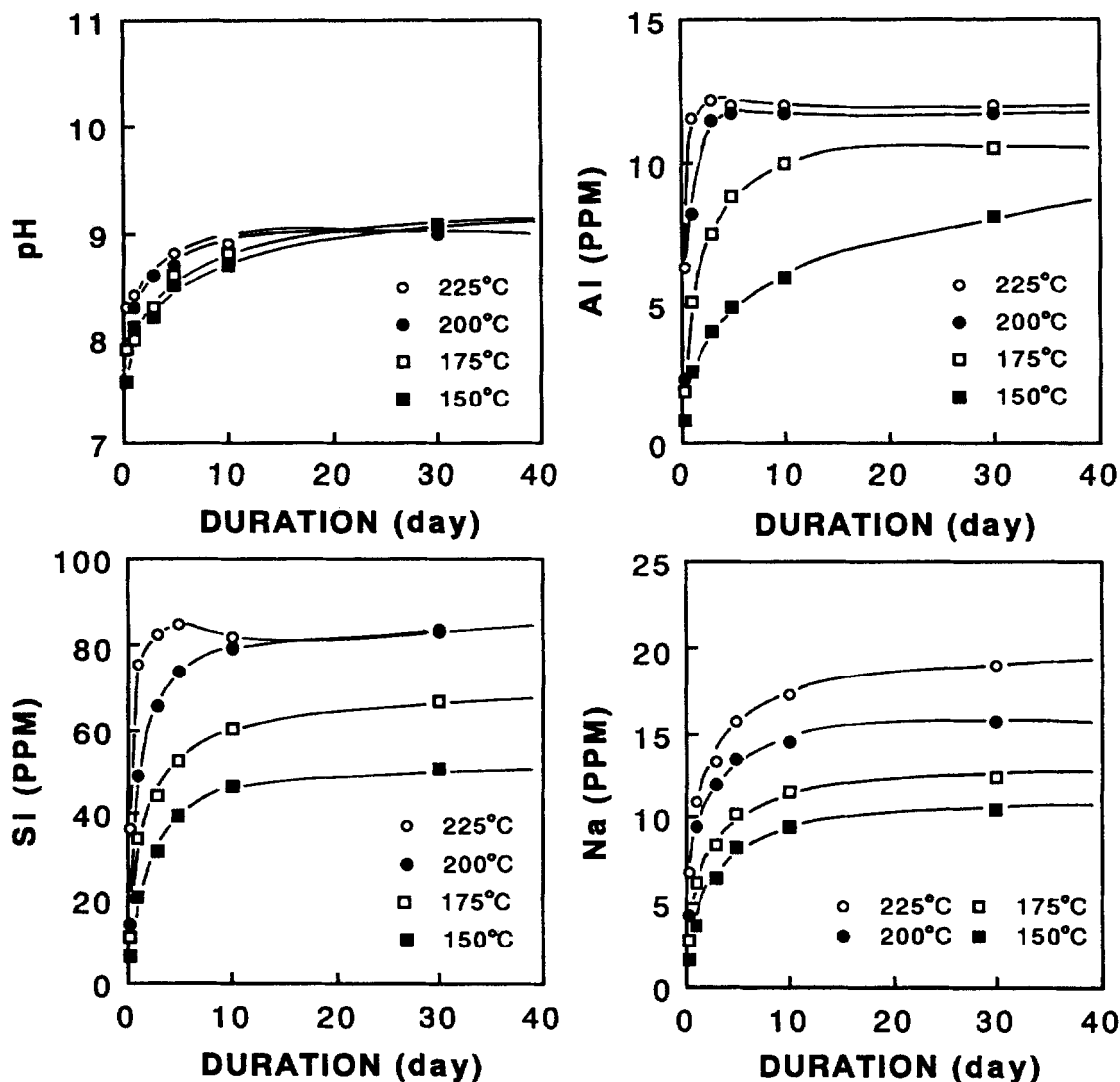


Figure 7. Changes in pH and concentrations of dissolved elements as a function of time for the 50-100 mesh sized albite in deionized-distilled water at 150°, 175°, 200°, and 225°C.

above. Therefore, the platy crystals may be K-mica because the d -value is closer to the basal spacing of muscovite than that of Na-mica (Bailey, 1984).

Surface alteration

The chemical composition of the albite surface changed during alteration. This change is strongly dependent on temperature and reaction time. XPS of original albite gave electron lines of Na_{1s} at 1076.6 eV, O_{KLL} at 750.0 eV, O_{1s} at 536.3 eV, Ca_{2p} at 352.5 eV, K_{2p} at 289.1 eV, C_{1s} at 284.6 eV, Na_{KLL} at 268.7 eV, Si_{2s} at 157.7 eV, Al_{2s} at 123.1 eV, Si_{2p} at 106.8 eV, Al_{2p} at 78.2 eV, and O_{2s} at 29.0 eV. Small peaks of satellite lines were also noted to the right of the strong O_{1s} , Si_{2s} , and Si_{2p} lines. The electron lines of Na_{1s} , Ca_{2p} ,

K_{2p} , and Na_{KLL} were weakened in the course of the reaction. Figure 6 shows variations of intensity ratios of $\text{Na}_{KLL}/\text{Si}_{2p}$ and $\text{Al}_{2p}/\text{Si}_{2p}$ as a function of time. The $\text{Na}_{KLL}/\text{Si}_{2p}$ ratio of original albite was 1.351, which decreased rapidly with time after 225°C alteration, whereas the ratios varied much less with decreasing reaction temperature. Similarly, the $\text{Al}_{2p}/\text{Si}_{2p}$ ratio of the original albite was 0.203, which increased linearly after 225°C reaction, where the ratios in lower temperature experiments increased slightly at the beginning of the reaction and then remained constant. The observations indicated that Na ions were preferentially leached from the albite surface with increasing temperature, and the dealcalized-leached layer tended to enrich in Al ions, especially for the 225°C experiments.

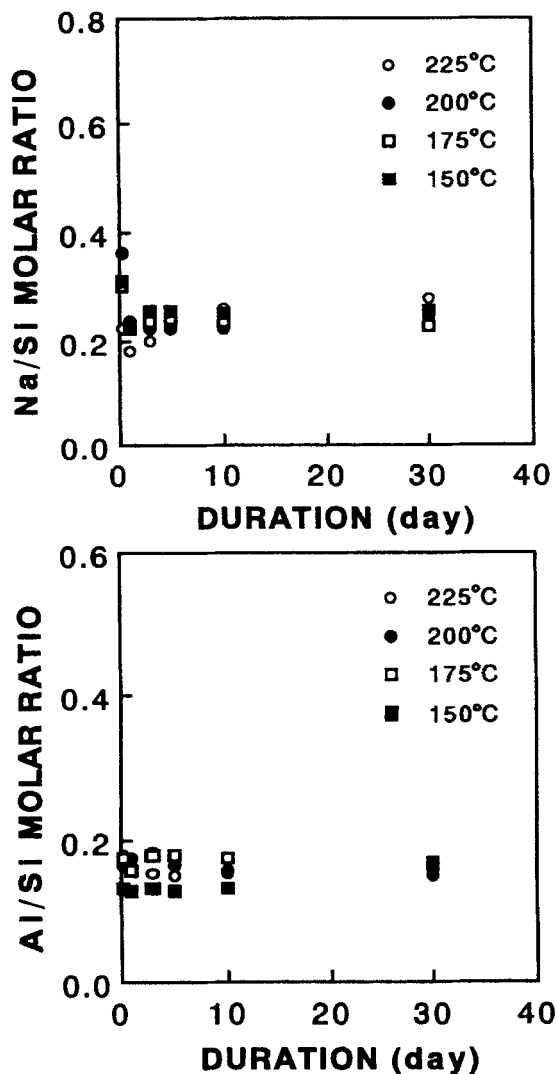


Figure 8. Variations of Na/Si and Al/Si molar ratios as a function of time in the solutions.

Chemistry of solution

The chemical composition of leachant solutions also changed progressively as the reaction progressed. Figure 7 shows variations of pH and concentrations of Na, Al, and Si ions in solutions during the alteration experiments. K values were below the detection limit of the instrument (0.01 ppm). The values of solution pH measured at 25°C increased rapidly at the beginning of the reaction and reached steady state at about pH 9.1 for all experiments after 30 days. The concentrations of leached elements showed parabolic dependence upon time: The rate of release of the element decreased gradually until a steady state was approached. The Na/Si and Al/Si molar ratios of solutions at 30 days were approximately 0.25 and 0.15,

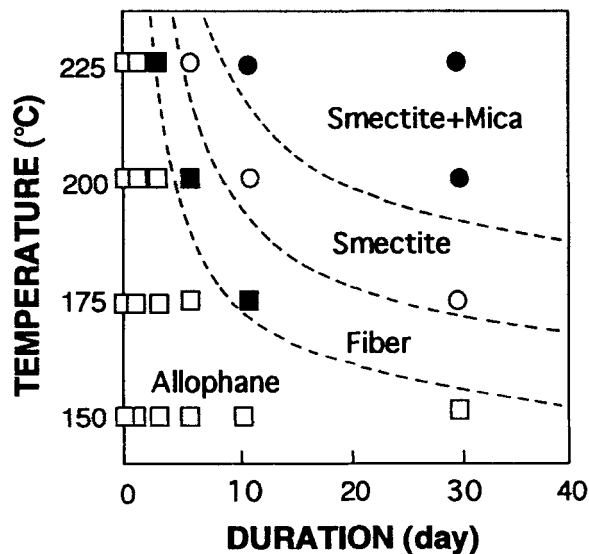


Figure 9. Phase diagram of alteration products in the system for albite and deionized-distilled water. □ = allophane; ■ = noncrystalline fiber; ○ = smectite; ● = smectite + mica.

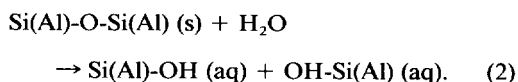
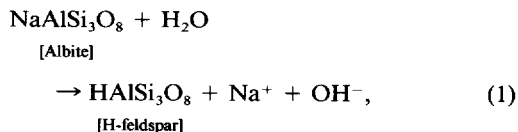
respectively (Figure 8). These values are apparently smaller than those of the stoichiometric ratio of albite (0.32 and 0.34, respectively), which is probably due to precipitation of alteration products.

DISCUSSION

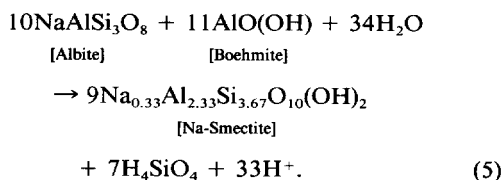
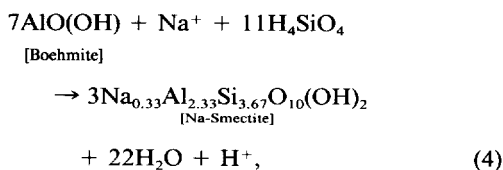
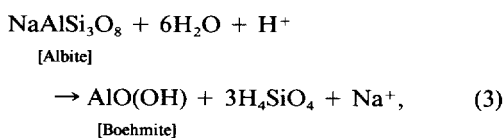
In the course of experimental alteration of albite in deionized-distilled water at 150° to 225°C, allophane, noncrystalline fiber, smectite, and K-mica were produced as alteration products. The phase diagram of this reaction system can be illustrated as shown in Figure 9. The noncrystalline fiber and smectite appeared to be the major alteration products of this experimental system. TEM clearly showed formation of the products as follows:

- 1) Formation of a leached layer less than 0.05 μm thick on the albite surface.
- 2) Growth of noncrystalline fibers in the leached layer matrix.
- 3) Development of flaky smectite from the fibrous materials.

Based on XPS, Na ions were preferentially leached from the albite surface as the reaction proceeded, producing a dealcalized-leached layer on the surface. The $\text{Al}_{2p}/\text{Si}_{2p}$ intensity ratio increased at the beginning of the reactions, indicating preferential leaching of Si over Al. This observation agrees with the suggestion of Chou and Wollast (1984, 1985). This leached layer was clearly visible by TEM and appeared noncrystalline to electron diffraction. The formation processes of the leached layer can be written as the following two steps:



Eq. 1 represents selective leaching of alkali ions from the albite surface by exchange of hydrogen in solution and formation of a dealcalized H-feldspar. Eq. 2 represents the breakdown of the silicate network of the H-feldspar by hydrolysis of the silicon-oxygen bonds, which produces a noncrystalline layer on the albite surface, and then the release of Si and Al ions from the crystal to aqueous solution. The first reaction raised the pH of the solution, which promoted more dissolution of Si and Al, and thereafter, precipitation of amorphous silica and allophane. As the reaction proceeded, the leached layer began to detach from the albite surface, and noncrystalline fibers appeared within the leached layer matrix as a transitional metastable phase that then grew to a flaky smectite. Figure 10 shows the solution compositions of 200°C experiments plotted on the stability diagram for the system of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. The solution compositions of this study moved as represented by small circles labeled 1 to 6, which almost fell in the stability field of Na-smectite. Assuming that albite dissolves congruently in aqueous solution, the theoretical paths of composition of the aqueous phase change along lines labeled CD in Figure 10. The chemical reactions in this theoretical system between pH 7 and 9 can be represented by:



Theoretically, during congruent dissolution, boehmite should precipitate initially as Reaction 3 progresses, and the composition of the aqueous phase should move to the boehmite-smectite stability field boundary (at D

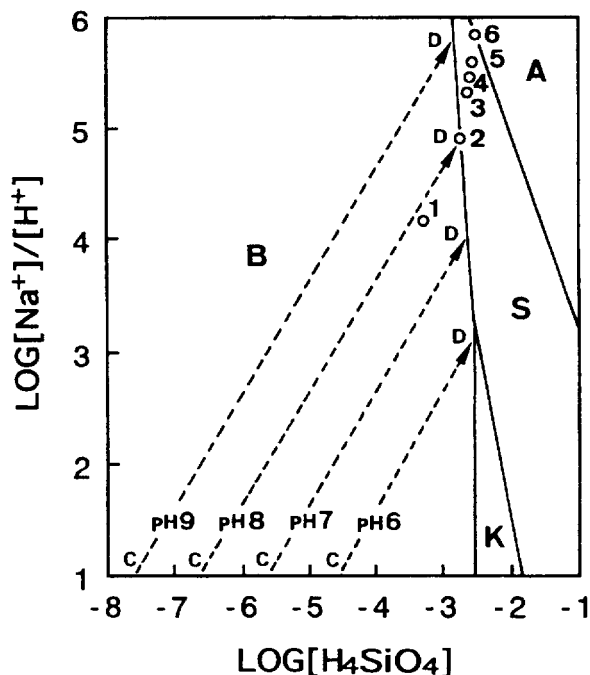


Figure 10. Plot of experimental data at 200°C on the activity diagram for the system of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 200°C. The symbols B, K, S, and A represent stability field of boehmite, kaolinite, Na-smectite, and albite, respectively. The positions of stability field boundaries were derived from Helgeson (1971). The labels 1 to 6 stand for aqueous compositions of 200°C experiments for 6 hr to 30 days. The CD lines are theoretical paths of aqueous composition during congruent dissolution of albite under different pH conditions.

in Figure 10). After that point, Na-smectite should appear as expressed by Eqs. 4 and 5. For the present experimental system, however, allophane and noncrystalline fiber appeared instead of boehmite at the initial alteration stage. These initial products disappeared, and new alteration phases of smectite and small amounts of K-mica were produced at the late stage. This observation suggests that the allophane and fibrous material appeared to occur as metastable phases. However, the smectite was formed in solution in the stability field of Na-smectite, suggesting that the smectite was also present as a stable phase. In early weathering stage of feldspar, poorly crystalline clay precursors exhibiting curled or circular forms have been reported (Eggleton and Buseck, 1980; Tazaki, 1986; Tazaki and Fyfe 1987a, 1987b). The results of this study strongly support the possibility that the clay precursors have been developed from leached layer on the feldspar surface, and grow to crystalline clays as weathering proceeds.

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