FORMATION OF MICA DURING EXPERIMENTAL ALTERATION OF K-FELDSPAR

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Abstract—Experimental alterations of K-feldspar in distilled-deionized water at 150°, 175°, 200°, and 225°C were performed. The alteration products and dissolution mechanism of K-feldspar were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), and X-ray photoelectron spectroscopy (XPS). SEM, TEM, and EDX clearly showed formation of fibrous boehmite less than 1.0 μm in length at the early alteration stages. The boehmite fibers decreased in abundance and rounded platy 1 M mica was produced as alteration proceeded. The mica exhibited initially angular shaped small flakes of 0.69 μm in average size, which developed to rounded platy particles of 1.97 μm. The main chemical reactions occurring in this experimental system can be expressed by:

$$KAlSi_3O_8 + 6H_2O + H^+ \rightarrow AlO(OH) + 3H_4SiO_4 + K^+,$$
[K-feldspar]　　　　　　　　　　　[boehmite]

$$3KAlSi_3O_8 + 12H_2O \rightarrow KAl_3Si_3O_{10}(OH)_2 + 2K^+ + 6H_4SiO_4 + 22H^+.$$
[K-feldspar]　　　　　　　　　[mica]

XPS showed no significant changes in intensities of photoelectron lines excited from K, Si, and Al in the K-feldspar surface before and after alteration, however the K/Si molar ratios in the solutions were considerably smaller than that of the original K-feldspar. The results of XPS strongly indicate that no dealkalized layer was produced on the surface, and that dissolution of K-feldspar in aqueous solution proceeded congruently by a surface-reaction mechanism. The discrepancy of mass balance in the solutions may be mainly caused by adsorption of K on the surface of boehmite.

Key Words—Dissolution mechanism, Experimental alteration, Fibrous boehmite, K-feldspar, Mica.

INTRODUCTION

Experimental alterations of K-feldspar in distilled-deionized water at temperatures between 150° and 225°C were performed to clarify dissolution mechanisms of K-feldspar and formation of alteration products. It is well known that dissolution of feldspar proceeds incongruently in aqueous solution, which has led to the hypothesis that a diffusion-inhibiting protective layer forms on the surface of the feldspar grain (Correns and von Englehardt 1938, Armstrong 1940). Since then, dissolution of feldspar has been investigated extensively and two main mechanisms have been proposed. One is a surface-reaction mechanism (Lagache *et al* 1961b; Lagache 1965; Petrović 1976; Petrović *et al* 1976; Aagaard and Helgeson 1982; Berner 1978, 1981; Holdren and Berner 1979; Dibble and Tiller 1981). The other is a diffusion-controlled mechanism which can be further divided into two categories: 1) diffusion through a leached layer (Wollast 1967; Pačes 1972, 1973; Nixon 1979; Fung *et al* 1980; Gardner 1983; Chou and Wollast 1984); and 2) diffusion through secondary precipitates (Helgeson 1971, 1972; Busenberg and Clemency 1976). Holdren and Berner (1979) investigated the dissolution mechanism of feldspar

etched in HF-H$_2$SO$_4$ solution by X-ray photoelectron spectroscopy. They reported that no protective layer appeared during dissolution and the observed non-linear rates of dissolution resulted from two stages: 1) ultrafine particles were produced during sample preparation which enhanced the rate of dissolution; and 2) dissolution of large grains occurred at dislocations and similar sites of excess energy on the surface. On the contrary, Chou and Wollast (1984, 1985) and Wollast and Chou (1985) argued against the above conclusion and suggested the formation of a protective layer of a few tens of angstroms at the feldspar surface from mass balance of dissolved elements in solution.

An experimental investigation on the decomposition of K-feldspar in aqueous solutions was carried out by Gruner (1944). This experiment was conducted in a large excess of 0.1 N HCl solutions at 300° to 400°C. The study of K-feldspar alteration in acid solutions under moderate temperature was performed by Norton (1939). Syntheses of clay minerals in the system of K$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O have been also reported by Yoder and Eugster (1955) and Velde (1965). Hemley (1959) studied phase equilibrium in the system of K$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O and showed alteration of K-feldspar to mica

　　　　397

Table 1. Experimental conditions and alteration products.

Run	Temp. (°C)	Duration	Products
A-1	225	6 h	Boehmite, (Mica)
A-2	225	1 day	Boehmite, (Mica)
A-3	225	3 days	Boehmite, (Mica)
A-4	225	5 days	Mica, (Boehmite)
A-5	225	10 days	Mica, (Boehmite)
A-6	225	30 days	Mica
A-7	225	60 days	Mica
B-1	200	6 h	Boehmite, (Mica)
B-2	200	1 day	Boehmite, (Mica)
B-3	200	3 days	Boehmite, (Mica)
B-4	200	5 days	Boehmite, (Mica)
B-5	200	10 days	Boehmite, (Mica)
B-6	200	30 days	Mica, (Boehmite)
B-7	200	60 days	Mica
C-1	175	6 h	Boehmite, (Allophane)
C-2	175	1 day	Boehmite, (Allophane)
C-3	175	3 days	Boehmite, (Allophane)
C-4	175	5 days	Boehmite, (Mica), (Allophane)
C-5	175	10 days	Boehmite, (Mica), (Allophane)
C-6	175	30 days	Boehmite, (Mica), (Allophane)
C-7	175	60 days	Boehmite, (Mica), (Allophane)
D-1	150	6 h	Boehmite, (Allophane)
D-2	150	1 day	Boehmite, (Allophane)
D-3	150	3 days	Boehmite, (Allophane)
D-4	150	5 days	Boehmite, (Allophane)
D-5	150	10 days	Boehmite, (Allophane)
D-6	150	30 days	Boehmite, (Allophane)
D-7	150	60 days	Boehmite, (Smectite)

( ) = trace product identified by transmission electron microscopy.

or kaolinite in aqueous solution of various K^+/H^+ activity at 200° to 550°C. Helgeson (1971) plotted experimental data on the activity diagram for the system of $K_2O-Al_2O_3-SiO_2-HCl-H_2O-CO_2$, and suggested that boehmite, kaolinite, and illite precipitated as reaction products under equilibrium conditions at 100°, 150°, and 200°C. Busenberg (1978) performed artificial weathering of feldspars in water at 25°C up to 1200 h and reported that a very poorly crystalline to amorphous materials, including a microcrystalline gibbsite or halloysite, appeared as an alteration product. On the other hand, the alteration processes of K-feldspar from the view point of thermodynamics have been reported (Lagache *et al* 1961a, 1961b; Lagache 1965; Helgeson *et al* 1969, 1984). However, alteration products of K-feldspar, especially at the initial alteration stage, and formation processes of the products have not been sufficiently confirmed by these studies.

The purposes of this study are to reveal the dissolution mechanism of K-feldspar in water using X-ray photoelectron spectroscopy, which provides the relative chemical composition less than few tens of angstroms beneath the surface layer, and to investigate formation of alteration products by electron microscopic observation.

EXPERIMENTAL METHODS

The K-feldspar used in this study is from Kurosaka, Ibaraki Prefecture, Japan. No impurities were detected by X-ray powder diffraction analysis or optical microscopy. The structural formula calculated from chemical analysis data obtained by electron microprobe analysis of a polished section is: $(K_{0.78}Na_{0.22})[Al_{1.00}Si_{3.00}]O_8$. The K-feldspar crystals were crushed in an agate mortar, and 50 to 100 mesh size grains were separated by dry sieving. Then, the material was cleaned ultrasonically in acetone more than five times to remove adhering ultrafine particles and was used as starting material.

All experiments were conducted using a Teflon bottle in which 4.0 g of starting material and 100 ml of distilled-deionized water were sealed, which was then placed in a pressure vessel. The alteration was performed under static conditions at 150°, 175°, 200°, or 225°C for 6 h, 1, 3, 5, 10, 30, or 60 days. The pressure was the equilibrium vapor pressure at the corresponding temperature. After reaction the vessel was quenched in water, and then solids and solutions were separated by centrifugation. Small amounts of solids (about 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). It was confirmed that this procedure gave no significant effect on an alteration layer formed on the feldspar surface (Kawano and Tomita 1994). The alteration products were collected by centrifugation and were washed with distilled-deionized water. The samples were used for X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). The concentrations of dissolved elements were measured by atomic absorption spectroscopy for Al and K, and by colorimetry for Si. The pH-values of leachant solutions were measured with a TOA HM-20S digital pH meter using a glass electrode at room temperature. The detailed analytical techniques were described in Kawano *et al* (1993). The experimental conditions and alteration products are summarized in Table 1.

RESULTS

Alteration products

The 225°C experiments produced fibrous boehmite less than 1.0 μm in length as a major alteration product of 6-h, 1-, 3- and 5-day reactions (Figure 1a) with minor product of mica. EDX indicated that the fibers consisted of Al and Si (Figure 2a), suggesting that the boehmite contained small amounts of Si as an adsorbed impurity. Figure 3a shows TEM of the aggregate of boehmite fibers produced for 5-day alteration, which clearly showed that the material exhibited a needle-like habit less than 1.0 μm in length. Electron diffrac-
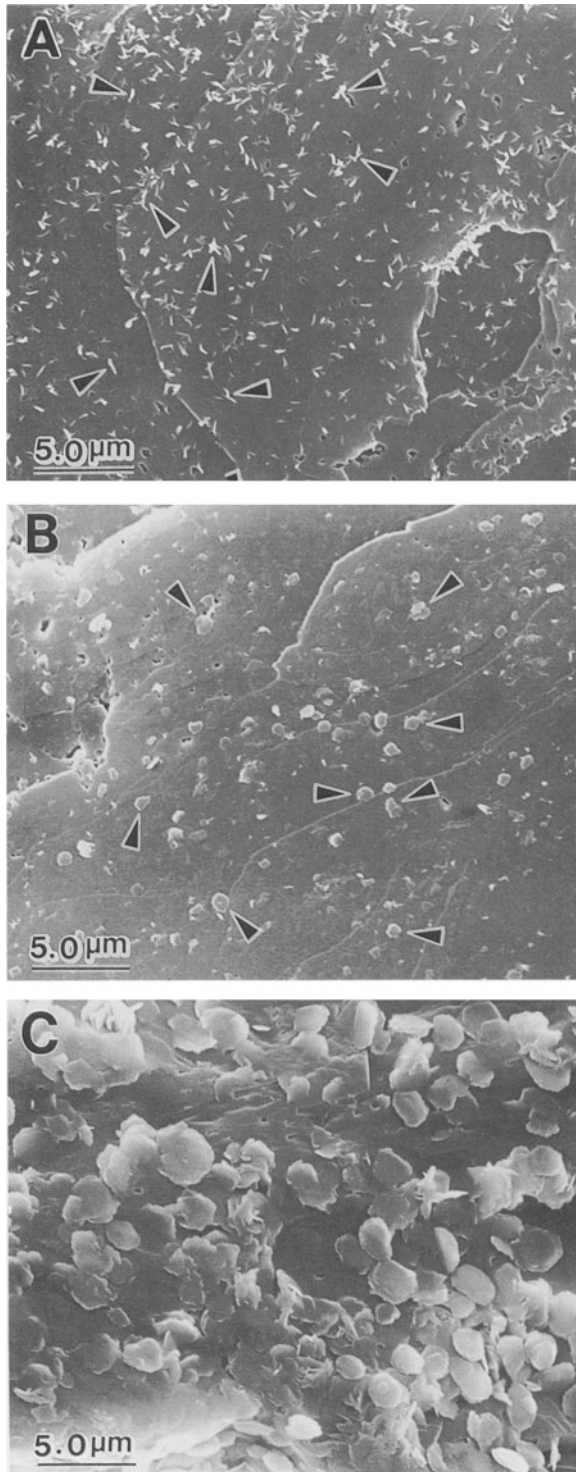
Figure 1. Scanning electron micrographs of alteration products at 225°C for (a) 1 day, (b) 10 days, and (c) 60 days. Arrows on photographs a and b indicate some examples of fibrous material and rounded mica, respectively.
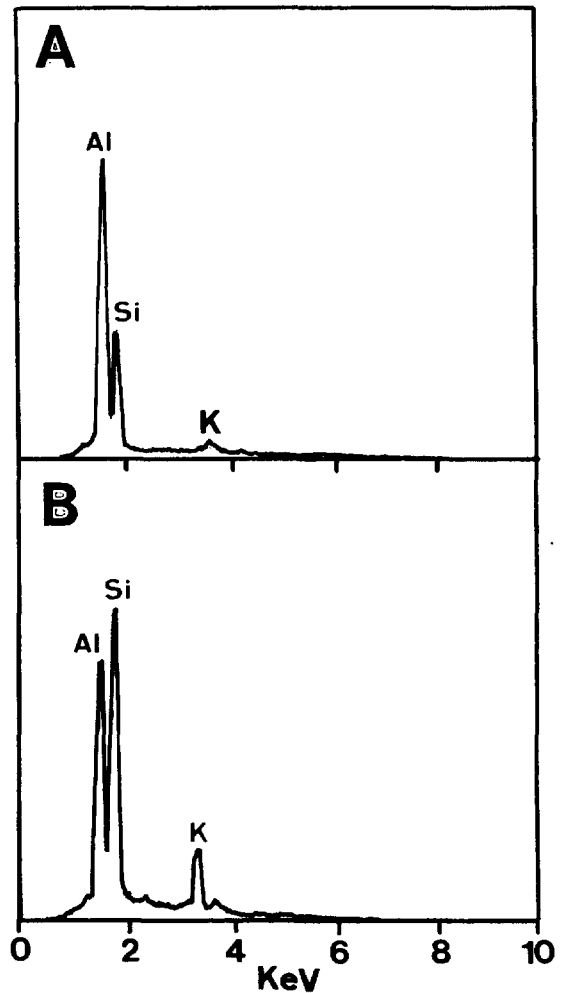

Figure 2. Energy dispersive X-ray analysis spectra of (a) fibrous boehmite formed at 225°C for one day and (b) mica formed at 225°C for 60 days.

tion of the fiber matrix displayed a diffuse halo (Figure 3e) indicating noncrystalline structure. After 10 days, the fibrous boehmite appeared to decrease in abundance and platy mica crystals exhibiting rounded outline developed as major alteration product (Figure 1b and 1c). EDX indicated that the mica consisted mainly of Si, Al, and K (Figure 2b). XRD showed sharp basal reflections at 10.0, 5.02, 3.34, and 2.51 Å (Figure 4), which did not shift after heating at 500°C or solvation with ethylene glycol. The value of d(060) spacing is 1.496 Å indicating dioctahedral structure. In the 22°–33°2 θ region, 3.661 and 3.069 Å reflections, which correspond to $11\bar{2}$ and 112 of 1 M mica, were observed. Figures 3b–d show TEMs of micas produced for 10-, 30-, and 60-day reactions, respectively. The mica flakes of the 10-day product had angular shapes with irregular outlines, however the form tended to change to rounded shapes with increasing reaction time. Both angular
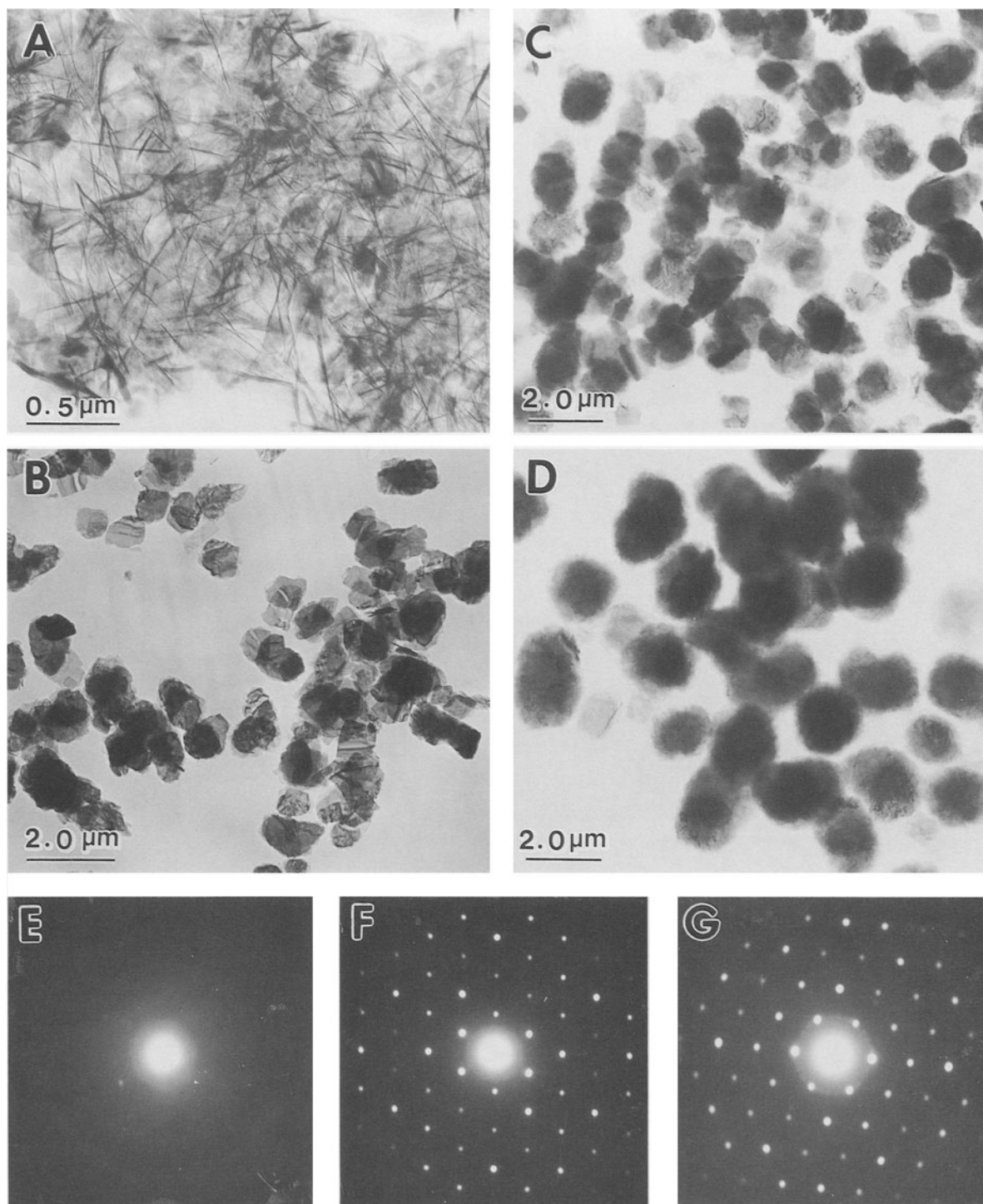
Figure 3. Transmission electron micrographs of alteration products at 225°C for (a) 5 days, (b) 10 days, (c) 30 days, and (d) 60 days, and electron diffraction patterns of the products for (e) 5 days, (f) 10 days, and (g) 60 days at 225°C.

and rounded flakes gave electron diffraction of hexagonal spot patterns (Figures 3f and 3g). Figure 5 shows variations of average particle size as a function of time for the micas produced by the reactions conducted from

5 to 60 days. The particle size was measured by TEM, and was defined as the longest distance of the edge of a particle. The average particle size was calculated from more than 200 particles, which increased progressively
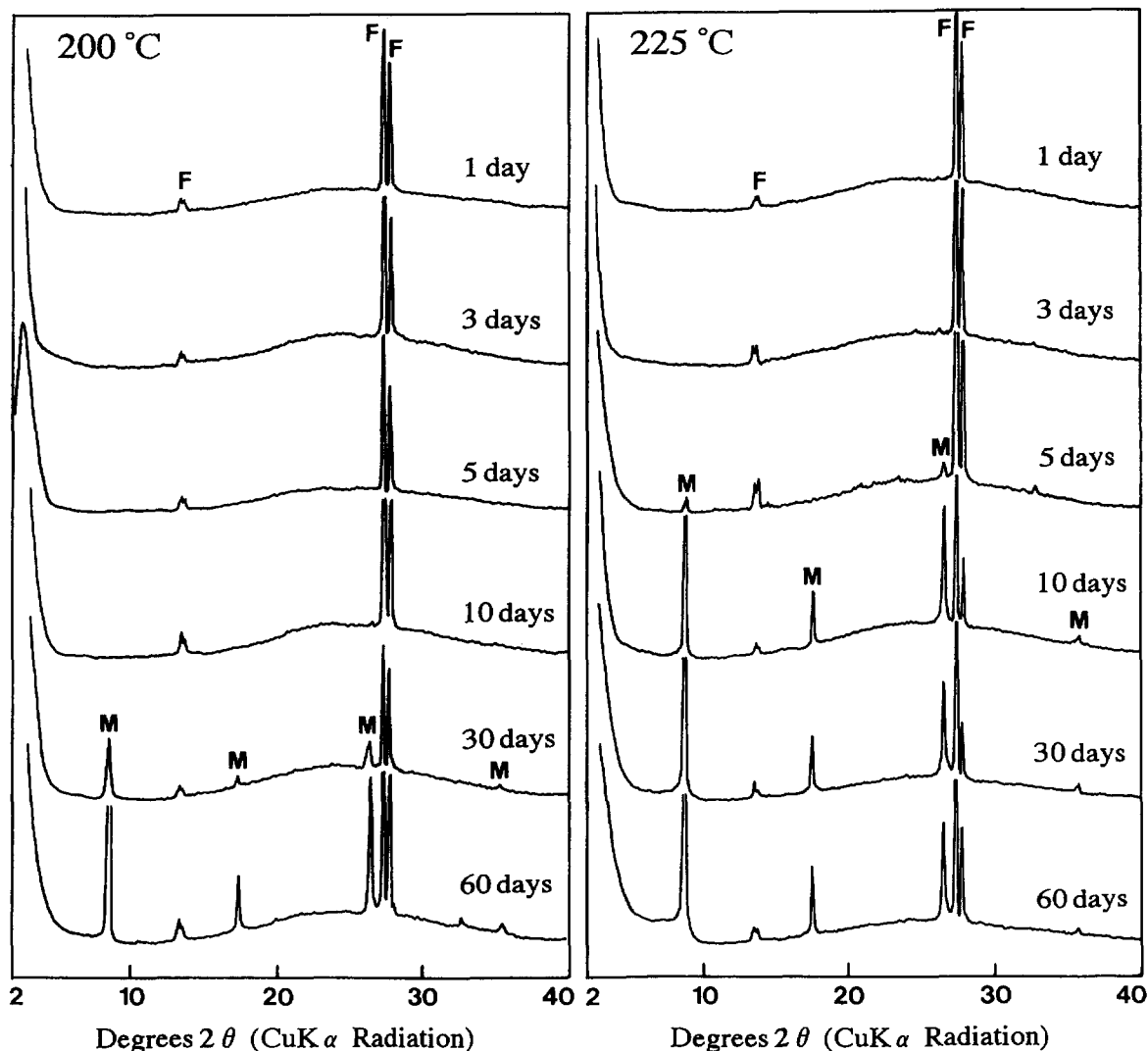
Figure 4.   X-ray powder diffraction patterns of alteration products at 200° and 225°C for 1 to 60 days. Symbols F and M indicate K-feldspar and mica, respectively.

with time: 5 days, 0.69 μm; 10 days, 1.26 μm; 30 days, 1.56 μm; 60 days, 1.97 μm.

Products similar to those of the 225°C experiments were formed by the 200°C experiments (Table 1). Noncrystalline fibrous boehmite less than 1.0 μm in length and trace amounts of angular-shaped micas were produced in an early reaction stage. With increasing reaction time, the fibers decreased and mica flakes appeared to increase (Figure 4). For the 175°C experiments, noncrystalline fiber was formed as the major alteration product together with small amounts of allophanes, and mica flakes appeared after reactions of 5 days. XRD showed small-angle scattering or small-angle diffraction at 30 to 40 Å which are characteristic features of allophanes (van der Gaast et al 1985). For the reactions at 150°C, mica could not be detected by

TEM but large amounts of noncrystalline fiber were observed.

Surface composition

The first reaction of feldspars with aqueous solution has been considered to be exchange of hydrogen ions from solution for alkali cations of the reactant mineral, and this reaction produces a dealkalized layer on the surface (Wollast 1967; Petrovic 1976; Petrović et al 1976; Berner 1978, 1981; Berner and Holdren 1979). Based on XPS analysis, the original K-feldspar gave electron lines of O_{KLL}, 749.7 eV; O_{1s}, 536.2 eV; K_{2s}, 382.2 eV; $K_{2p1/2}$, 300.1 eV; $K_{2p3/2}$, 297.3 eV; C_{1s}, 284.0 eV; Na_{KLL}, 268.5 eV; Si_{2s}, 157.6 eV; Al_{2s}, 123.5 eV; Si_{2p}, 106.9 eV; Al_{2p}, 78.0 eV; and O_{2s}, 28.4 eV (Figure 6a). If a dealkalized layer is formed on the K-feldspar
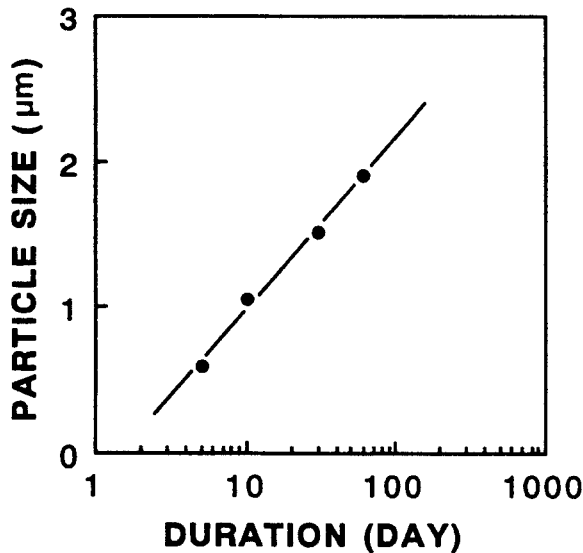
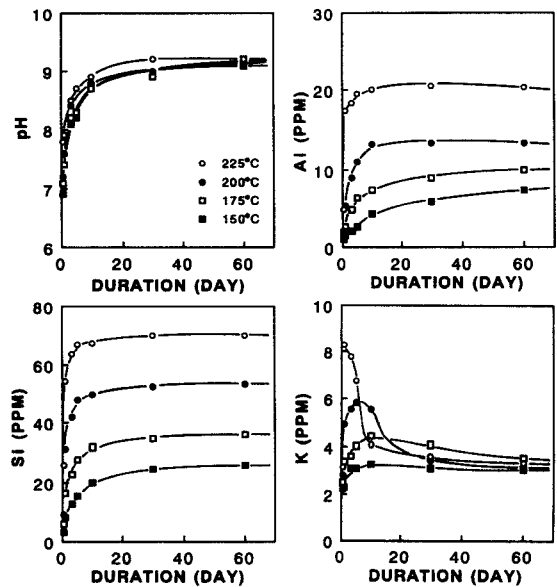Figure 5.   Variations of average particle size as a function of log time for mica formed by reactions at 225°C.
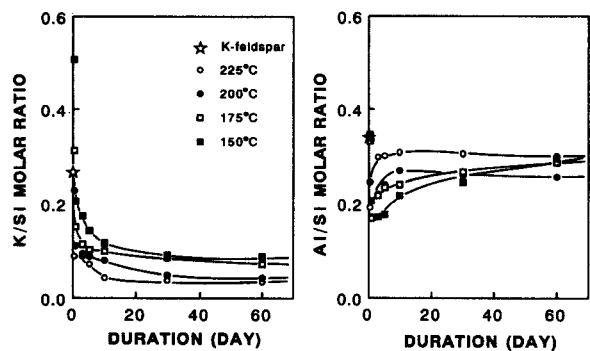

Figure 7.   Variations of pH and dissolved elements in solutions during hydrothermal reactions at 150°, 175°, 200°, and 225°C.

surface during the reactions, decrease in intensities of K_{2s} and K_{2p} lines would be expected (Holdren and Berner 1979, Berner *et al* 1985). Figure 6b shows variations of intensity ratios between K_{2s} and Si_{2s} electron lines, in which no significant changes were recognized during the reactions. The result indicates that no dealkalized layer could be present on the K-feldspar surface. There were also no significant changes in Al_{2s}/Si_{2s} intensity ratios in all the experiments.

Chemistry of solutions

The evolution of pH and concentrations of Si, Al, and K in solutions during the alterations are shown in Figure 7. The pH values increased at the beginning of the reactions and reached steady-state at a pH of approximately 9.0 after 30 days. Similarly, the concentrations of Si and Al increased rapidly in the early stage, but rates of increase declined progressively with time

to reach steady-state after 30 days. The concentrations of K increased at the beginning of the reactions, but the values decreased more rapidly with increasing the reaction temperature. Figure 8 shows variations of K/Si and Al/Si molar ratios in the solutions. These values were mainly in the range below 0.1 for K/Si and 0.2 to 0.3 for Al/Si. The K/Si ratios are noticeably smaller than that of original K-feldspar (K/Si = 0.26). For the 150°C reaction, K ion is not consumed during reaction because no precipitation of mica appeared. Therefore, leaching rate of K from the surface of K-feldspar must be slower than those of Si and Al. This observation is not compatible with the result of XPS analysis (Figure 6). The probable reason for this will be discussed in next section.

Figure 6.   XPS wide-scan spectrum of (a) original K-feldspar and (b) variations of K_{2s}/Si_{2s} intensity ratios of K-feldspars during hydrothermal reactions at 150°, 175°, 200°, and 225°C.

Figure 8.   Variations of K/Si and Al/Si molar ratios in solutions during hydrothermal reactions at 150°, 175°, 200°, and 225°C.
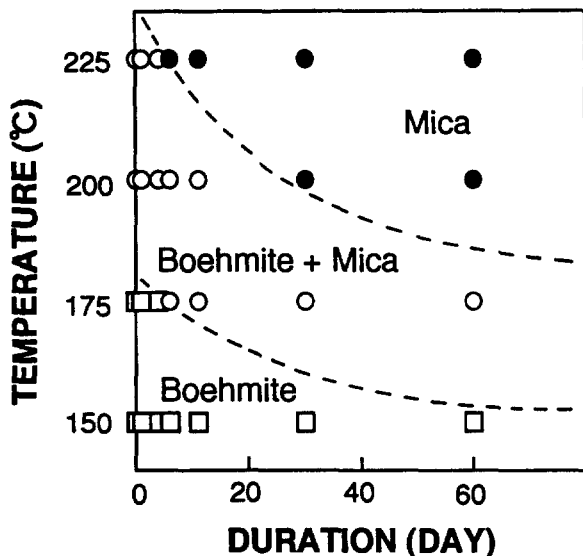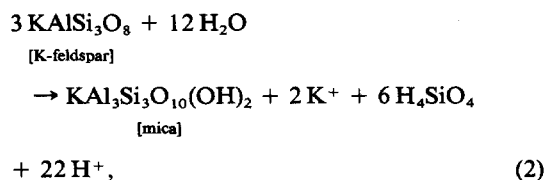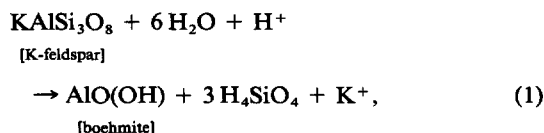
Figure 9. Schematic representation showing phase diagram of alteration products for the system of K-feldspar and distilled-deionized water. □ = boehmite, ○ = boehmite and mica, ● = mica.

DISCUSSION

The present study revealed that initially noncrystalline fibrous boehmite appeared and subsequently mica was formed during the dissolution of K-feldspar in distilled-deionized water at 175° to 225°C. The phase diagram of this reaction system represented schematically is illustrated in Figure 9. The fibrous boehmite appeared mainly at low temperature and in the early alteration stages, and decreased in abundance with increasing reaction time. The observation suggested that the fibrous boehmite must be a metastable phase in this system. On the contrary, the mica tended to be produced at higher temperature and later stages of reaction, and increased in abundance and particle size with time. The morphology of the mica characteristically changed from angular-shaped plates to rounded platy shapes with time. The rounding or smoothing of a crystal surface indicates a decrease in the surface-energy anisotropy which is generally caused by a dissolution-recrystallization process controlled by an Ostwald ripening mechanism under decreasing supersaturation (Baronnet 1982). The micas produced for 200°C experiments gave no obvious XRD peaks except for 003 reflection in the 22° to 33°2 θ region, which probably suggests that the products belong to the 1 M_d polytype. However, 1 M was clearly preserved in the 225°C experiments. The transformation sequence of polytypes of mica appears as 1 M_d → 1 M → 2 M_1 by increasing either temperature, pressure, or time (Yoder and Eugster 1955, Velde 1965). According to Yoder and Eugster (1955), the 1 M_d polytype occurs as metastable phase, 1 M is stable phase below 200°–350°C,

and 2 M_1 above this range. The present results are consistent with their report. Figure 10 shows experimental data from runs conducted at 200°C plotted on the stability diagram for the system of K_2O-Al_2O_3-SiO_2-H_2O at 200°C, which suggests that boehmite and mica should precipitate theoretically as the reaction progresses. These reactions can be represented by:

$$KAlSi_3O_8 + 6 H_2O + H^+$$
[K-feldspar]

$$\rightarrow AlO(OH) + 3 H_4SiO_4 + K^+, \qquad (1)$$
[boehmite]

$$3 KAlSi_3O_8 + 12 H_2O$$
[K-feldspar]

$$\rightarrow KAl_3Si_3O_{10}(OH)_2 + 2 K^+ + 6 H_4SiO_4$$
[mica]

$$+ 22 H^+, \qquad (2)$$

$$3 AlO(OH) + 3 H_4SiO_4 + K^+$$
[boehmite]

$$\rightarrow KAl_3Si_3O_{10}(OH)_2 + 6 H_2O + H^+. \qquad (3)$$
[mica]
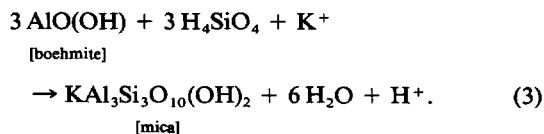
In the course of the K-feldspar dissolution, boehmite appears initially as reaction (1) which stimulates ac-
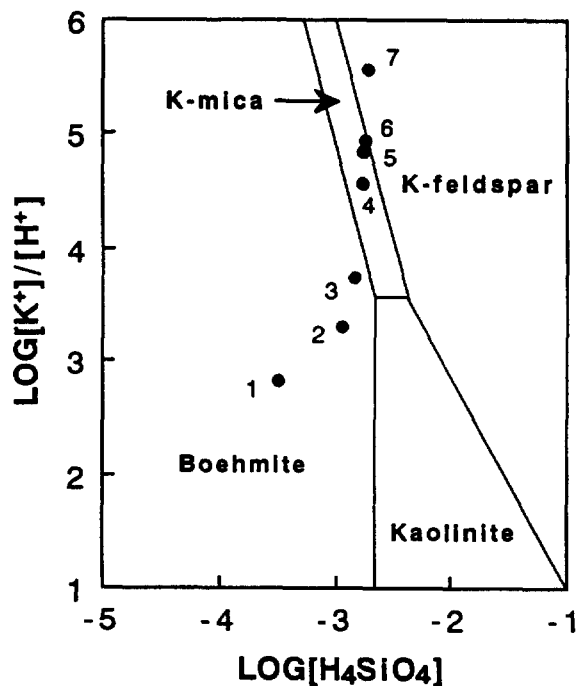

Figure 10. Plot of experimental data at 200°C on the activity diagram for the system of K_2O-Al_2O_3-SiO_2-H_2O at 200°C. The positions of field boundaries were derived from Helgeson (1971).

tivities of SiO_2 and K^+ in the solution. Then, mica begins to precipitate as expressed by Eqs. (2) and (3).

The dissolution mechanism should be an important factor controlling the formation of early stage alteration products such as noncrystalline materials and clay minerals. For instance, it is widely accepted that dissolution of glasses is incongruent overall and produces an amorphous leached layer on the glass surface (Doremus 1975, Lanford *et al* 1979, Houser *et al* 1980, Smets and Lommen 1982). This leached layer changes progressively to secondary crystalline phases (e.g., smectite, serpentine) as the reaction progresses (Abrajano *et al* 1989, 1990; Murakami *et al* 1989; Banba *et al* 1990). Similar observation was confirmed during the dissolution of albite in distilled-deionized water at 175° to 225°C (Kawano and Tomita 1994). For the K-feldspar, XPS showed that the surface composition remained unchanged during hydrothermal reactions, which implies that no dealkalized layer has been produced on the surface and that the dissolution has proceeded congruently. This result indicates that the dissolution of K-feldspar in aqueous solution is controlled by surface reaction instead of a transport-controlled mechanism. The surface reaction controlled dissolution can be simply defined as detachment of ions from the surface of the crystal (Berner 1978) in which dissolution proceeds linearly if concentration in solution and surface area of solid remain constant. The nonlinear rate of dissolution observed in this study may be caused by the following factors as discussed by Velbel (1986): 1) formation of secondary precipitates; 2) presence of ultrafine particles produced during sample preparation; 3) presence of high energy sites of the K-feldspar surface; and (4) changes in composition of the solutions.

The Al/Si molar ratios in the solutions were roughly compatible with a stoichiometric ratio in the original K-feldspar, whereas the K/Si molar ratios were considerably smaller than that required by congruent dissolution. These values vary with the secondary product as well as dissolution process of the starting material, they therefore could not be used for interpretation of dissolution process of the K-feldspar. However, the deficiency of K is apparently not caused by utilization with precipitation of mica, because the K/Si molar ratios of solutions of 150°C reactions also showed considerably smaller values than that of the original K-feldspar. We performed experimental alterations of K-feldspar in 0.01 N HCl solution at 150° and 200°C for 1 to 60 days. In this case, fibrous boehmite, kaolinite, or halloysite were the major products, and mica could not be detected by XRD and TEM. However, it was found that deficiency of K in solutions occurred depending on the amounts of boehmite (Kawano and Tomita, unpublished data). These observations probably suggest that the deficiency is due to adsorption of K^+ ions on the surface of boehmite.

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