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SYNTHESIS OF KAOLINITE FROM MICAS AND K-DEPLETED MICAS

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Abstract—The weathering stages of K-depleted biotite, K-depleted phlogopite, and natural biotite were investigated using hydrothermal treatment with $AlCl_3$ solution at 200ºC for 12 to 72 h. Although there were some differences in the degree of weathering of the two K-depleted micas, both first transformed to hydroxy-Al interlayered vermiculite (HIV), which then altered to kaolinite. In case of the natural biotite, the biotite first transformed to a K-depleted mica-like phase, which then altered to kaolinite. The natural biotite had resisted weathering to kaolinite more than did the K-depleted biotite, as expected. The K-depleted phlogopite had less resistance in weathering to kaolinite than the K-depleted biotite. The transformation process changed the color of the micas. The K-depleted biotite changed from greenish-black through yellow to pale gray whereas the natural biotite changed from greenish-black through beige to yellow. However, in the case of K-depleted phlogopite, there was no significant color change during the transformation process. The presence of the interlayer K^+ ions and the structural Fe^{2+} ions in mica appear to have contributed to the differences in the degree of weathering to kaolinite among the micas investigated.

Key Words—Hydrothermal Treatment, Hydroxy Al-interlayered Vermiculite (HIV), Kaolinite, K-depleted Biotite, K-depleted Phlogopite, Transformation, Weathering.

INTRODUCTION

The transformation of soil constituents is an important soil-formation process (Allen and Hajek, 1989; Brady and Weil, 2002). The chemical weathering of primary minerals such as micas and feldspars is a typical transformation process. Understanding the weathering of minerals under environmental conditions can help in predicting the final weathering products as well as evaluating the soil conditions, including the stability of the minerals and the properties of soil solutions.

The weathering of micas such as biotite, muscovite and phlogopite in soil environments is certainly related to the genesis of soils (Rebertus *et al.*, 1986). Many researchers have studied the weathering mechanisms and products of mica. The weathering products of mica are dependent on weathering environments (Rebertus *et al.*, 1986). There are two types of transformations of biotite to vermiculite. The structure of biotite can be modified to form vermiculite, while two biotite layers can also be rearranged to form one vermiculite layer in the presence of sufficient H_3O^+ and O_2 (Banfield and Eggleton, 1988). Further weathering processes result in the transformation of the vermiculite to kaolinite (Graham *et al.*, 1989). Biotite can also be directly transformed to kaolinite (Ahn and Peacor, 1987; Kretzschmar *et al.*, 1997; Jolicoeur *et al.*, 2000). On the other hand, muscovite was reported to transform to kaolinite directly (Singh and Gilkes, 1991) and F-rich phlogopite was reported to form the vermiculitized phlogopite by alteration processes (Toksoy-Koksal *et al.*, 2001). The alteration of minerals commonly involves dissolution which can be congruent or incongruent. The dissolution of phlogopite was reported to be incongruent in the range of pH 4–5 (Lin and Clemency, 1981). Although numerous investigations on weathering of micas have been carried out under laboratory and field conditions, few efforts have been made in relation to the tropical environments where Al-rich, high-temperature, and acidic conditions are common (Murphy *et al.*, 1998; White, 2002).

Here we report the artificially enhanced transformation of K-depleted biotite, K-depleted phlogopite and natural biotite in the Al-rich acidic solutions similar to those encountered in tropical conditions. The experiments were carried out under acidic hydrothermal conditions (3 N $AlCl_3$ at 200ºC) because the transformation reactions of micas are very slow under natural conditions. Although micas in natural systems are less commonly exposed to hydrothermal conditions, the results obtained from the present studies on the transformation of these micas are expected to be useful in understanding the weathering mechanism of micas under natural conditions over a long period of time.

MATERIALS AND METHODS

Clays and reagents

Three different micas were used in this study. Natural biotite from Bancroft, Ontario and K-depleted biotite were provided by the late Dr A.D. Scott. Their particle sizes were <50 μm. K-depleted phlogopite was prepared from natural phlogopite purchased from Ward's Natural Science Establishment, Inc. (Rochester, NY, USA). All

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reagents were of analytical grade, and were used without further purification.

Preparation and characterization of K-depleted phlogopite

In order to control particle size, natural phlogopite was wet ground in a blender with deionized water. Phlogopite <50 μm in size was obtained using a standard sieve. Potassium removal from the <50 μm fraction of phlogopite was carried out by the method developed by Scott and Smith (1966). A 15 g portion of the <50 μm material was stirred in a dark bottle containing 300 mL of 1.0 M NaCl – 0.2 N sodium tetraphenylborate (NaTPB) – 0.01 M disodium ethylenediaminetetraacetic acid (EDTA) solution at room temperature for 1 day. After equilibration, the mica slurry was filtered through Whatman 50 filter paper under vacuum. The collected solid portion was washed with 40% 0.5 N NaCl – 60% acetone (volume basis) solution several times. The product was then washed repeatedly with deionized water. This series of procedures were repeated four times to remove the K completely from phlogopite.

Powder X-ray diffraction (XRD) analysis, using a Scintag diffractometer with CuKα radiation, was carried out to confirm removal of K from natural phlogopite. X-ray diffraction patterns reported by Stout and Komarneni (2002) made it possible to confirm the presence of the K-depleted phlogopite without the analysis of K in solution, which is removed from natural phlogopite. The K-depleted micas produced by the K-removal treatment give a d_{001} spacing of ~12 Å (11–13 Å). The variation in the d_{001} spacing values is related to the mica type and the degree of occupancy of water molecules in the interlayers, *i.e.* the hydration state.

Transformation of micas under hydrothermal conditions

100 mg of mica (K-depleted biotite, K-depleted phlogopite, or natural biotite) were treated with 10 mL of 3 N $AlCl_3$ in a stainless steel Parr reactor with a teflon vessel at 200ºC for 12, 48 and 72 h. In the case of natural biotite, the hydrothermal reaction was carried out for an additional 24 h. Then, the solid phase was separated from the solution by centrifugation (HT centrifuge, IEC) at 5000 rpm. The solid phases were analyzed by XRD to investigate the weathering stages of the micas by the hydrothermal treatment. Scanning electron microscopy (SEM) images, using an Hitachi S-3500N microscope, were taken to investigate the morphologies of the transformed micas.

RESULTS AND DISCUSSION

Transformation of the K-depleted biotite

Figure 1 shows the XRD patterns of K-depleted biotite at the different weathering stages. The d_{001} spacing of untreated K-depleted biotite is 12.14 Å, and 11.27 Å under dry condition (Figure 1a). The presence of the 11.27 Å material is probably due to dehydration leading to smaller numbers of water molecules occupying the interlayers. Hydrothermal treatment for 12 h caused the 12.14 Å peak in the original K-depleted biotite to expand to 13.98 Å, which is attributed to the formation of HIV (Barnhisel and Bertsch, 1989; Rebertus *et al.*, 1986). This spacing did not change with ethylene glycol treatment but collapsed after heat treatment at 500ºC for 4 h, showing a broad set of peaks at 12.69, 11.04 and 10.32 Å (Figure 2a). This collapse suggests incomplete filling of the interlayers with hydroxy Al species. At the initial stage of the weathering, the formation of HIV as an intermediate is favored in acid conditions (Karathanasis, 1988). In order to determine whether the HIV (which is derived from the trioctahedral mica) retains the trioctahedral 2:1 layer characteristic, the *b*-axis dimension was measured (Fanning *et al.*, 1989). However, it was found to be difficult to identify the 060 peak as the HIV seems to be a poorly crystallized intermediate. At the same time a broad peak at ~7.09 Å with relatively low intensity appeared. This probably indicates the presence of kaolinite as it has a d_{001} spacing at ~7.1 to 7.4 Å (Murphy *et al.*, 1998).

The HIV transformed to kaolinite after hydrothermal treatment for 48 h (Figure 1c). The peak at ~14 Å attributed to the HIV disappeared, while the kaolinite phase increased as indicated by the much greater intensity of the 7.20 Å peak when compared to the

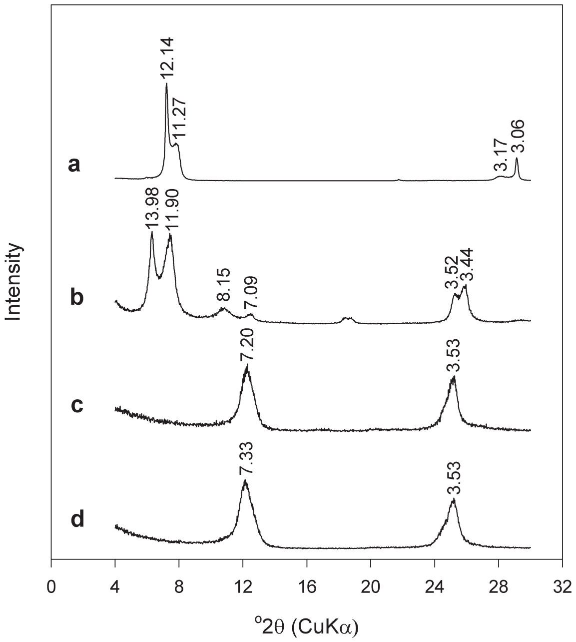

Figure 1. XRD patterns of the K-depleted biotite at the different stages of the transformation process: (a) original K-depleted biotite; (b) K-depleted biotite treated for 12 h; (c) K-depleted biotite treated for 48 h, and (d) K-depleted biotite treated for 72 h. *d* spacing values given in Å.

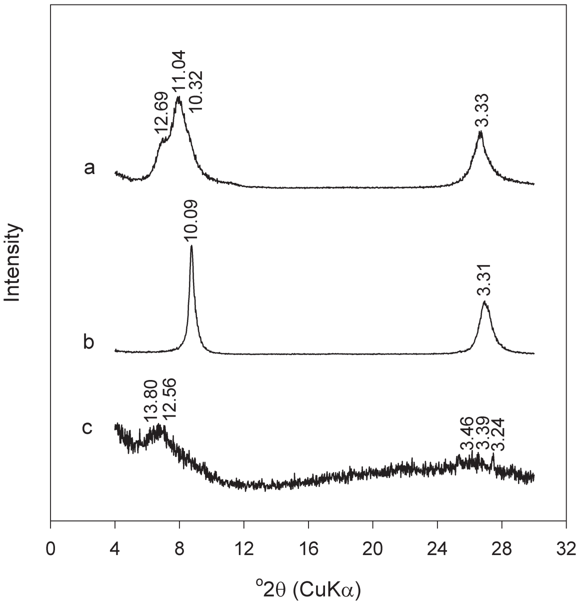

Figure 2. XRD patterns after ethylene glycol and heat treatment at 500ºC for 4 h using the micas treated with $AlCl_3$ for 12 h: (a) K-depleted biotite; (b) natural biotite; and (c) K-depleted phlogopite. *d* spacing values given in Å.

sample treated for 12 h. There was no difference in the XRD patterns between the treatments for 48 and 72 h. In order to determine whether halloysite (~7 Å) rather than kaolinite is present in the final product, the final products after the hydrothermal treatments for 3 days were solvated with ethylene glycol (Hillier and Ryan, 2002). According to those authors, the presence of halloysite could be determined by the change in intensity ratios of the ~7 Å to ~3.5 Å peak before and after the ethylene glycol solvation. There is no significant change in the intensity ratio of the peak heights of our ~7 Å materials. Thus, this result suggests that the transformation products are kaolinites.

In addition, there is no evidence of the formation of Mg silicates during the transformation. There are no peaks in the XRD patterns to indicate Mg silicates such as $MgSiO_3$, $Na_2Mg_2Si_6O_{15}$, $(Fe,Mg)SiO_3$, *etc*. Furthermore, 3 N $AlCl_3$ solution provides sufficient amounts of Al^{3+} for the formation of kaolinite through hydroxy-Al interlayer formation. The amount of Al^{3+} required for the formation of kaolinite can be estimated. Mica has a stoichiometric composition of Si:Al = 3:1, while kaolinite has an equivalent value of 1:1. Two additional moles of Al^{3+} are required for stoichiometric formation of kaolinite. In the case of our experimental system, addition of 3 N $AlCl_3$ provides sufficient amounts of Al^{3+} to form kaolinite in solution. In such an Al-rich acid environment, the transformation pathway of the K-depleted biotite to kaolinite was found to be through the hydroxy-Al interlayers.

Transformation of the K-depleted biotite through hydroxyl-Al interlayered vermiculite to kaolinite is a complicated series of reactions. The transformation mechanism of K-depleted bioitite under Al-rich and acidic conditions is assumed to include topotactic alteration, dissolution, precipitation and layer rearrangement (Figure 1). Based on the model that Rebertus *et al.* (1986) proposed, the transformation of the K-depleted biotite can be expressed as the following equation, where HIV is omitted because it is a poorly crystallized intermediate:

$$Na_2(Si_6Al_2)(Fe_3Mg_3)O_{20}(OH)_4 + 4Al(OH)_2(H_2O)_4^+ + 10H^+ \rightarrow 1.5Al_4Si_4O_{10}(OH)_8 + 2Na^+ + 3Mg^{2+} + 3Fe^{2+} + 21H_2O$$

Hydroxy-Al^{3+} can be formed by Al^{3+} ions that are either released by dissolution of the biotite or pre-existing dissolved Al species in solution. The hydroxy-Al^{3+} replaces interlayer Na^+, resulting in the formation of HIV. Here, the formation of HIV is facilitated because of the absence of Al complexing agents (Ranger *et al.*, 1991). It is much easier for the hydroxy-Al^{3+} species to replace exchangeable Na^+ ions than fixed K^+ ions in mica. In the early stages of mica transformation, topotactic exchange and precipitation are considered to be dominant reactions. It is reasonable to assume that HIV is necessary to form kaolinite under the present hydrothermal conditions. The hydroxy-Al^{3+} interlayers in the vermiculite serve as sources of Al and OH for octahedral sheets during the formation of kaolinite. The transformation mechanism of HIV to kaolinite seems to be a layer rearrangement. This explanation is supported by the study of Poncelet and Brindley (1967). They reported that the hydroxy-Al interlayered montmorillonite transformed to well crystallized kaolinite under acidic hydrothermal conditions (1 N HCl at 220ºC for 7 days). However, Al-saturated montmorillonite (Al-montmorillonite) under the same conditions yielded little or no kaolinite. Even the addition of gibbsite to Na-saturated montmorillonite (Na-montmorillonite) did not yield more kaolinite. They suggested that hydroxy-Al polymers in the interlayers are necessary to form kaolinite, but external gibbsite seems not to affect the formation of kaolinite.

The hydrothermal treatment leads to a color change in the K-depleted biotite. The change in color of the K-depleted biotite was dependent on the degree of weathering (Table 1). After treatment for 12 h, the color changed from greenish-black (the color of the original K-depleted biotite) to beige. After the treatment for 48 h, the beige color changed to yellow. Then, the yellow became gray which is typical of kaolinite (Rebertus *et al.*, 1986). The beige and yellow colors are probably due to the oxidation of structural Fe^{2+}. There is no evidence of the formation of Fe hydroxides or oxides in the XRD patterns. The results suggest that kaolinite may contain some Fe^{3+} in octahedral sheets.

Transformation of the natural biotite

The XRD patterns of the natural biotite at different weathering stages are shown in Figure 3. Although there

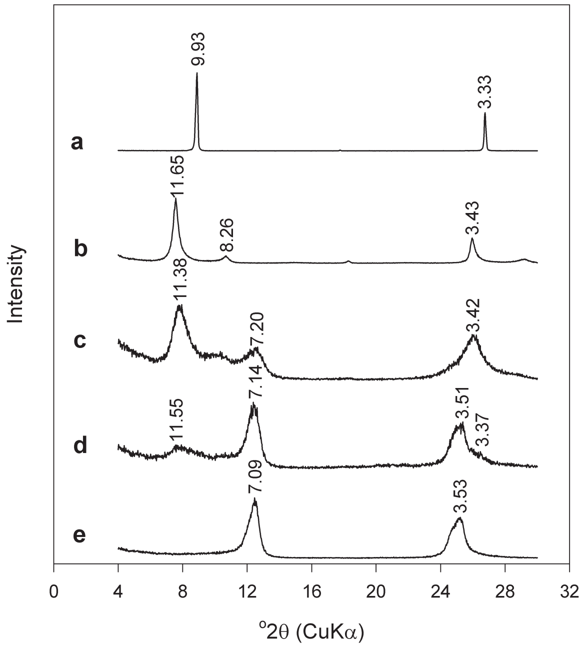

Figure 3. XRD patterns of the natural biotite at different stages of the transformation process: (a) original natural biotite; (b) natural biotite treated for 12 h; (c) natural biotite treated for 24 h; (d) natural biotite treated for 48 h; and (e) natural biotite treated for 72 h. *d* spacing values given in Å.

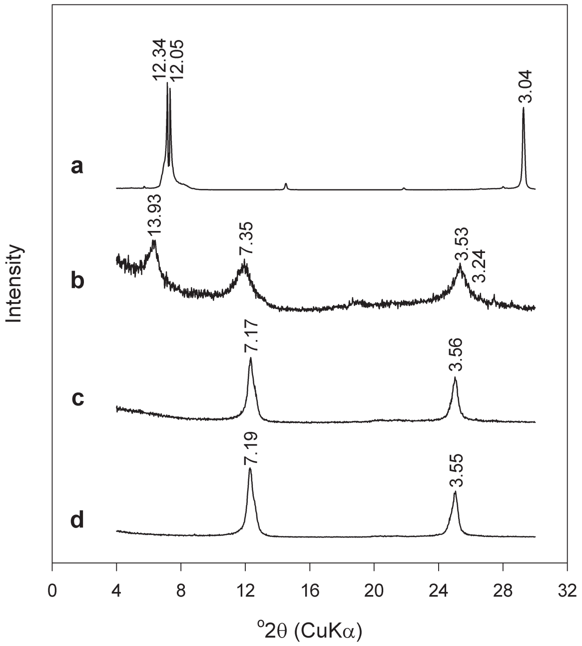

Figure 4. XRD patterns of K-depleted phlogopite at different stages of the transformation process: (a) original K-depleted phlogopite; (b) K-depleted phlogopite treated for 12 h; (c) K-depleted phlogopite treated for 48 h; and (d) K-depleted phlogopite treated for 72 h. *d* spacing values given in Å.

was some difference in the degree of weathering between the natural biotite and the K-depleted biotite, the natural biotite was also ultimately transformed to kaolinite. The d_{001} spacing of the original natural biotite was 9.93 Å under dry conditions, as revealed by the XRD pattern (Figure 3a). The hydrothermal treatment for 12 h caused a shift of the 9.93 Å peak to 11.65 Å, indicating a K-depleted mica-like phase (Figure 3b). This 11.65 Å peak did not change upon ethylene glycol solvation but collapsed to 10.09 Å upon heat treatment at 500°C (Figure 2b) suggesting that Al^{3+} saturation and hydration occurred in this sample. However, there is no appearance of a ~7.0 Å kaolinite phase (Figure 3b) after biotite transformed for 12 h, unlike the K-depleted biotite which showed a kaolinite-like phase (Figure 1b). After the hydrothermal treatment of biotite for 24 h, a broad peak at 7.20 Å appeared, indicating a kaolinite-like phase. At this point, the 11.38 Å phase was still present, indicating a K-depleted mica-like phase. There was no appearance of the ~14 Å peak attributed to HIV even though hydrothermal treatment was carried out for 24 h (Figure 3c). The presence of a HIV-like phase was not detected by XRD after treatments ranging from 12 to 48 h. After the treatment for 48 h, the 7.14 Å peak increased in intensity, while the 11.55 Å peak attributed to a K-depleted mica-like phase persisted. After treatment for 72 h, the 11.55 Å peak disappeared, resulting in complete transformation of the biotite to kaolinite (Figure 3e).

The rate of weathering of the natural biotite was found to be slower than that of the K-depleted biotite as can be seen from Figures 1 and 3. The natural biotite transformed completely to kaolinite after hydrothermal treatment for 72 h, while the K-depleted biotite transformed completely to kaolinite after only 48 h. These results suggest that the presence of interlayer K ions leads to a slower weathering rate of micas. The interlayer K^+ is not easily replaced by another cation such as Mg^{2+} in solution as K is fixed in the ditrigonal cavity. The replacement of the interlayer K^+ with exchangeable cations occurs over a long period of time in natural systems. In the early weathering stages of

Table 1. Color changes of micas at the different stages of transformation.

Samples	Untreated	12 h	48 h	72 h
K-depleted biotite	greenish-black	beige	yellow (ochre)	pale gray
Natural biotite	greenish-black	beige	beige	yellow
K-depleted phlogopite	white	white	white	white

mica, the weathering rate depends on the interlayer K content. Ion exchange in the K-depleted biotite is more rapid than that in the natural biotite because Na^+ can be replaced more easily than K^+ with hydroxyl-Al^{3+}.

The color of the natural biotite changed according to the degree of the weathering. After hydrothermal treatment for 12 h, the color changed from greenish-black to beige whereas after treatment for 72 h, the beige color changed to yellow (Table 1).

Transformation of the K-depleted phlogopite

The K-removal process used in this study resulted in an increase in the d_{001} spacing of the natural phlogopite from ~10 to 12.34 and 12.05 Å (Figure 4a) as shown earlier by Stout and Komarneni (2002). The hydrothermal treatment for 12 h caused the 12.34 and 12.05 Å peaks to shift to a broad 13.93 Å peak indicating HIV. This 13.93 Å peak changed little upon ethylene glycolation or heat treatment at 500ºC (Figure 2c) suggesting stable hydroxyl Al in the

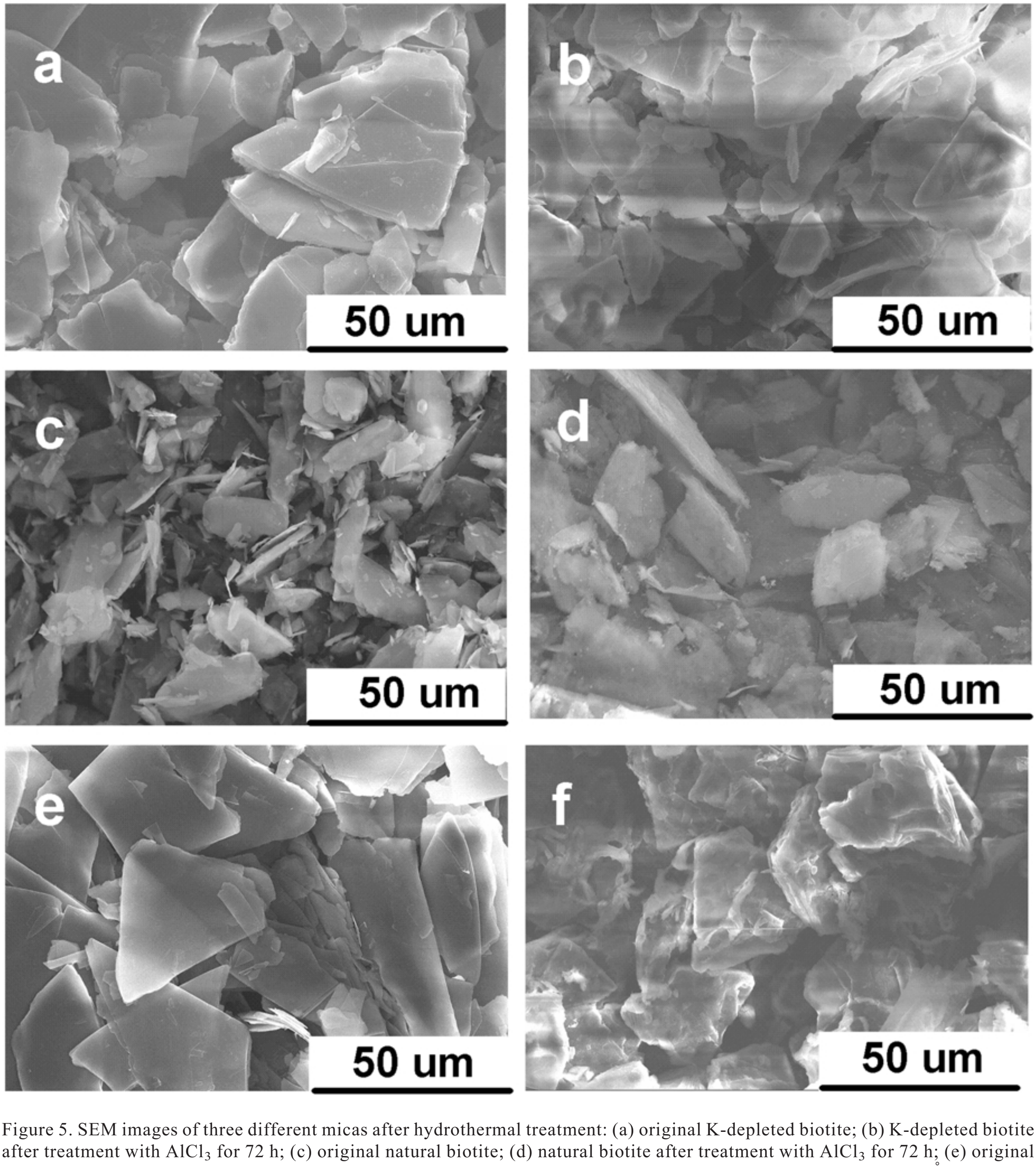

Figure 5. SEM images of three different micas after hydrothermal treatment: (a) original K-depleted biotite; (b) K-depleted biotite after treatment with $AlCl_3$ for 72 h; (c) original natural biotite; (d) natural biotite after treatment with $AlCl_3$ for 72 h; (e) original K-depleted phlogopite; and (f) K-depleted phlogopite after treatment with $AlCl_3$ for 72 h. *d* spacing values given in Å.

interlayers. At the same time, a broad peak at 7.35 Å appeared which has a greater intensity than the corresponding peak (7.09 Å) of K-depleted biotite treated for 12 h (Figure 1b). These results suggest that the weathering rate of the K-depleted phlogopite is more rapid than that of the K-depleted biotite. The chemical composition could contribute to the difference in the weathering rate between K-depleted phlogopite $[Na(Si_3Al)(Mg)_3O_{10}(OH)_2{\cdot}H_2O]$ and K-depleted biotite $[Na(Si_3Al)(Mg,Fe^{2+})_3O_{10}(OH)_2{\cdot}H_2O]$. The Fe^{2+} in octahedral sheets may be oxidized to Fe^{3+} in acid conditions during the weathering process (Kalinowski and Schweda, 1996). The structural Fe^{3+} transforms the biotite from trioctahedral sheets to dioctahedral sheets, which leads to more resistance in their weathering (McBride, 1994). After the treatment for 48 h, the 7.17 Å peak increased in intensity. There was no significant difference between the treatment for 48 and 72 h, suggesting that the transformation was complete by 48 h. There is no significant color change during the transformation process of K-depleted phlogopite (Table 1).

Figure 5 shows the morphologies of three different starting micas and after their hydrothermal treatment for 72 h. There were no significant changes in particle size after the treatment of the biotite micas, which may suggest pseudomorphism. The SEM images do not show Fe oxides or Al oxides as crusts on the plate-like particles, the morphology of which is typical of phyllosilicates such as kaolinite. In case of the K-depleted phlogopite, extensive etch pits were clearly observed after treatment for 72 h and recrystallization may have occurred. The etch pits were not observed for the biotite samples. These SEM images also suggest that the transformation rate of the K-depleted phlogopite is greater than that of the others as indicated by etch pits.

CONCLUSIONS

In an Al-rich acid environment under hydrothermal conditions, the transformation of K-depleted biotite followed the pathway; K-depleted biotite → HIV → kaolinite. The transformations of K-depleted phlogopite also followed the same pathway. However, the rate of transformation of K-depleted phlogopite was found to be more rapid than that of the K-depleted biotite because of the oxidation of structural Fe^{2+} in the K-depleted biotite. The transformation of natural biotite was slower than that of the K-depleted biotite due to the interlayer K ions in the former, as these needed to be replaced before transformation. The variation in weathering rate among the three micas was dependent on their structural and chemical properties.

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