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SILICATION OF HYDROXY-Al INTERLAYERS IN SMECTITE

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Abstract—The reaction of hydroxy-Al interlayers in montmorillonite with monosilicic acid was studied by chemical analysis, X-ray diffractometry (XRD), and Fourier-transform infrared (FTIR) spectroscopy. Hydroxy-Al interlayers in montmorillonite was prepared by treating Ca-montmorillonite (<2 μm) with hydroxy-Al solutions at an initial Al concentration of 0.5 mM and OH/Al molar ratios of 1.0, 2.0, and 2.5. The resultant partially interlayered montmorillonite was reacted with 0.5, 0.9, and 1.4 mM monosilicic acid solutions.

A substantial amount of monosilicic acid was adsorbed by the interlayer hydroxy-Al polymers through the reaction of Si-OH groups with mainly Al-OH groups, resulting in the formation of silicated Al-interlayers with Si/Al molar ratios up to 0.19. The adsorption of silicic acid by interlayer hydroxy-Al polymers increased the basal spacings of the partially interlayered montmorillonite. This effect was most pronounced for the hydroxy-Al interlayered montmorillonite formed in the systems at an OH/Al ratio of 2.0, in which the d(001) reflections (110°C) shifted from 13.6 Å before silication to 14.1 Å with a shoulder at 17.0 Å after silication. The differential IR spectrum of the silicated hydroxy-Al interlayers in montmorillonite exhibited absorption bands at 935 and 3730 cm^{-1}, which can be assigned to Si-O and Si-OH, respectively, of the adsorbed $Si(OH)_4$. An interlayer structure analogous to that of "proto-imogolite" was, thus, proposed for the silicated interlayer hydroxy-Al polymers in montmorillonite. This study revealed a new mechanism through which Si enters the interlayer spaces of smectite. The silication of hydroxy-Al-interlayered clays in natural environments and the related modifications in surface properties of the clays should receive increasing attention.

Key Words—Al-interlayer, Interlayer adsorption, Montmorillonite, Silication, Silicic acid.

INTRODUCTION

Siliceous Al-interlayers in smectite can be formed through the intercalation of hydroxy-aluminosilicate (HAS) cations or "proto-imogolite" (Lou and Huang, 1988) as well as that of imogolite tubes (Johnson *et al.*, 1988). These interlayer complexes may have potential application in industrial catalysis. Furthermore, HAS interlayering has been reported to have implications in natural systems (Lou and Huang, 1988). Since HAS ions ("proto-imogolite") are known as one of the major forms of soluble Al and Si and as the precursor of noncrystalline aluminosilicates in acidic environments (Farmer *et al.*, 1979, 1980; Wada and Wada, 1980), the interlayer adsorption of HAS ions may result in the formation of siliceous interlayer materials in natural systems.

HAS ions are reaction products of hydroxy-Al ions with monosilicic acid. Compared to hydroxy-Al ions, however, HAS ions have a lower positive charge density (Wada and Wada, 1980), which may make HAS ions less competitive than hydroxy-Al ions in their interactions with expandable layer silicates. Nevertheless, since soluble Si concentrations (e.g., 0.04–1.0 mM, as reported in Karathanasis, 1988, and Farmer *et al.*, 1979) usually exceed Al (e.g., 0.02–0.2 mM, as in Manley *et al.*, 1987) in the solutions of acid soils, a substantial portion of hydroxy-Al ions is bound to react with monosilicic acid to form HAS ions before entering the interlayer spaces of expandable layer silicates.

Other pathways by which Si enters the interlayers of expandable clays, however, remain to be explored. Hydroxy-Al interlayers of soil clays can also form through the *in situ* hydrolysis and polymerization of the previously adsorbed Al^{3+} ions in the interlayer spaces of smectites and vermiculites or as a result of the partial weathering of primary chlorites. Although noncrystalline aluminum oxides are known to be effective adsorbents of $Si(OH)_4$ (McKeague and Cline, 1963; Jones and Handreck, 1963; Beckwith and Reeve, 1963), little information is available on the interaction of interlayer hydroxy-Al polymers in expandable layer silicates with monosilicic acid in solution.

The objectives of this study were to examine the reaction of soluble silica as $Si(OH)_4$ with interlayer hydroxy-Al polymers in montmorillonite, the products of the interlayer reactions, and their implications for the mineralogy and chemistry of acidic environments. Hydroxy-Al-interlayered montmorillonite with an incomplete interlayer filling was prepared and used in this study since partially interlayered clays are common in acid soils and sediments (Rich, 1968; Barnhisel and Bertsch, 1989).

MATERIALS AND METHODS

Preparation of hydroxy-Al interlayered montmorillonite

Partially interlayered montmorillonite was prepared from the <2 μm fraction of Ca-saturated montmoril-

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lonite (Crook, Wyoming) and the solutions of hydroxy-Al ions. The solutions of hydroxy-Al ions with an Al concentration of 0.5 mM and OH/Al molar ratios of 1.0, 2.0, and 2.5, respectively, were prepared by titrating dilute solutions of $AlCl_3$ with 0.05 M NaOH solution at the rate of 0.5 ml min^{-1}. The pH readings of the hydroxy-Al solutions with OH/Al molar ratios of 1.0, 2.0, and 2.5 after standing for 1 hr were 4.60, 4.85, and 5.12, respectively. Aliquots of 200 ml of the hydroxy-Al solutions were mixed with a 20 ml clay suspension containing 90 mg montmorillonite and then agitated at 25°C for 24 hr. The resultant clay complexes were collected by filtration through a Sartorius cellulose nitrate membrane filter with a 0.01 μm pore size. Aluminum concentrations in the initial solutions and the filtrates were determined colorimetrically (Hsu, 1963). The amounts of Al fixed by montmorillonite were calculated by taking the difference between the initial and final Al concentrations. The clay complexes on the filters were washed three times with deionized distilled water and then transferred to polyethylene bottles for the following silication study.

Reactions of hydroxy-Al-montmorillonite with monosilicic acid

Monosilicic acid was prepared by passing Na-metasilicate solution through a H^+-form Dowex 50W-X8 ion-exchange resin column. Monosilicic acid solutions (200 ml at pH 5.28, with initial Si concentrations of 0.48, 0.94, and 1.37 mM, respectively) or 200 ml of deionized distilled water (adjussted to pH 5.28 with 0.1 M HCl) were added to the hydroxy-Al-montmorillonite complexes in polyethylene bottles. The pH of the resulting suspensions varied with the OH/Al ratio of the hydroxy-Al solutions that were used to prepare the hydroxy-Al-montmorillonite complexes. The suspension pH values of the clay complexes with OH/Al molar ratios of 1.0, 2.0, and 2.5 were 5.33, 5.62, and 6.05, respectively. The final pHs of these suspensions were measured at the end of the reaction period. Since the magnitude of pH change during the reaction might be a useful indication of the reaction mechanism, no attempts were made to control the suspension pH during the reaction period. The resulting suspensions were then agitated at 25°C for 5 d.

Examinations of the reaction products

The solid reaction products were collected by filtration through membrane filters of 0.01 μm pore size; they were washed three times with deionized distilled water and then once with 50% acetone. Clays were air-dried at 25°C on glass slides or heated at 110° and 350°C for 2 hr, then analyzed on a computer-aided Rigaku D/Max-RBX X-ray diffractometer. Infrared spectra were recorded on a Bio-Rad FTIR spectrometer with KBr (200 mg) discs containing 1 mg of the freeze-dried clays. The amounts of Si adsorbed by the hydroxy-Al-montmorillonite complexes were calculated by taking the difference between the initial and final Si concentrations that were determined colorimetrically according to the method of Weaver *et al.* (1968).

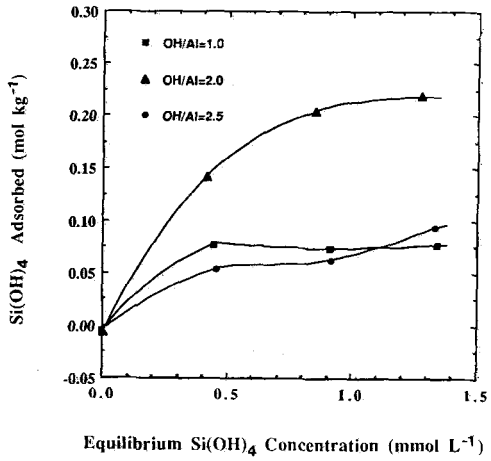


Figure 1. Adsorption isotherms for monosilicic acid on hydroxy-Al-montmorillonite complexes at 25°C.

RESULTS AND DISCUSSION

Adsorption of monosilicic acid by hydroxy-Al-montmorillonite

Figure 1 shows the removal of substantial amounts of $Si(OH)_4$ from solutions upon its reaction with hydroxy-Al-montmorillonite complexes. Since the pure montmorillonite does not adsorb any $Si(OH)_4$ at pH <7 (Lou and Huang, 1988), the $Si(OH)_4$ removed in the present study must be adsorbed by the hydroxy-Al polymers that are associated with the montmorillonite. The pH values (Table 1) at which the adsorption of $Si(OH)_4$ occurred were those commonly reported in acidic soils and sediments.

The largest amount of $Si(OH)_4$ was adsorbed by the hydroxy-Al-montmorillonite complexes prepared at an OH/Al molar ratio of 2.0 (Figure 1). The smaller amounts of $Si(OH)_4$ adsorbed by the hydroxy-Al-montmorillonite complexes prepared at an OH/Al molar ratio of 1.0 can be attributed to the lower pH and the lower degree of interlayer filling (Table 1). The hydroxy-Al-montmorillonite complexes formed at an OH/Al molar ratio of 2.5 had the highest degree of polymerization among the OH/Al ratios studied. Although the exact sizes are not known, hydroxy-Al polymers increase in size as the OH/Al ratio increases (Hsu, 1989). The lower capacity of these clay complexes to adsorb $Si(OH)_4$ may be related to their large polymer sizes, which will be discussed later.

Two mechanisms have been proposed by Jackson (1965) for the adsorption of monosilicic acid on aluminum hydroxides: first, the reaction between the Si-

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Table 1. Initial and final pH of the suspensions containing hydroxy-Al-montmorillonite complexes[1] and various amounts of $Si(OH)_4$.

OH/Al molar ratio	Initial pH	Final pH Initial $Si(OH)_4$ concentration (mM)			
		0.00	0.48	0.94	1.37
1.0	5.33	5.32	5.26	5.25	5.26
2.0	5.62	5.54	5.54	5.50	5.54
2.5	6.05	5.89	5.89	5.90	5.92

[1] The amounts of Al adsorbed by montmorillonite from the solutions with OH/Al ratios of 1.0, 2.0, and 2.5 were 0.76, 1.15, and 1.15 mol kg^{-1}, respectively.

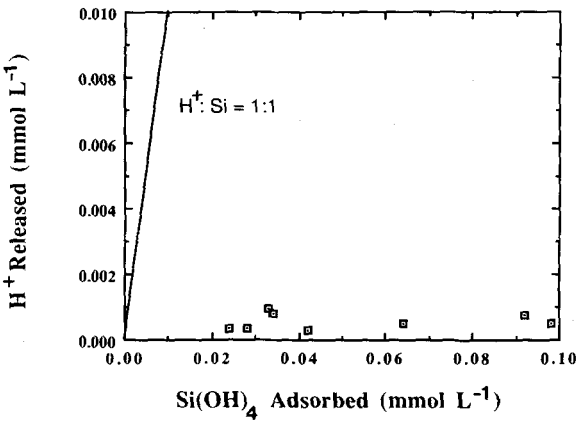


Figure 2. H^+ release as a function of $Si(OH)_4$ adsorption on interlayer hydroxy-Al polymers in montmorillonite.

OH group and the Al-OH-Al hydroxyl group, releasing one H_2O molecule; and second, the reaction between the Si-OH group and the edge water group of the Al-polymers (Al-H_2O), accompanied by the release of a proton as hydronium. In addition, we propose a third mechanism: The adsorption of monosilicic acid could proceed through the reaction of Si-OH with the edge hydroxyl group of the Al-polymers (Al-OH), releasing one water molecule. The pH change during the reaction should, thus, give some indication of the reaction mechanisms.

The adsorption of $Si(OH)_4$ through the second reaction mechanism necessitates the release of 1 mole H^+ ions for the adsorption of every 1 mole of $Si(OH)_4$ molecules (Figure 2, solid line). Such a relationship, however, was not observed in the present study. Since the amount of the released H^+ that was calculated from the pH differences (Table 1) was very small relative to the amount of the adsorbed $Si(OH)_4$ (H^+/Si molar ratios 0.005–0.03) and no definite relationship was found between the amount of H^+ released and the amount of $Si(OH)_4$ adsorbed (Figure 2), the reaction between Si-OH group and the edge water group of the Al-polymers (Al-H_2O) was probably not the dominant reaction mechanism.

$Si(OH)_4$ adsorption by a discrete phase of aluminum hydroxides has been shown in several cases to increase with increasing pH from 4 to 9 (e.g., Jones and Handreck, 1963; McKeague and Cline, 1963; Beckwith and Reeve, 1963). At a pH (e.g., pH 5) well below the PZC of aluminum hydroxides, the surfaces are dominantly positively charged; the reaction of $Si(OH)_4$ with edge water groups (Al-H_2O) is unfavorable because of the high H^+ activity in solution (Mott, 1970). In the present study, the acidic condition (pH 5.3–6.1) apparently inhibited such a reaction mechanism to a large extent. Accordingly, the slight decrease in pH during the 5 d reaction period (Table 1) was likely a result of the further hydrolysis of interlayer hydroxy-Al species. Thus, the $Si(OH)_4$ should have been adsorbed on the hydroxy-Al polymers mainly through the reaction of Si-OH groups with hydroxyl groups of the Al polymers, which does not cause pH change because only H_2O molecules are released.

Interlayer hydroxy-Al polymers appear to have a gibbsite-like multiple-ring structure (Barnhisel and Bertsch, 1989). It has been shown that the edge surfaces [Al-(H_2O)(OH)] of gibbsite are much more reactive than its 001 faces (Al-OH-Al hydroxyls) (Parfitt *et al.*, 1977). Thus, $Si(OH)_4$ molecules were likely to be adsorbed through the reaction of Si-OH groups with edge Al-OH groups of the interlayer hydroxy-Al polymers. However, poorly ordered interlayer hydroxy-Al polymers are expected to have more structural defects than gibbsite on their 001 faces, and the Al-OH groups around the defect sites should be as reactive as their edge counterparts.

Nature of the silication products

The adsorption of $Si(OH)_4$ by hydroxy-Al-montmorillonite complexes resulted in an increase in their basal spacings (Figures 3A and 3B, 25°C and 110°C). This effect was most pronounced for the silication of the Al-interlayered montmorillonite prepared from the hydroxy-Al solutions with an OH/Al molar ratio of 2.0, which is consistent with the effect of the OH/Al ratio on $Si(OH)_4$ adsorption (Figure 1). Figure 3B (110°C) shows the shift of d(001) reflections of the Al-interlayered montmorillonite (OH/Al = 2.0) from 13.6 Å before silication to 13.8–14.1 Å (standard deviation = ±0.05 Å) after silication. A smaller shifting of d(001) values was observed after silication of hydroxy-Al-interlayered montmorillonite prepared at OH/Al molar ratios of 1.0 (from 12.7 Å to 12.9–13.0 Å) and 2.5 (from 13.1 Å to 13.2–13.3 Å) (Figure 3B, 110°C). The magnitude of shifting (Figures 3A and 3B, 25°C and 110°C) increases with the increasing initial $Si(OH)_4$ concentration and the amount of $Si(OH)_4$ adsorbed (Figure 1). The increase in the interlayer d-spacing upon silication indicated that $Si(OH)_4$ was adsorbed in the

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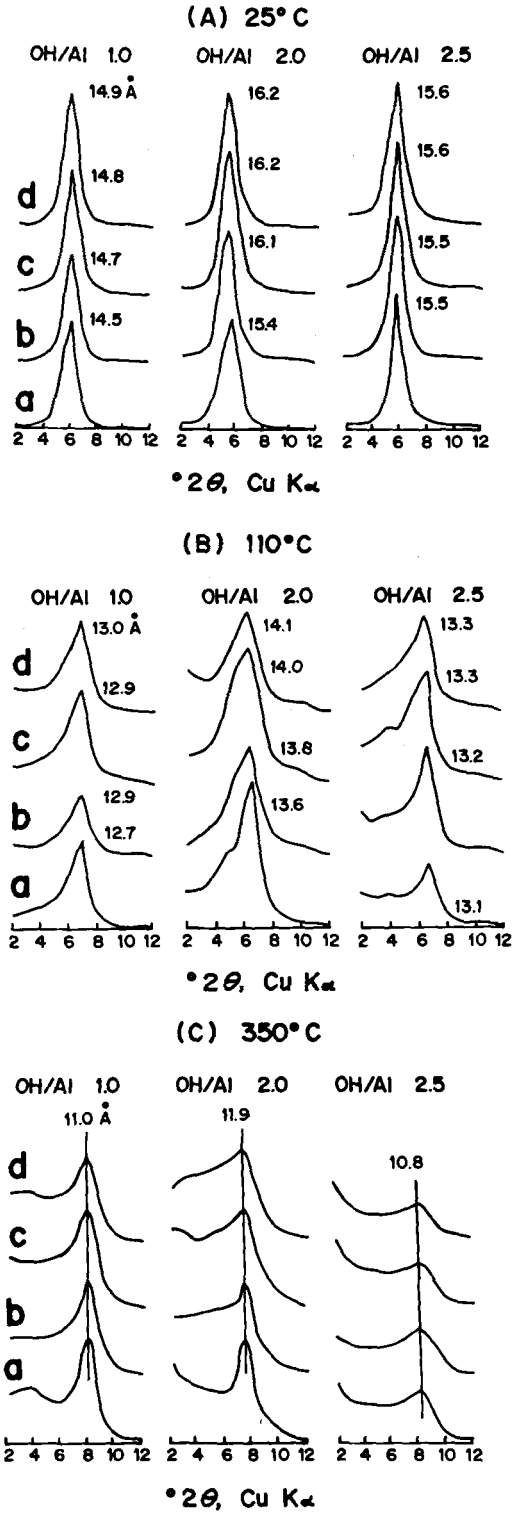


Figure 3. X-ray diffractograms of the hydroxy-Al-montmorillonite reacted with $Si(OH)_4$ solutions for 5 d (25°C) at the initial $Si(OH)_4$ concentration of a) 0.00, b) 0.48, c) 0.94, and d) 1.37 mM. Parallel-oriented specimens were A) air-dried at 25°C, B) heated at 110°C for 2 hr, and C) heated at 350°C for 2 hr.

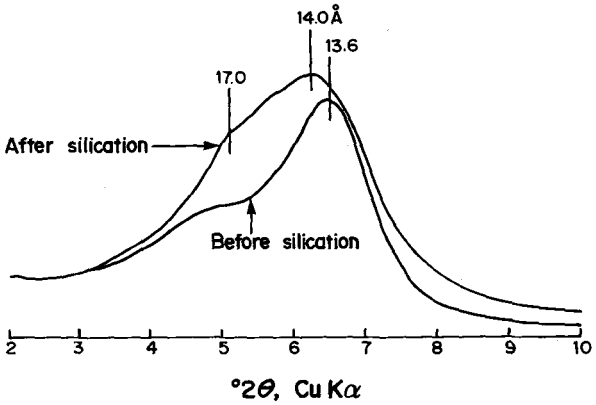


Figure 4. Effect of silication [initial $Si(OH)_4$ concentration = 0.94 mM] on the d(001) spacing (110°C) of the hydroxy-Al-montmorillonite complex (OH/Al molar ratio = 2.0). Parallel-oriented specimens were heated at 110°C for 2 hr.

interlayer spaces of the hydroxy-Al-montmorillonite complexes. The adsorption of $Si(OH)_4$ on the surfaces of interlayer hydroxy-Al polymers apparently strengthened the interlayer "pillars" and hence reduced the interlayer collapsibility. The effect of silication on the interlayer features of hydroxy-Al-montmorillonite prepared at an OH/Al ratio of 2.0 was still evident after heating at 350°C, as indicated by the asymmetric nature of the X-ray diffraction peak (Figure 3C, 350°C). The lower thermal stability of the silicated hydroxy-Al montmorillonite complexes formed at OH/Al molar ratios of 1.0 and 2.5 (Figure 3C, 350°C) is consistent with the lower capacity of these clay complexes to adsorb $Si(OH)_4$ (Figure 1).

It is noteworthy that the silicated hydroxy-Al-montmorillonite complexes not only gave 001 reflections with larger d-spacings than those without silication but also showed a shoulder at 17 Å (average I/I_1 = 76 ± 6) (Figure 4), which indicated the expansion of some of the interlayers to 7.4 Å upon the silication. The 7.4 Å interlayer spacing is close to the thickness of a monolayer of HAS cations, i.e., an aluminum hydroxide sheet plus a Si-tetrahedron (Lou and Huang, 1988). Such expansion, therefore, resulted from the reaction of $Si(OH)_4$ molecules with Al-OH groups on the 001 face of the interlayer hydroxy-Al "islands."

The differential FTIR spectrum (Figure 5c) of the hydroxy-Al-montmorillonite complexes after silication showed absorption bands at 3730, 935, 700, and 453 cm^{-1}. These bands arose from the adsorption of $Si(OH)_4$ since the 3730 cm^{-1} band can be assigned to Si-OH groups (Russell *et al.*, 1969) and the 935, 700, and 453 cm^{-1} bands are apparently related to the 1100, 800, and 470 cm^{-1} bands, respectively, of silica gel. The downshift of the frequencies is attributed to the bonding of $Si(OH)_4$ onto hydroxy-Al polymers, which inhibits the polymerization of the Si-O tetrahedron. Farmer *et al.* (1979) found that the 1100, 800, and 470

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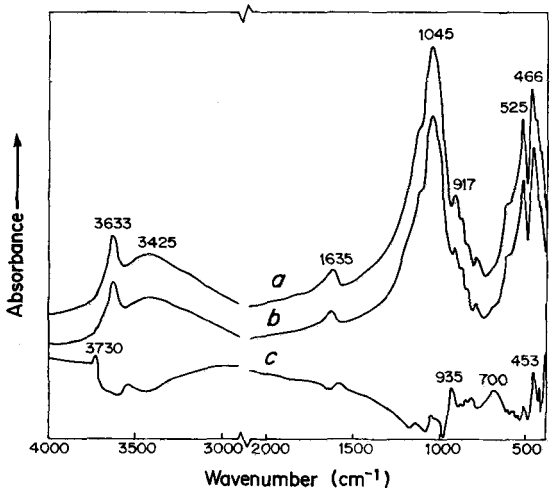


Figure 5. FTIR spectra of a) hydroxy-Al-montmorillonite complex (OH/Al molar ratio = 2.0) and b) the hydroxy-Al-montmorillonite complex reacted with 1.37 mM $Si(OH)_4$ solution for 5 d at 25°C, and c) the differential FTIR spectrum (spectrum b minus spectrum a, ordinate scale expanded 6 times).

cm^{-1} bands of silica gel in the coprecipitates of $Si(OH)_4$-hydroxy-Al shifted gradually to 1000, 700, and 450 cm^{-1}, respectively, as the Al/Si ratio increased from 0 to 2.0. Such decrease in the frequency is apparently caused by Al substitutions in silicate frameworks that make Si-O tetrahedra less polymerized.

Furthermore, the Si-O band at 935 cm^{-1} and the Si-OH band at 3730 cm^{-1} (Figure 5c) of the silicated hydroxy-Al-montmorillonite complexes coincide with those of imogolite, an orthosilicate (Cradwick *et al.*, 1972). The Si-OH vibration occurs at 3730 cm^{-1} because the Si-O tetrahedra in imogolite are isolated; hence, the apical hydroxyl of each tetrahedron is well separated from the other (Cradwick *et al.*, 1972). The $Si(OH)_4$ adsorbed in the present study should, therefore, occur as isolated tetrahedra on the surfaces of the interlayer hydroxy-Al polymers in montmorillonite. Moreover, the Si-O vibration at 935–940 cm^{-1} and Si-OH vibration at 3730 cm^{-1} have also been found in the "proto-imogolite" (HAS ions) adsorbed in the interlayer of smectites (Lou and Huang, 1988; Lou, 1991). Thus, during silication of the interlayer hydroxy-Al polymers, a hydroxy-aluminosilicate structure analogous to that of "proto-imogolite" has formed at defect sites of interlayer hydroxy-Al polymers. "Proto-imogolite" is the precursor or molecular fragment of imogolite (Farmer *et al.*, 1979), in which an orthosilicate group replaces three hydroxyls around a vacant Al site in the aluminum hydroxide sheet. The interlayer spacing of 7.4 Å, as indicated by the XRD analysis (Figure 4), agrees well with the thickness of a monolayer of proto-imogolite or HAS ions. Instead of three Si-O bonds in the typical imogolite structure proposed by Cradwick *et al.* (1972), some of the adsorbed $Si(OH)_4$ molecules may be bound to the edge hydroxyls of the interlayer hydroxy-Al polymers through one Si-O bond.

Table 2. Si/Al molar ratios of the silicated hydroxy-Al interlayers in montmorillonite.

OH/Al molar ratio	Initial $Si(OH)_4$ concentration (mM)			
	0	0.48	0.94	1.37
1.0	0	0.10	0.10	0.10
2.0	0	0.12	0.18	0.19
2.5	0	0.05	0.05	0.08

The siliceous Al-interlayer materials in the present study have a maximum Si/Al molar ratio of 0.19 (Table 2), which is lower than the theoretical ratio of proto-imogolite (0.5). The partial silication may be attributed to many factors. The adsorption of $Si(OH)_4$ by the interlayer hydroxy-Al polymers might not have reached the maximum. Some of the Al-OH groups around the defect sites on the 001 faces of interlayer hydroxyl-Al polymers might not be available for the adsorption of $Si(OH)_4$ due to strong bonding of these polymers in the interlayer space. In addition, the Al-OH-Al hydroxyls on the 001 faces of hydroxy-Al polymers are not as reactive as edge hydroxyls (Parfitt *et al.*, 1977). Edge sites and defective sites of interlayer hydroxyl-Al polymers were apparently more accessible and reactive for the adsorption of $Si(OH)_4$, which created a Si-deficient central region of these polymers. Farmer *et al.* (1979) suggested that the Si/Al molar ratio of soluble proto-imogolite could be either lower or higher than 0.5, because proto-imogolite fragments could either be deficient in silica or adsorb excess silica on edge sites. The lower thermal stability of hydroxy-Al interlayers (Figure 3) indicated marginal distribution of polymers forming an "atoll" structure (Dixon and Jackson, 1962; Frink, 1965). The atoll structure could result in a steric blocking of the adsorption sites for $Si(OH)_4$ within the center of the particles.

Therefore, the reaction products were expected to have a lower Si/Al molar ratio than that of an ideal proto-imogolite structure. Compared with the interlayer hydroxy-Al polymers formed at an OH/Al molar ratio of 2.0, the large hydroxy-Al polymers formed at an OH/Al molar ratio of 2.5 are expected to have higher positive charge per hydroxy-Al polymer, fewer edge sites per mole of Al, and, therefore, a lower capacity to adsorb $Si(OH)_4$ as well as a lower Si/Al molar ratio in the hydroxy interlayers. Furthermore, the interlayer hydroxy polymers formed at an OH/Al molar ratio of 2.5, which are expected to have larger polymers and hence have a larger central area, are less accessible to $Si(OH)_4$ than the polymers formed at an OH/Al ratio of 2.0.

CONCLUSIONS

The present study revealed a new mechanism by which Si is introduced into the interlayer spaces of

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expandable layer silicates. This study also indicated the formation of a "proto-imogolite" structure on the interlayer surfaces of montmorillonite. Farmer and Fraser (1982) and Farmer (1987) postulated that a simultaneous equilibrium exists between $Si(OH)_4$ in solution and gibbsite and imogolite and that an imogolite or proto-imogolite structure can form if the level of $Si(OH)_4$ in solution exceeds 0.03–0.1 mM. Soluble Si levels in acid soils commonly range from 0.04–1.0 mM (Karathanasis, 1988; Farmer *et al.,* 1979). The present study indicated that a significant amount of $Si(OH)_4$ was adsorbed by interlayer hydroxy-Al polymers within this concentration range. Silication of interlayer hydroxy-Al in expandable layer silicates can, therefore, be considered inevitable in most of the acid soils. The adsorption of $Si(OH)_4$ onto the surfaces of interlayer hydroxy-Al polymers in expandable layer silicates, thus, merits attention in the study of the mineralogy and chemistry of acid soils and sediments. The degree of silication is expected to be affected by a number of factors. As shown in the present study, soluble Si level and OH/Al molar ratio (or pH) are important factors. The silication mechanism also provided an interpretation for the siliceous nature of the Al-interlayer materials suggested in selective dissolution studies of the expandable layer silicates from some acidic soils (Wada *et al.,* 1987; Matsue and Wada, 1988, 1989).

Hydroxy-Al interlayers in expandable layer silicates are noted for their importance in affecting the availability and dynamics of plant nutrients and pollutants in acidic environments (Huang, 1988; Barnhisel and Bertsch, 1989) and for their application in industrial catalysis (Pinnavaia, 1983) due to the high surface reactivity of the interlayer materials. The modifications in surface properties of the hydroxy-Al interlayers upon silication, thus, deserve future study.

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