

ELECTRIC CHARGE AND SURFACE CHARACTERISTICS OF HYDROXYALUMINOSILICATE- AND HYDROXYALUMINUM-VERMICULITE COMPLEXES

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Abstract—Hydroxyaluminosilicate (HAS) ions prepared from hydroxy-Al (HyA) ions and orthosilicic acid at different NaOH/Al molar and Si/Al atomic ratios were fixed in the interlayer spaces of vermiculite (Vt). The electric charge and surface characteristics of HAS-Vt and HyA-Vt complexes formed were investigated in the pH range of 4 to 8. At pH 4 to 6, the magnitude of negative charge (CEC) of HAS-Vt and HyA-Vt complexes was drastically reduced by a HAS- or HyA-interlayer formation of Vt. At pH 7 to 8, especially in NaOH/Al molar ratio of 2.5, the magnitude of negative charge was from 62 to 89% of CEC in untreated Vt, suggesting that part of HAS or HyA ions fixed on Vt was excluded from its interlayer spaces. The positive charge did not develop on HAS-Vt and HyA-Vt complexes at pH between 4 and 8. The fixation of HAS or HyA ions on Vt caused the significant reduction of its total and internal surface areas as well as the slight increase of its external surface area. The HAS- or HyA-fixation in the interlayer spaces of Vt was confirmed by X-ray diffraction analysis. Our results provided evidence of a possibility that Vt could fix HAS ions in the same way as HyA ions, transforming to chloritized-Vt. These interlayer materials could play a significant role in modifying the surface and mineralogical properties and cation exchange capacity of clays and soils.

Key Words—Electric charge characteristics, Fixation, Hydroxy-Al, Hydroxyaluminosilicate, Specific surface area, Vermiculite.

INTRODUCTION

Vermiculite (Vt) and smectite in soils are frequently partially interlayered or chloritized. Fixation of hydroxy-Al (HyA) ions in the interlayer spaces of Vt was investigated by Rich (1960) and Hsu and Bates (1964). HyA ions appear to be the principal components of the non-exchangeable interlayer materials (Rich, 1968; Barnhisel, 1977). These interlayer materials play significant roles in modifying the surface and mineralogical properties and cation exchange capacity of clays. Modifications of these characteristics depend upon the degree of filling of the interlayer space with HyA ions and the relative stability of the interlayer components (Barnhisel, 1977; Barnhisel and Bertsch, 1989).

Recent studies involving various soils in humid temperate regions and the characteristics of interlayered materials have been reported by Wada and Kakuto (1983), Wada *et al.* (1987), and Matsue and Wada (1988). Matsue and Wada (1988) reported that the materials dissolved by the citrate treatment had a Si/Al ratio ranging from 0.72 to 0.24 for 15 Dystrichrepts derived from Tertiary sediments. They suggested that the formation of a HyA sheet partially bonded with Si-tetrahedra was a possible model for the interlayer structure of hydroxy-interlayered Vt. However, it is estimated that some interlayer materials, especially those with low Si/Al ratios, are composed of hydroxy-aluminosilicate (HAS) ions and their polymers.

HAS ions are easily formed in soil solutions by the interaction of HyA ions with orthosilicic acid (Farmer

et al., 1979; Wada and Wada, 1980), which have a proto-imogolite structure and a positive charge in the acid condition (Farmer, 1981). Farmer *et al.* (1980) and Farmer (1981) proposed that proto-imogolite was transported from the E horizon in Spodosols as a HyA-orthosilicate complex and formed allophane, proto-imogolite allophane, and imogolite in the Bs horizons. Chloritized-Vt clays commonly occur in podzolic Bs horizons in Canada (McKeague *et al.*, 1976; Ross, 1980). Farmer *et al.* (1980) estimated that chloritized-Vt clays could be formed by interaction between vermiculites and percolating proto-imogolite (HAS) solutions.

Inoue *et al.* (1988) and Lou and Huang (1988) demonstrated that HAS ions were fixed in the interlayer spaces of montmorillonite (Mt). The fixation of HAS ions by Mt caused a marked decrease in its swelling ability, total and internal surface areas, and negative charges, but a great increase in external surface area (Inoue *et al.*, 1988). Inoue *et al.* (1988 and 1990) also indicated that a large amount of phosphate and humic substances was adsorbed by HyA-Mt or HAS-Mt complexes. These marked changes of physical and chemical properties caused by the interlayer formation are based on the electric charge and surface characteristics of HAS-Mt or HyA-Mt complexes (Inoue and Satoh, unpublished data).

The 2:1 and 2:1:1 layer silicate intergrades were extensively isolated from acidic and nonallophanic Andisols in Japan and USA (Shoji and Ono, 1978; Shoji

Table 1. The NaOH/Al and Si/Al ratios, pH, and Al concentration of the solutions containing hydroxy-Al (HyA) or hydroxyaluminosilicate (HAS) ions after passing through a membrane filter of 0.2 μm pore size.

Ions	NaOH/Al ratio	Si/Al ratio	pH	Al concentration (mM)
HyA	1.0	0.00 \pm 0.00 ¹	4.34 \pm 0.09	3.96 \pm 0.06
	2.0	0.00 \pm 0.00	4.48 \pm 0.16	3.91 \pm 0.02
	2.5	0.00 \pm 0.00	5.12 \pm 0.17	3.89 \pm 0.09
HAS	1.0	0.27 \pm 0.00	4.02 \pm 0.01	3.97 \pm 0.04
	1.0	0.52 \pm 0.01	3.96 \pm 0.02	3.96 \pm 0.02
	1.0	0.98 \pm 0.03	3.88 \pm 0.03	3.97 \pm 0.01
	2.0	0.27 \pm 0.02	4.26 \pm 0.15	3.90 \pm 0.19
	2.0	0.54 \pm 0.03	4.09 \pm 0.13	3.89 \pm 0.20
	2.0	0.99 \pm 0.04	4.03 \pm 0.09	3.94 \pm 0.06
	2.5	0.28 \pm 0.00	4.57 \pm 0.09	3.79 \pm 0.05
	2.5	0.55 \pm 0.01	4.28 \pm 0.05	3.82 \pm 0.01
	2.5	1.03 \pm 0.02	4.16 \pm 0.07	3.90 \pm 0.03

¹ Mean and standard error.

et al., 1985, 1987). These intergrades in Andisols were predominantly transformed from Vt and micas derived from Asian long-range transported eolian dust (Inoue and Mizota, 1988; Inoue and Naruse, 1991). Chloritized-Vt could be pedogenically formed by the interaction of expansible 2:1 layer silicates weathered from micas with HyA or HAS ions, which are transformed from volcanic ash during weathering processes. The cation exchange and anion adsorption reactions by soil clays in nonallophanic Andisols would be influenced by the electric charge and surface characteristics of hydroxy interlayered Vt or smectite. However, little information is available on the interaction of HAS ions with Vt, or electric charge and surface characteristics of HAS-Vt and HyA-Vt complexes formed in different Si/Al atomic and NaOH/Al molar ratio solutions with different pH ranges. Our objective was to investigate the fixation of HAS and HyA ions by Vt and selected physical and chemical properties of the HAS-Vt and HyA-Vt complexes formed.

MATERIALS AND METHODS

Hydroxyaluminum and hydroxyaluminosilicate ions

Orthosilicic acid prepared from tetraethyl orthosilicate (Farmer *et al.*, 1979) was mixed with an AlCl_3 solution to obtain Si/Al atomic ratios of approximately 0.00, 0.25, 0.50, and 1.00 (Inoue *et al.*, 1990). The solutions were titrated with 0.1 M NaOH at the rate

of 0.2 ml/min with continuous stirring to give a NaOH/Al molar ratio of 1.0, 2.0, or 2.5. The solutions were diluted to 2000 ml (final Al concentration = 4 mM) and aged for 7 d at 20°C. The terms Si/Al atomic and NaOH/Al molar ratios will henceforth be stated as Si/Al and NaOH/Al ratios for the sake of brevity. The pH was recorded and clear filtrates were obtained by passing through a cellulose nitrate membrane filter of 0.2 μm pore size. The amount of Al and Si in the filtrates was determined according to the methods described by Inoue and Huang (1984, 1985). Table 1 represents NaOH/Al and Si/Al ratios, pH, and Al concentration of the solutions containing HyA or HAS ions used in this study.

Vermiculite complexes

Vermiculite (Zonolite) obtained from near Libby (Montana, USA) was used in this study. It was ground in an agate mortar with a small amount of water, and the clay fraction of Vt (<2 μm) was collected by repeated dispersion, sedimentation, and siphoning. The Vt clay was treated successively with dithionite-citrate (Mehra and Jackson, 1960), 2% Na_2CO_3 (Jackson, 1979, p. 73), and 1 M CH_3COONa -1 M NaCl (pH 5, 4 times). The Na-saturated Vt clay was washed with 80% (v/v) methyl alcohol (until Cl^- was eliminated), treated with acetone, air-dried, and then gently ground in an agate mortar. The 060 reflection of Vt lay in the range of 1.53 to 1.55 Å. The chemical composition of the Vt clay was determined after the Na_2CO_3 fusion or $\text{HF-H}_2\text{SO}_4$ digestion (Table 2). The structural formula of the Vt clay was obtained on the basis of its chemical composition (Table 2). The Vt used in this study is trioctahedral and the clay contains a significant amount of interstratified biotite-vermiculite (See Figure 4).

Four grams of Na-saturated Vt were treated with 200 ml of the solutions containing HyA or HAS ions. After centrifugation at 7500 g for 10 min, the supernatant was collected. This treatment was repeated 8 more times. HyA-Vt or HAS-Vt complexes were collected by centrifugation. Free salts were removed from the complexes by washing with 80% (v/v) methyl alcohol until Cl^- was eliminated, followed by washing with acetone. The HyA-Vt or HAS-Vt complexes prepared were air dried and gently ground in an agate mortar and passed through 60 mesh sieve. The amount of Al and Si fixed on Vt was calculated as the difference

Table 2. The chemical composition and the structural formula of vermiculite used in this study.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	Chemical composition		K_2O	Na_2O	P_2O_5	IL ¹	Total
					CaO	MgO					
Oven dry basis (%)											
41.50	14.50	10.30	0.82	0.06	0.30	20.42	3.90	3.90	0.07	4.24	99.51
Structural formula											
$\text{K}_{0.35}\text{Na}_{0.53}\text{Ca}_{0.02}(\text{Al}_{0.09}\text{Fe}_{0.54}\text{Mg}_{2.12})(\text{Si}_{2.90}\text{Ti}_{1.04}\text{Al}_{1.06})\text{O}_{10.00}(\text{OH})_{2.00}$											

¹ Ignition loss.

between that present in the solution initially and that remaining after centrifugation.

Negative and positive charges

The electric charge characteristics of the samples were determined by measuring the retention of Ca^{2+} and Cl^- , on the basis of the procedure described by Wada and Okamura (1980) at pH between 4 and 8, except that CaCl_2 was used for the CEC and AEC determinations instead of NH_4Cl . The clay samples (0.20 g) were treated 5 times with 8 ml of 0.5 M CaCl_2 and equilibrated 5 times with 0.025 M CaCl_2 . The equilibrium pH was measured using the supernatant obtained by the final centrifugation. The amounts of Ca^{2+} and Cl^- in the interstitial solution were estimated by gravimetric procedures. The Ca^{2+} and Cl^- retained by the clay samples were replaced by washing with 1 M NaNO_3 , and were determined using a Hitachi 207 atomic absorption spectrometer and a chloride electrode (Orion 94-17B), respectively. The magnitudes of negative and positive charges of the samples were shown as cation and anion exchange capacities (CEC and AEC, meq/100 g), respectively.

Specific surface areas

The total and external surface areas of Na-saturated samples were determined by the EGME method (El-tantawy and Arnold, 1973) and by adsorption of N_2 gas at -195°C in conjunction with the BET equation, using a Shibata P-850 surface area measurement apparatus. The internal surface area was calculated as the difference between total and external surface areas.

X-ray diffraction

HyA-Vt and HAS-Vt complexes were treated with 1 M KCl and 1 M MgCl_2 . Then parallel oriented clay specimens were prepared. X-ray diffraction analysis was carried out according to the procedure described by Inoue *et al.* (1988). Instead of $\text{CuK}\alpha$ radiation, however, Fe-filtered $\text{CoK}\alpha$ radiation was used in this study. In order to dissolve interlayer materials (HAS ions) fixed in interlayer spaces of Vt, the 1/3 M Na-citrate treatment was carried out according to the method described by Tamura (1958).

RESULTS AND DISCUSSION

Vermiculite complexes

When Vt was treated with the HyA and HAS solutions prepared at the different Si/Al and NaOH/Al ratios, the amount of Al and Si fixed on Vt was influenced by the Si/Al and NaOH/Al ratios of solutions. The amount of Si fixed slightly increased with an increase in the Si/Al ratio (Figure 1), whereas fixed Al was variable and ranged from 0.69 to 0.97 mmol/g except for HAS ions formed at a Si/Al ratio of 1.0 and a NaOH/Al ratio of 2.5. In the case of a NaOH/Al ratio of 2.5,

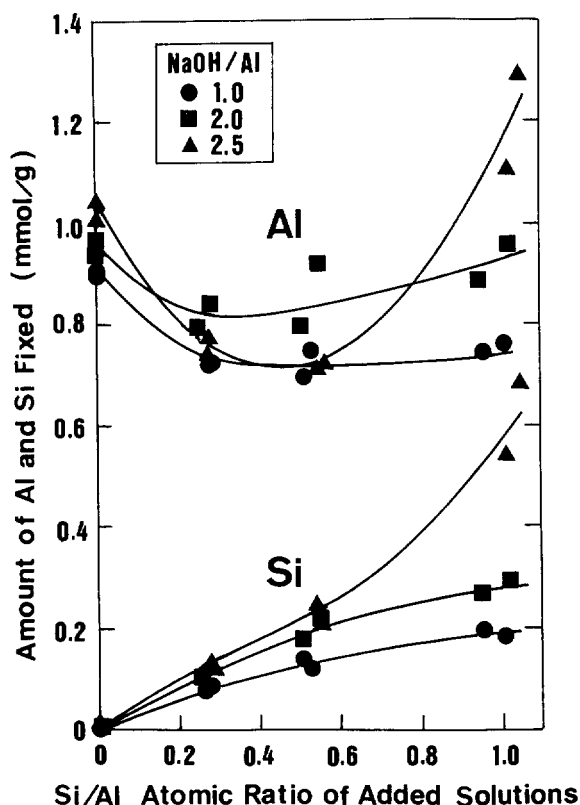


Figure 1. Relationships between the amount of Al and Si fixed on vermiculite and the Si/Al ratio of the hydroxy-Al (HyA) or hydroxyaluminosilicate (HAS) solutions prepared at the different NaOH/Al ratios.

the increased amounts of Si and Al adsorbed by Vt were substantial at the Si/Al ratio of 1.0. This great increase of Al and Si was probably due to the precipitation of amorphous aluminosilicates formed during the interaction of Vt with HAS ions.

The amount of Al and Si fixed on Vt (Al: 0.69 to 1.29; Si: <0.68 mmol/g) was smaller than that on Mt (Al: 0.72 to 1.73; Si: <0.82 mmol/g). Since the interlayer spaces of Vt complexed with HyA or HAS ions did not expand as compared with HyA- or HAS-Mt complexes, relatively large HyA or HAS polymerized ions formed at higher NaOH/Al and Si/Al ratios could not penetrate into the interlayer spaces of Vt.

Figure 2 shows the relationships between the Si/Al ratio of HyA or HAS ions fixed on Vt and the Si/Al ratio of the HyA or HAS solutions. The Si/Al ratio of HAS ions fixed on Vt increased with increasing Si/Al ratio of the solutions. Its ratio was close to 0.5 in the HAS solution with a Si/Al ratio of approximately 1.0 and a NaOH/Al ratio of 2.5, suggesting that the dominant HAS ion has a proto-imogolite structure with a Si/Al ratio of 0.5 (Farmer, 1981). When Vt was treated with the HyA or HAS solution with Si/Al ratios of 0.00, 0.25 to 0.28, 0.51 to 0.56, and 0.95 to 1.04, the

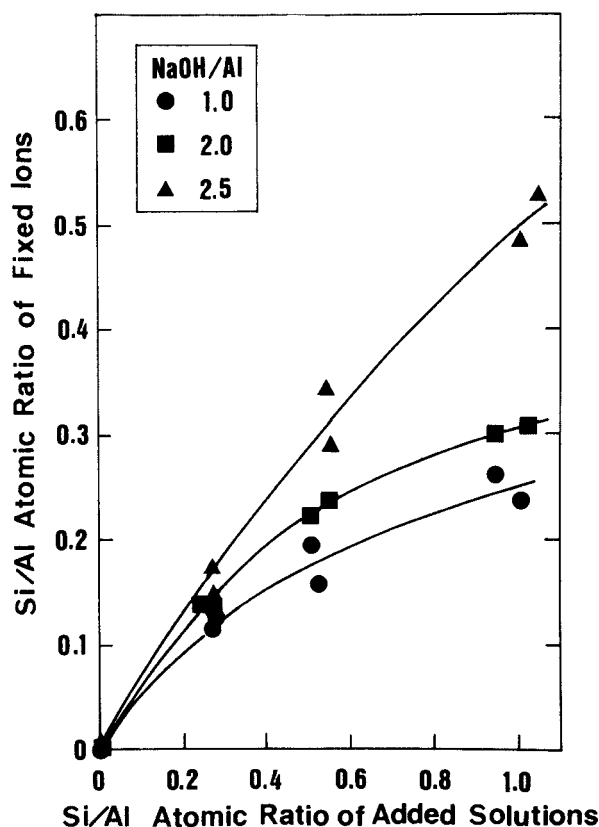
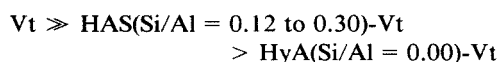


Figure 2. Relationships between the Si/Al ratio of hydroxy-Al (HyA) or hydroxyaluminosilicate (HAS) ions fixed on vermiculite and the Si/Al ratio of the HyA or HAS solutions prepared at the different NaOH/Al ratios.

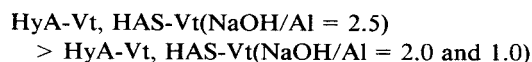
Si/Al ratio of HAS ions fixed on Vt was 0.00, 0.12 to 0.17, 0.16 to 0.35, and 0.24 to 0.53, depending on the NaOH/Al ratio. The Si/Al ratio of fixed HAS or HyA ions increased with increasing NaOH/Al or Si/Al ratios of the HAS or HyA solutions. The Si/Al ratio of fixed HAS ions on Vt was slightly lower than for Mt.

Electric charge characteristics

Figure 3 shows the relationships between the CEC or AEC of HyA-Vt and HAS-Vt complexes formed at the different Si/Al and NaOH/Al ratios and the equilibrium pH value. The negative charge of Vt was predominantly occupied by the permanent negative charge in the pH range of 4 to 8. On the contrary, the negative charge characteristics of HyA-Vt or HAS-Vt complexes were quite different from that of Vt. The CEC of HyA-Vt and HAS-Vt complexes greatly depended on Si/Al and NaOH/Al ratios and was strongly influenced by an equilibrium pH value. At pH 4 to 6, the CEC of HyA-Vt and HAS-Vt complexes formed at NaOH/Al ratios of 1.0 and 2.0 was in the following order:



The negative charge of HyA-Vt or HAS-Vt complexes was characterized by the great increase of pH-dependent charge and the drastic decrease of permanent negative charge (Figure 3). The trend of reduction of negative charge in HyA-Vt or HAS-Vt complexes was more prominent than that of HyA-Mt or HAS-Mt complexes. The CEC of HyA-Vt and HAS-Vt complexes at Si/Al ratios of approximately 0.00, 0.25, 0.50, and 1.00 was in the following order:



This trend suggests that polymerized HyA and HAS ions formed at the higher NaOH/Al ratio cannot penetrate into the interlayer spaces of Vt.

When the NaOH/Al ratio was 2.5, the Si/Al ratio of HAS ions fixed by Vt was strongly influenced by the Si/Al ratio of HAS solutions (Figure 2). The decrease of CEC in the complexes depended on the Si/Al ratio of HyA or HAS ions fixed by Vt and decreased with increasing Si/Al ratio.

The decrease of CEC by the complexation of Vt with HyA or HAS ions could be based on the physical blocking effect (Rich, 1968) of permanent negative charge sites of Vt by HyA or HAS ions in interlayer spaces and on planar surfaces. Polymerized HyA or HAS ions with a large molecular size could not penetrate into the interlayer spaces of Vt. With increasing NaOH/Al and Si/Al ratios or by raising the equilibrium pH, HyA and HAS ions gradually increase in size, decrease in net positive charge per Al atom (Hsu, 1977; Wada and Wada, 1980), and produce gibbsite or amorphous aluminosilicates such as allophane.

Rich (1968) estimated that the optimum pH(H₂O) for the interlayer formation was between 4.5 and 5.0 for Vt. The CEC values in Figure 3 indicated that the observed optimum equilibrium pH for the HAS or

Table 3. Specific surface areas of vermiculite (Vt), hydroxy-Al-vermiculite (HyA-Vt), or hydroxyaluminosilicate-vermiculite (HAS-Vt) complexes formed at pH 5 ± 0.3.

Sample	NaOH/Al ratio	Si/Al ratio	Specific surface areas (m ² /g)		
			Total	External	Internal
HyA-Vt	1.0	0.00	319	53	266
	2.0	0.00	312	66	246
	2.5	0.00	342	58	284
HAS-Vt	1.0	0.12	262	46	216
	1.0	0.20	296	39	257
	1.0	0.27	291	38	253
	2.0	0.14	328	59	269
	2.0	0.24	336	55	281
	2.0	0.30	317	29	288
	2.5	0.15	341	34	307
	2.5	0.29	399	26	373
	2.5	0.48	479	43	436
Vt	—	—	397	33	364

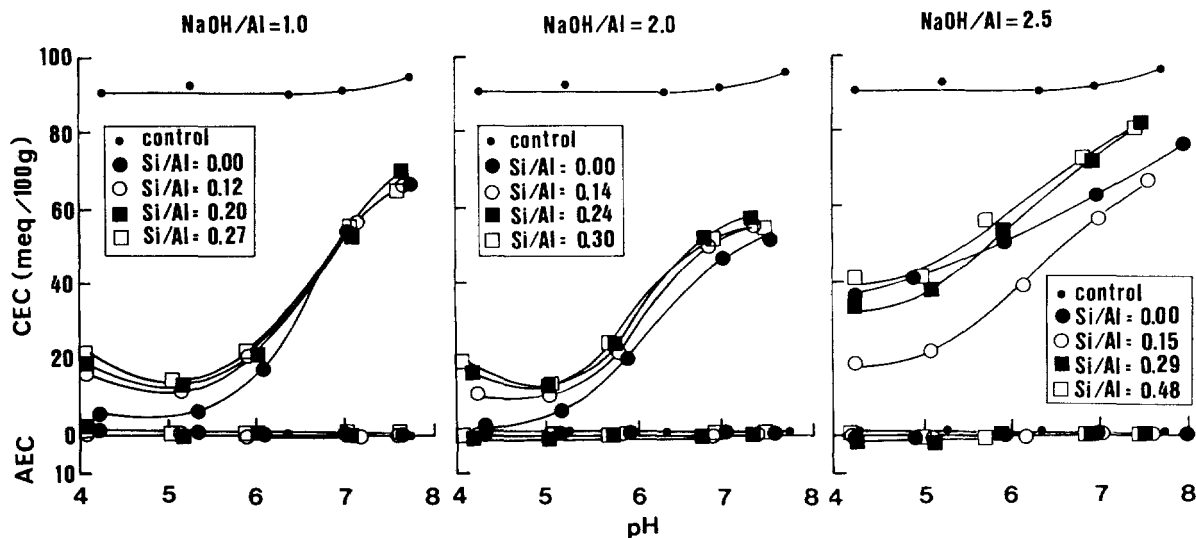


Figure 3. Relationships between the magnitude of negative and positive charges and the pH value of hydroxy-Al-vermiculite (HyA-Vt) or hydroxyaluminosilicate-vermiculite (HAS-Vt) complexes formed at the different Si/Al and NaOH/Al ratios. Control: untreated vermiculite.

HyA interlayer formation of Vt was in the range of 4.1 to 5.3.

The retention of Cl^- by the HAS-Vt and HyA-Vt complexes was not observed even in lower pH ranges, because of the electrostatic repulsion of Cl^- by the permanent negative charge of Vt. The AEC values of Mt complexes with HAS and HyA ions with Si/Al ratios of 0.00 to 0.51, which are formed at NaOH/Al ratios of 2.0 and 2.5, ranged from 0.0 to 2.9 meq/100 g for HyA-Mt complexes, and from 1.7 to 8.3 meq/100 g for HAS-Mt complexes at the pH range of 4 to 7. Therefore, the anion adsorption by HAS-Vt or HyA-Vt complexes was quite different from that of HAS-Mt or HyA-Mt complexes, probably because of its higher negative charge density and because the dominant negative charge sites of Vt are located in tetrahedral sheets. These are nearer to interlayer surfaces as compared to the octahedral sheets of Mt.

Surface characteristics

Table 3 indicates total, external, and internal surface areas of HyA-Vt or HAS-Vt complexes formed at around pH 5. The total surface area of Vt used in this study was $397 \text{ m}^2/\text{g}$ and falls within the ranges of Vt (380 to $410 \text{ m}^2/\text{g}$) as reviewed by Egashira (1987). The specific surface area of Vt was predominantly occupied by an internal surface area.

Total surface areas of HyA-Vt and HAS-Vt complexes were also calculated on the assumption that the monolayer of EGME was intercalated in their interlayer spaces. The fixation of HyA and HAS ions by Vt caused the great reduction of its total and internal surface areas. Total and internal surface areas of HyA-Vt and HAS-Vt complexes formed at NaOH/Al ratios of

1.0 and 2.0 significantly decreased. The reduction in total surface area was 66 to 86%, while reduction of internal surface was 59 to 79% of that in Vt. The decline in total surface area in the complexes was predominantly due to the decrease of internal surface area caused by the fixation of HyA and HAS ions. On the contrary, the external surface area of the complexes slightly increased as compared with that of Vt, probably because of the formation of an irregular external surface by the fixation of HyA and HAS ions on the planar surface of Vt, and/or the formation of amorphous aluminosilicates and aluminum hydroxides during the interaction of Vt with HAS and HyA ions.

The internal surface area of the HAS-Vt complexes formed at NaOH/Al ratios of 2.0 and 2.5 slightly increased with increasing Si/Al ratio of HAS ions fixed on Vt. The slight increase of internal surface area in HAS-Vt complexes formed at a NaOH/Al ratio of 2.5 and Si/Al ratios of 0.29 and 0.48 could be based on the development of HAS polymers. These forms have large molecular size and low positive charge, thereby making it difficult to penetrate into the interlayer spaces of Vt. In the process, the HAS could be excluded from its interlayer spaces of Vt. The great increase of specific surface areas in HAS(Si/Al = 0.48; NaOH/Al = 2.5)-Vt complexes could be mainly related to the coexistence of amorphous aluminosilicates formed.

Dixon and Jackson (1962) and Frink (1965) indicated that the interlayer material was concentrated near the edges of soil clays. Small ions such as Ca^{2+} or Al^{3+} , therefore, could penetrate deeper into the interlayer spaces, but the penetration of a large EGME molecule could be limited due to the physical blocking by HyA and HAS ions fixed near the edges of Vt.

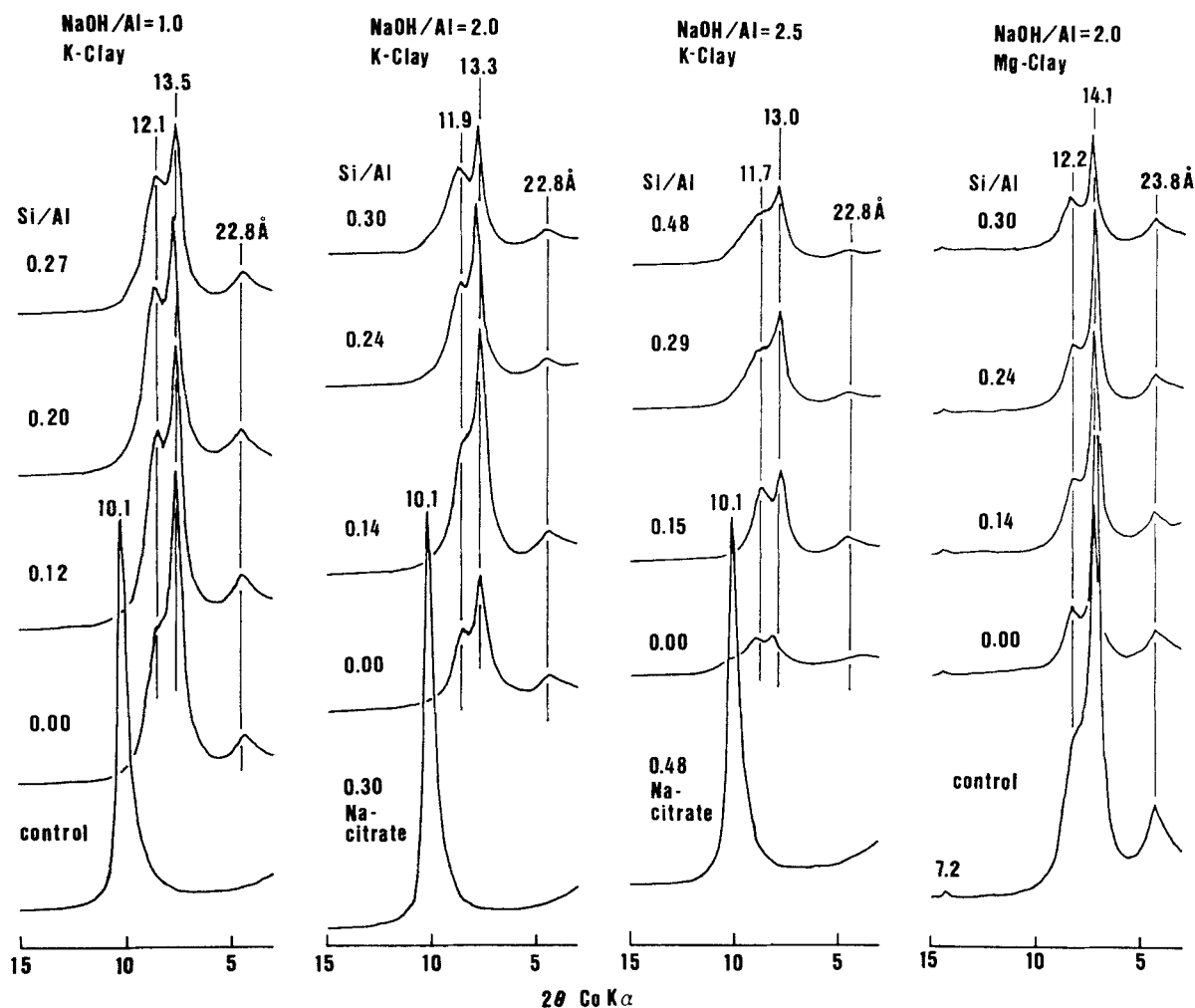


Figure 4. X-ray diffractograms of K- or Mg-saturated and air-dried hydroxy-Al- or hydroxyaluminosilicate-vermiculite complexes and Na-citrate treated samples. Control: vermiculite.

X-ray diffraction

Rich (1960) and Hsu and Bates (1964) used XRD to reveal that HyA ions were fixed in interlayer spaces of Vt. The fixation of HAS ions in the interlayer spaces of Vt was confirmed by our X-ray diffraction analysis. The X-ray diffractograms of K-saturated and Mg-saturated and parallel oriented samples are given in Figure 4. The reflection at 23.8 Å and the shoulder or weak reflection at 12.2 Å in Mg-saturated specimens were due to the interstratified biotite-vermiculite present in the original clay.

The X-ray diffractograms of Mg-saturated HAS-Vt complexes formed at NaOH/Al ratios of 1.0 to 2.5 gave a reflection at 13.0 to 14.1 Å. The product, when K-saturated, had a spacing of 13.0 to 13.5 Å at 20°C (Figure 4). These results suggest that the thickness of HAS ions is almost the same as that of HyA ions (Hsu and Bates, 1964) and indicate that HAS ions are fixed as a monolayer in the interlayer spaces of Vt.

After heating the K-saturated specimens with NaOH/Al ratio of 2.0, the reflection at 13.3 Å collapsed to 10.8–11.5 Å at 110°C and to 10.5–10.8 Å for HAS-Vt and HyA-Vt complexes at 300°C (Figure 5). The d_{001} -spacings of the specimens at 110 and 300°C were decreased with increasing Si/Al ratio.

HAS and HyA ions were fixed in the interlayer spaces of Vt, resulting in the expansion of its d_{001} -spacing. After treatment of HAS (Si/Al = 0.30)-Vt and HAS (Si/Al = 0.48)-Vt complexes with Na-citrate, however, the reflection at 13.0 to 13.5 Å shifted to a sharp reflection at 10.1 Å, indicating that HAS ions adsorbed in the interlayer spaces of Vt were completely dissolved by the Na-citrate treatment (Figure 4).

Pedogenic implications

The present data revealed that Al and Si were adsorbed as HAS ions in the interlayer spaces of Vt and that the fixation of HAS and HyA ions on Vt greatly

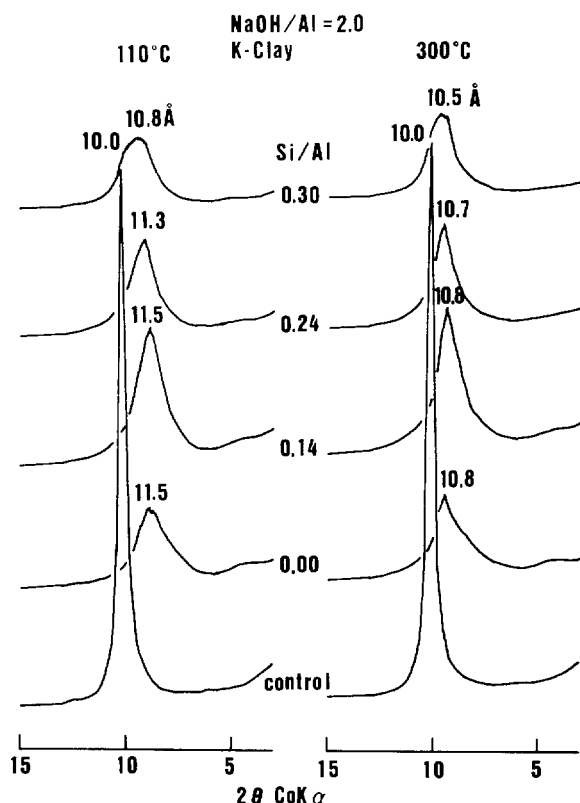


Figure 5. X-ray diffractograms of K-saturated and heated hydroxy-Al- or hydroxyaluminosilicate-vermiculite complexes. Control: vermiculite.

changed its electric charge and surface characteristics. The expanded d_{001} spacings (13 to 14 Å) of HAS-Vt complexes provide evidence of a possibility that, in addition to HyA ions, interlayer materials of chloritized-Vt are partially composed of HAS ions. Our findings also suggest that the formation of chloritized-Vt in the nonallophanic Andisols could be formed by the interaction of Vt, transformed from muscovite and transported as eolian dust from China, with HAS and/or HyA ions formed in soil solutions during weathering and pedogenic alteration of volcanic ash.

Furthermore, our data indicate that the cation exchange capacity is strongly reduced by the formation of hydroxy-interlayered Vt, especially in the pH range of 4 to 5.5. HyA and HAS ions and their polymers fixed on Vt would be important as active Al components in soils. These active Al components in chloritized-Vt could contribute to accumulation and stabilization of humus and phosphate retention in acidic and nonallophanic Andisols (Inoue and Higashi 1988, Inoue 1990). These interlayer materials could play a significant role in modifying the surface and mineralogical properties of clays and soils and their cation exchange and anion fixation reactions.

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