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CHARGE HETEROGENEITY AND NANOSTRUCTURE OF 2:1 LAYER SILICATES BY HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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Abstract—Several soil and reference smectites and vermiculites and one reference illite were examined by high-resolution transmission electron microscopy (HRTEM) to decipher the nanostructure and layer charge heterogeneity in these minerals. HRTEM results were compared with those obtained from powder X-ray diffraction (XRD) analysis. Samples were either exchanged with Na^+ ions followed by equilibration with a very dilute solution of NaCl in a pressure membrane apparatus at 316 hPa (pF = 2.5) to see the effect of hydration and applied pressure on layer organization, or exchanged with dodecylammonium ions to see the expansion behavior. Oriented samples were embedded in a low viscosity resin and cut approximately 500 Å thick perpendicular to d(001) using an ultramicrotome fitted with a diamond knife. In general, Na-saturated soil clays possessed crystallites that were thinner (c-direction) and shorter (ab-direction) as compared with reference clays. In all cases, samples treated with dodecylammonium chloride exhibited nanostructures that were more disintegrated as compared with Na-saturated samples. In a soil vermiculite, dodecylammonium ion exchange showed frayed edges indicating the initiation of mica transformation to vermiculite from edge toward core. In a reference vermiculite (Transvaal) treated with dodecylammonium ions, in addition to completely expanded crystallites, a regular interstratification between expanded vermiculite and mica (phlogopite) layers was clearly observed in some crystallites. Such nanostructural details were not detected by XRD. HRTEM of the Na-treated illite showed thick crystallites having 10 Å layer separations, whereas the dodecylammonium-exchanged illite showed three types of layers with different degrees of expansion indicating charge heterogeneity in illite: 1) unexpanded (10 Å, highest charge) crystallites; 2) expanded high-charge vermiculite-like (24 Å) crystallites; and 3) occasionally expanded high-charge vermiculite-like (24 Å) layers interspersed in the matrix of 10Å crystallites.

Key Words—Charge heterogeneity, Clays, High-resolution transmission electron microscopy, Illite, Montmorillonite, Nanostructure, Smectite, Vermiculite.

INTRODUCTION

Clay minerals such as smectite, vermiculite and mica are very important constituents of soils and sediments. A better characterization, and hence a better understanding, of these minerals is important from several standpoints: plant nutrient (and environmentally hazardous chemical species) dynamics in soils, land use for various purposes, understanding past and present environmental conditions, extraction of oil from sedimentary basins, and applications to fabricate industrially useful products.

Layer charge, layer organization, and interstratification are very important properties of 2:1 clay minerals. Layer charge has also been used for the identification of these minerals (Bailey, 1980). It is observed that the swelling of these minerals with organic molecules, such as glycerol or ethylene glycol, is inversely proportional to the layer charge and, hence, this property is used for their identification (MacEwan, 1944; Brindley, 1966). More recently, the magnitude and distribution of layer charge of reference (Lagaly and Weiss, 1969, 1970) and soil clays (Malla and Douglas, 1987a, 1987b; Ruehlicke and Niederbudde, 1985; Ghabru *et al.*, 1989) has been deduced from the exchange of the mineral with alkylammonium ions followed by measurement of d(001) spacings by X-ray powder diffraction (XRD). Although XRD techniques have been successfully employed for both structural analysis and routine identification of clay minerals, they do not provide as much detailed information from a very small area as does transmission electron microscopy (TEM). Information is averaged over many unit cells involving a large number of particles in XRD; and consequently, certain nanostructural details are lost. TEM, on the other hand, can give detailed information from a very small area, e.g., one 50–100 Å particle. In high resolution mode (phase contrast image), TEM gives the direct image of the specimen that bears a 1:1 relation to structural information (Iijima and Allpress, 1974). High-resolution TEM (HRTEM), in recent years, has

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Table 1. Sample characteristics.

Sample symbol	Particle size (μm)	Layer charge/half unit cell[1]			2:1 expandable clay type
		Upper	Lower	Mean	
SWy-1[2]	—	0.37[3]	0.21[3]	0.28	Na-montmorillonite
SAz-1[2]	—	0.49[3]	0.31[3]	0.39	Ca-montmorillonite
IMt-1[2]	<2.0	—	—	0.72[5]	Illite
Libby	<0.5	0.82[4]	0.59[4]	0.70,	Trioctahedral vermiculite
Transvaal	<0.5	0.82[4]	0.64[4]	0.73, 0.75[6]	Trioctahedral vermiculite
6201	<0.2	0.65[4]	0.49[4]	0.57	Smectite (soil clay)
21	<0.2	0.78[4]	0.60[4]	0.69	Vermiculite (soil clay)
320	<2.0	0.78[4]	0.60[4]	0.70, 0.75[6]	Hydroxy Al-interlayered vermiculite (soil clay)
7150	<0.2	0.78[4]	0.56[4]	0.66	Hydroxy Al-interlayered vermiculite (soil clay)

[1] Malla and Douglas (1987a and 1987b).
[2] Samples obtained from the Source Clay Repository of the Clay Minerals Society.
[3] Upper and lower limits of charge heterogeneity determined from monolayer to bilayer transition.
[4] Bilayer to pseudotrimolecular transition.
[5] Hower and Mowatt (1966).
[6] From paraffin-type structure.

proven to be a powerful tool in pinpointing the precise mechanism of mineral alteration due to its ability to capture each stage of a reaction (Page and Wenk, 1979; Veblen and Ferry, 1983; Olives Banos and Amouric, 1984; Eggleton and Banfield, 1985, Banfield and Eggleton, 1988; Ahn and Peacor, 1986, 1987; Bell, 1986). Malla and Komarneni (1990) have reviewed the usefulness of HRTEM in the study of soils and clays.

Tessier (1984) demonstrated that HRTEM in conjunction with small angle X-ray scattering (SAXS) can be used to study the effect of interlayer cations, hydration state, and applied pressure on organization of layers including the size of crystallites. In this study, the state of hydration and applied pressure of real-life field conditions were simulated by equilibrating the samples with known concentrations of salt solution and gas pressure in an ultrafiltration device. Where the equilibration of clays with dilute salt solution and applied pressure provides the information on layer organization (thickness of crystallites, domains, etc.) as a result of mechanical and hydration forces, exchange of large organic cations provides information on layer charge heterogeneity and the ease with which the alteration of clay minerals can occur. The main objectives of this study were, therefore, to gain better insight on layer charge heterogeneity and nanostructure of both soil and reference clays and to compare the nanostructural properties of these clays after they have been exchanged with small inorganic cations (Na^+) to those treated with large organic cations (alkylammonium ions).

MATERIALS AND METHODS

Samples

Both soil and reference clays were selected for this study (Table 1). Sources and layer charge properties of these samples were previously reported (Malla and Douglas, 1987a, 1987b). Mineralogically, the soil samples selected were a smectite (with a small quantity of kaolinite or halloysite and without mica, i.e., sample 6201), a vermiculite (with a small amount of kaolinite and trace of mica, i.e., sample 21), and hydroxy aluminum interlayered vermiculites (with considerable amounts of kaolinite and with mica, i.e., sample 320, or without mica, i.e., sample 7150).

Pretreatment, saturation, and orientation

Clay fractions (<2.0 or <0.2 μm) were extracted from the soil samples (<2 mm) by centrifugation methods (Jackson, 1969). Reference montmorillonites obtained from the Clay Minerals Society were used as received.

Homoionic, Na^+-saturated clay was obtained by washing 200 mg of sample four times with 10 ml of 0.5 M NaCl. Samples were then washed four additional times with a very dilute 10^{-3} M NaCl. After the last wash, they were equilibrated with a very dilute (10^{-3} M) NaCl solution at a hydration potential fixed by an applied air pressure of 316 hPa (pF = 2.5) in an ultrafiltration device for a minimum of 40 hr (Tessier and Berrier, 1979; Tessier, 1984; Ben Rhaiem *et al.*, 1987). This technique was originally designed by Tessier (1984) for soils to avoid aggregation artifacts due to drying. The technique was also adopted by Środoń *et al.* (1990) for embedding harder and more compacted samples, such as bentonites. In addition to preserving the sample fabric throughout the embedding process, this method also oriented the clay layers parallel to each other.

Additional aliquots of Na^+-saturated clay were exchanged with dodecylammonium ions by treating 200 mg samples with 20 ml of 0.1 M dodecylammonium chloride solution at 65°C, either for 24 hr in the case of smectites or for 3 days with vermiculite. Samples

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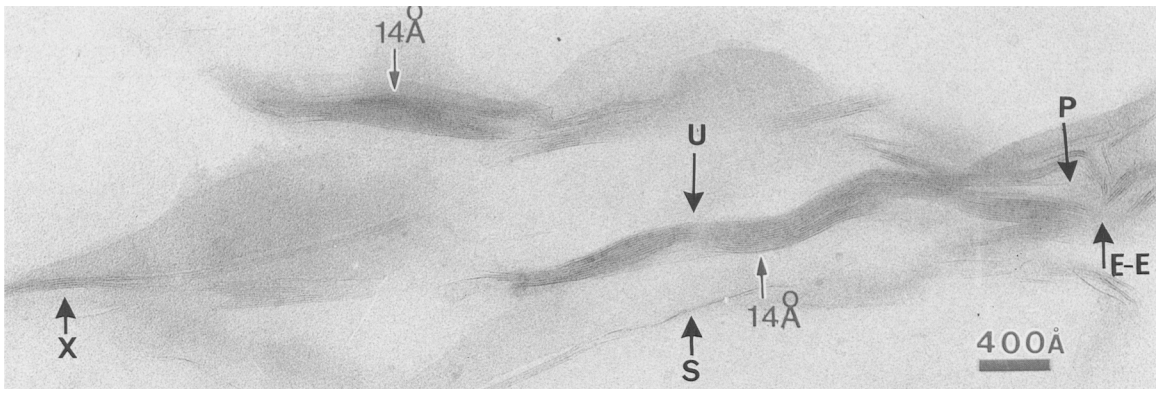


Figure 1. Lattice-fringe images of Na-saturated Wyoming montmorillonite (SWy-1) showing crystallites made up of long and parallel but undulated layers (U). Pore (P) associated with layer organization is shown. S = single layer; X = thin crystallite.

were further incubated with 10 ml of 95% ethanol at 65°C for 24 hr after centrifuging and decanting the dodecylammonium chloride solution. Samples were then washed five times by centrifugation with 95% ethanol to remove the excess salts. The last centrifugation was performed at high speed (10,000 rpm) and the alcohol was decanted completely. The high-speed centrifugation also oriented the clay layers parallel to each other.

Sample preparation for HRTEM and XRD examination

1) Na (from ultrafiltration device) or dodecylammonium ion (from centrifuge tubes) exchanged clays were placed in 1 cm^3 porous containers.

2) Water was removed from the samples by methanol by placing the porous containers in a beaker containing 100% methanol for 1 hr and renewing the methanol.

3) Methanol was replaced from the samples with propylene oxide. For a period of 1 hr, samples were placed in each of the following methanol-propylene oxide mixtures: 25% methanol plus 75% propylene oxide; 50% methanol plus 50% propylene oxide; 25% methanol plus 75% propylene oxide; and 0% methanol plus 100% propylene oxide.

4) Propylene oxide was replaced with Spurr low-viscosity resin (hard type) by placing the porous containers in a 1:1 mixture of propylene oxide and Spurr low-viscosity resin overnight.

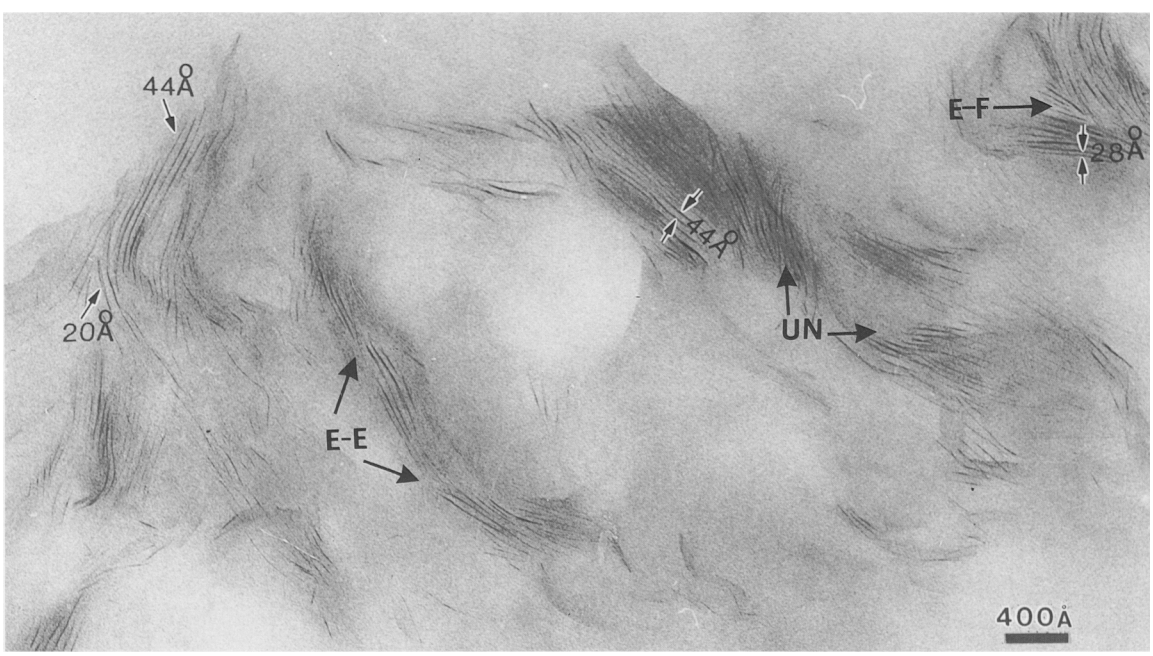


Figure 2. Lattice-fringe images of Arizona montmorillonite (SAz-1) exchanged with dodecyl-ammonium ions showing a large degree of layer disorganization. E-E = edge-to-edge association.

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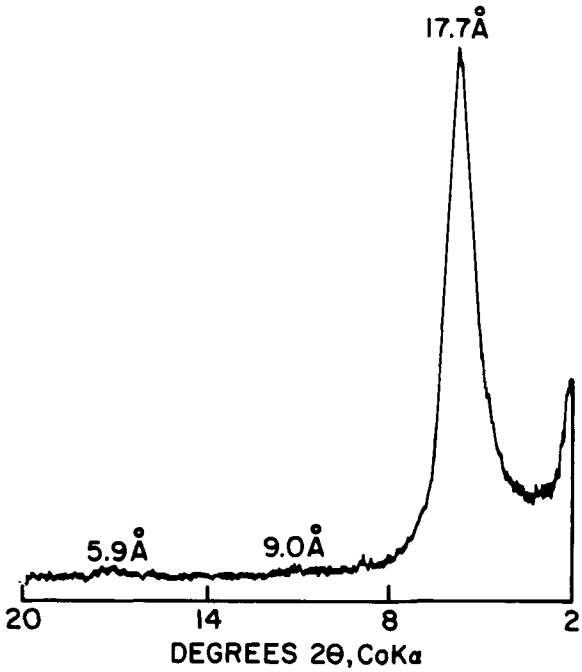


Figure 3. XRD pattern of SAz-1 exchanged with dodecylammonium ions.

5) A small amount of the sample was placed in a mold that was partially filled with Spurr resin, and the mold was then completely filled with the Spurr resin.

6) The mold was placed in an oven at 60°C for a minimum of 40 hr for curing and hardening.

7) And after curing the resin, thin slices of about 500 Å were cut using a diamond knife fitted in a Reichert Ultramicrotome. The slices were collected in a small water-filled container and then captured on carbon films supported on TEM grids.

HRTEM one-dimensional and bright field lattice-fringe imaging were performed with a Philips 420 STEM (120 kV) at magnifications ranging from 51,000 to 135,000. To insure the proper collection of data, images were taken following the conditions described by Środoń *et al.* (1990).

For X-ray powder diffraction analyses, a small amount of sedimented clay paste was smeared on a glass slide and allowed to dry at room temperature. The XRD analyses were performed with a Philips diffractometer using Fe-filtered, CoKα radiation.

RESULTS

Smectites

A lattice fringe image of Na-saturated sample Swy-1 is given in Figure 1. Parallel, but somewhat undulated layers (U) are observed. As many as 20 layers constituted a crystallite that truncated to only about 4 with a great lateral extension (200–4000 Å). The edge-to-edge (E–E) and face-to-face (F–F) associations of crystallites have resulted in a pore system indicated by P in Figure 1. Sporadically, a single layer (S) or a crystallite made up of only a few layers (X) were observed. The layer separation was about 14 Å.

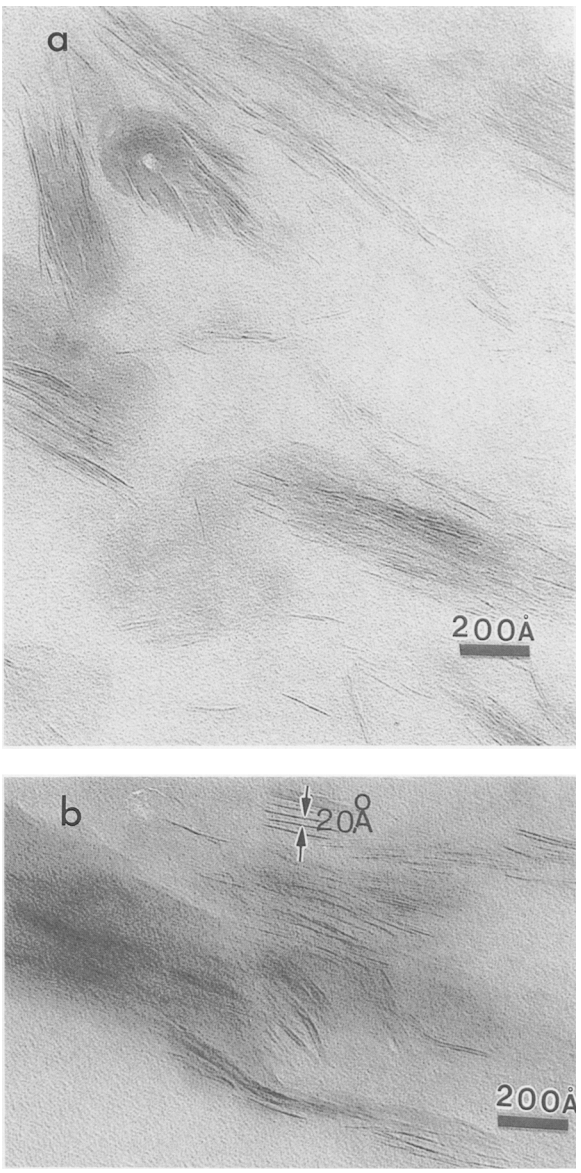


Figure 4. Lattice-fringe images of a) Na-exchanged and b) dodecylammonium ion-exchanged sample 6201.

Dodecylammonium ion-exchanged Sample SAz-1(Cheto type) (Figure 2) showed a large degree of layer disorganization. Layers in crystallites were not always parallel (UN). Both edge-to-edge (E–E) and edge-to-face (E–F) layer associations were observed. Although some degree of disorder in layer organization was observed in the original Cheto type montmorillonite (Vali and Köster, 1986), the further layer disorganization observed in Figure 2 compared with that observed for

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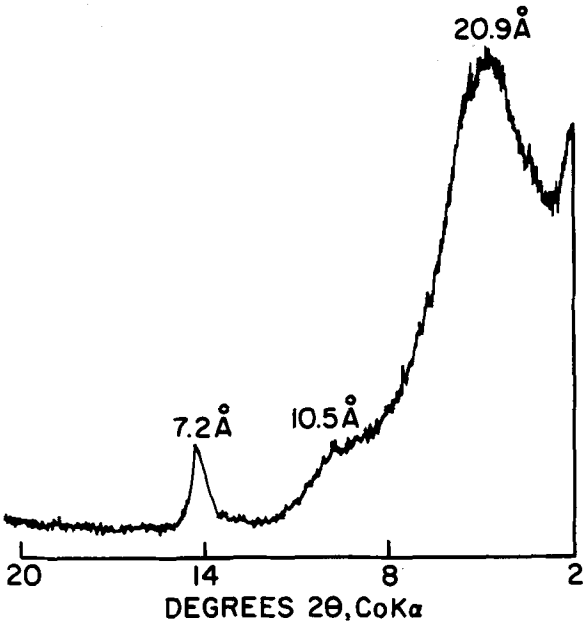


Figure 5. XRD pattern of 6201 exchanged with dodecylammonium ions.

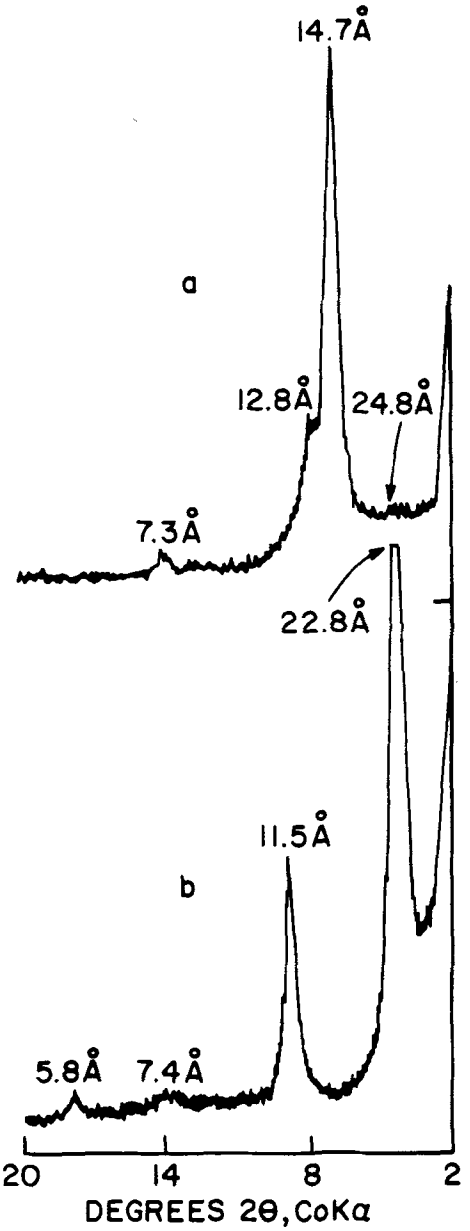


Figure 6. XRD patterns of a) Na-exchanged and b) dodecylammonium ion-exchanged Libby vermiculite.

the original clay by Vali and Köster is apparently a consequence of the layer disintegration (both c- and ab-direction) caused by alkylammonium chloride solution. Very large layer spacings of about 40–45 Å were observed. Additionally, a smaller population of layers with spacings of 20 and 28 Å were observed. The above layer spacings are too large to account for a bilayer adsorption of flatly lying dodecylammonium ions. XRD, however, showed the d-value of only 17.7 Å (Figure 3), indicating a bilayer adsorption of the alkylammonium ions (Lagaly and Weiss, 1969). The larger spacing in the HRTEM image observed in this sample as compared with XRD (17.7 Å, Figure 3) may be due to the adsorption of embedded resin (Vali and Koster, 1986; Laird *et al.*, 1989). The adsorption of resin molecules in smectite may have been facilitated by a pre-expansion of layers with large organic ions (alkylammonium ions), and/or it may have been caused by the hydrophobic surface offered by alkyl groups of the alkylammonium ions.

TEM images of sample 6201 treated with NaCl or dodecylammonium chloride solutions are given in Figure 4 and X-ray diffractograms of the same are given in Figure 5. In both figures, the crystallites are short with less than perfect parallelism between the layers. Unlike smectites discussed previously, layers in this sample appeared less distinct from one another. Such a nanostructure may reflect an origin from the partial crystallization of glassy materials. The XRD spacings (20 Å) in this case correlate well with those observed from TEM images, and this spacing indicates the pseudotrimolecular adsorption of the alkylammonium ions (Malla and Douglas, 1987a; Lagaly and Weiss, 1969).

Vermiculites

XRD analysis showed that Libby vermiculite is in fact not a pure vermiculite, but is interstratified with some 10 Å biotite layers (Sawhney, 1967; Figure 6a). HRTEM image of the Na-saturated sample (Figure 7a) showed relatively thick crystallites with great lateral extension similar to that of illite (Figure 14a). Although XRD showed an intense peak at 14.7 Å, only about

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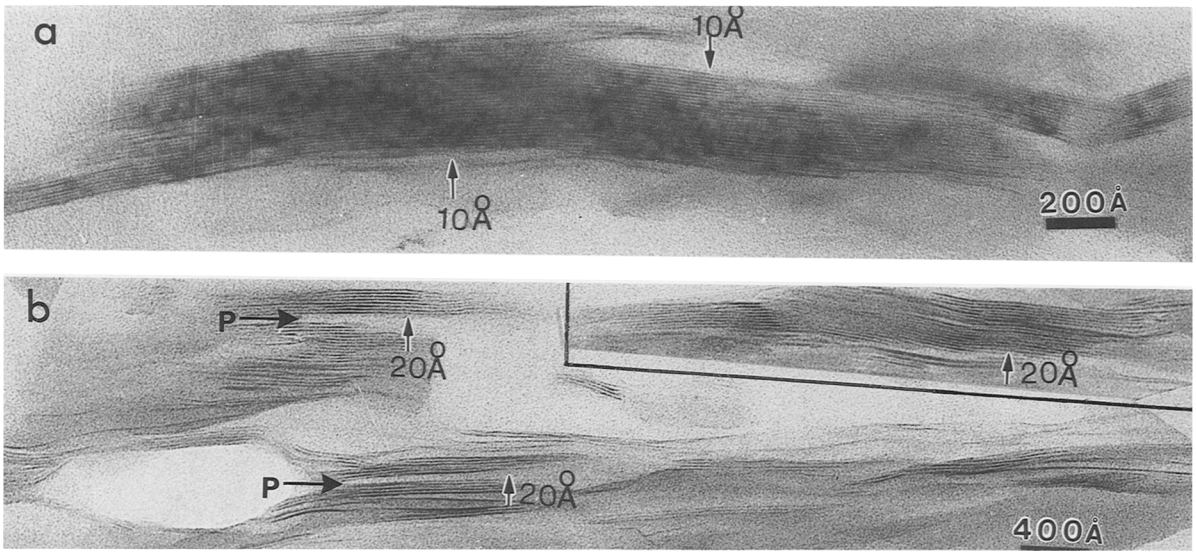


Figure 7. Lattice-fringe images: a) Na-exchanged and b) dodecylammonium ion-exchanged Libby vermiculite. In inset (b), a crystallite from different area is also shown. Pores are indicated by (P).

10 Å layer separations are seen in the TEM micrograph (Figure 7a). Both XRD (22.8 Å in Figure 6b) and TEM (20Å in Figure 7b) showed similar d(001) values for dodecylammonium chloride-treated samples. The dodecylammonium-treated sample, however, gave a nanostructure that is somewhat different from that observed for the Na-saturated sample. The former treatment apparently caused the disintegration of crystallites leading to fewer layers per crystallite with smaller lateral extension.

Transvaal vermiculite treated with both Na and dodecylammonium chloride solution (Figure 8) exhibited XRD patterns similar to those of Libby vermiculite. TEM images of dodecylammonium-exchanged samples, however, showed considerable variation in the expansion properties of these two vermiculites. The crystallites were almost completely expanded in Libby vermiculite. In Transvaal, however, three types of expansion behavior of crystallites (Figure 9) were apparent: fully expanded (20 Å), expanded with a few interspersed unexpanded (10 Å) layers, and regularly interstratified between expanded and unexpanded layers. Edge-to-edge (E–E) associations and pores (P) are indicated.

Sample 21 is a soil vermiculite with an average layer charge of 0.69/half unit cell (Malla and Douglas, 1987a). Only a trace of mica and a small quantity of kaolinite are present in this sample. The XRD patterns of samples treated with NaCl and dodecylammonium chloride are given in Figure 10. These treatments indicated spacings which are typical for a vermiculite. The lattice fringe images are presented in Figure 11. The Na-saturated sample showed that crystallites are thin but have a considerable lateral extension (ab-direction) typical of mica or illite (Figure 14a). The layer separations observed are about 10–12 Å. The dodecylammonium chloride-treated samples showed both expanded (as large as 36 Å) and unexpanded (10 Å) layers in the same crystallite. Some of the layers expanded only at edges (wedge, indicated by arrow) showing resistance to expansion towards the core. This is a typical example of weathering of mica to vermiculite. The extension in the ab-direction has been considerably shortened by alkylammonium chloride treatment.

Hydroxy-interlayered vermiculites

Both samples 320 and 7150 are typical hydroxy-interlayered soil vermiculites as evidenced by their resistance to collapse upon K-saturation and heat treatments (Malla *et al.*, 1989). Sample 320 contains both kaolinite and mica as a mixture, whereas sample 7150 contains kaolinite only. Both of these vermiculites expanded to about 23 Å upon exchange with dodecylammonium ions (Figure 12). The lattice fringe image of sample 320 showed parallel layers with uniform layer separations of 20 Å (Figure 13). Some discrete kaolinite crystallites with layer separation of 7 Å were observed (Figure 13a) adjacent to an expanded vermiculite crystal. The micrograph of sample 7150 (Figure 13b) showed that the layers in this sample were more disorganized than in sample 320 (Figure 13a) with less than perfect parallelism between the layers.

Illite

IMt-1 is an illite sample from Silver Hill, Montana. This sample was originally described as an I Md polytype by Hower and Mowatt (1966) and later as a pure 1M polymorph, free of expandable smectite layers, by

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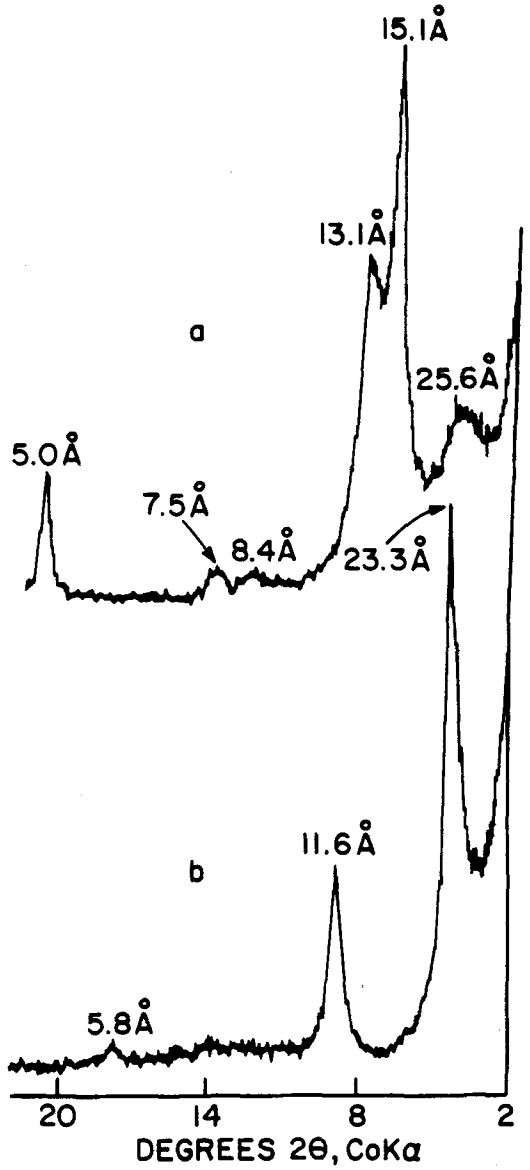


Figure 8. XRD patterns of a) Na-exchanged and b) dodecylammonium ion-exchanged Transvaal vermiculite.

Reynolds and Hower (1970). Lattice-fringe imaging of NaCl-treated sample showed relatively thick (100–200 Å) crystallites with a great lateral extension (ab-direction) (Figure 14a). The layer separation is 10 Å (Figure 14a). The image of the sample treated with dodecylammonium chloride solution for 2 days is given in Figure 14b. Both unexpanded (10Å) and expanded (24 Å) crystallites were observed. The expanded d-value is in line with the paraffin-type packing of dodecylammonium ions in the interlayers (Lagaly, 1982). Occasionally, a few expanded layers having frayed edges were interspersed with crystallites composed of 10 Å layers. The XRD pattern (Figure 15) corroborates the HRTEM

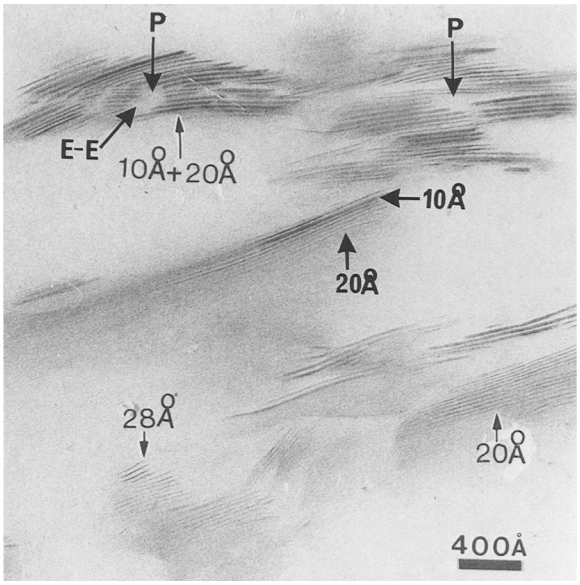


Figure 9. Lattice-fringe images of Transvaal vermiculite exchanged with dodecylammonium ions showing expanded (20 Å) and unexpanded layers (10 Å). Pores are indicated by (P). E–E = edge-to-edge association.

results, i.e., both expanded (23.1 Å) and unexpanded (10 Å) d(001)-values with high order integral reflections were observed.

DISCUSSION

Charge heterogeneity

Layer charge in 2:1 layer silicates, in general, originates from the cationic substitution of Si^{4+} by Al^{3+} in tetrahedral sheet and/or of Al^{3+} by Mg^{2+} or of Mg^{2+} by Li^{+} in octahedral sheet. Sites of cationic substitution are not uniformly distributed, but differ from one layer to another or within a layer. Consequently, the strength of a clay in holding, releasing, or exchanging cations and solvation complexes varies from layer to layer and from one part of a layer to the other. The net result of charge heterogeneity is to affect the rate of mineral transformation and the physical and chemical properties of a clay. Charge heterogeneities in smectite and vermiculites have been deduced 1) by reacting the clay with hydroxy Al-polymer solution and determining the ease with which these polymeric cations are exchanged with small inorganic cations (Hsu, 1968) and 2) by exchanging with alkylammonium ions followed by determining the packing of these cations in the clay interlayers by XRD (Lagaly and Weiss, 1970; Lagaly, 1982; Malla and Douglas, 1987a, 1987b). Alkylammonium ions in the interlayers of 2:1 clays may assume a monolayer (13.6 Å), a bilayer (17.7 Å), a pseudotrimolecular layer (21.7 Å), or a paraffin-type configuration depending on the magnitude of the layer charge and the size of the alkyl chain. In a mineral with ho-

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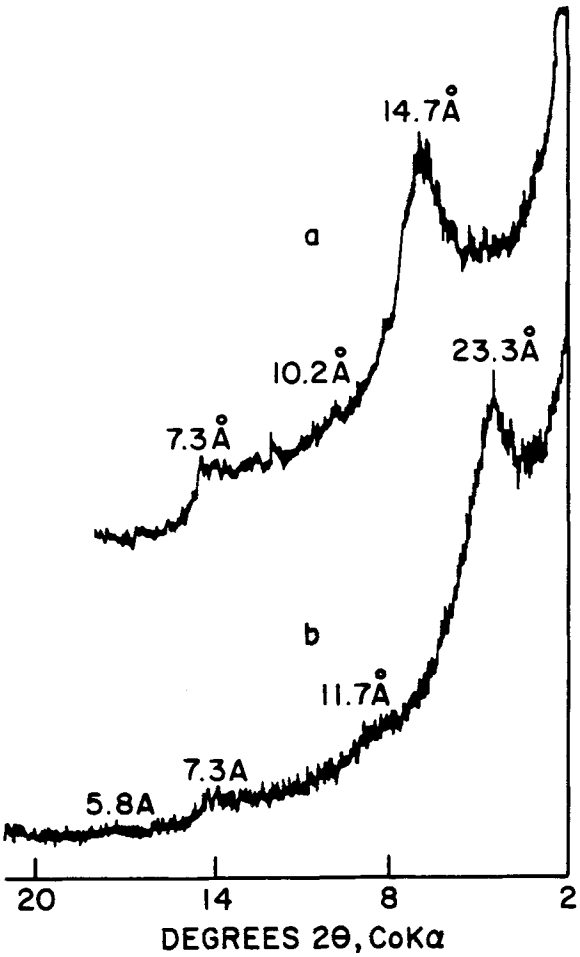


Figure 10. XRD patterns of sample 21: a) Na-exchanged and b) dodecylammonium ion-exchanged.

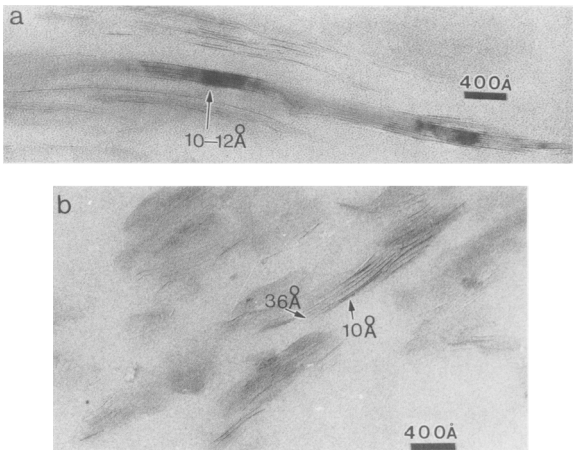


Figure 11. Lattice-fringe images of sample 21: a) Na-exchanged and b) dodecylammonium ion-exchanged. In (b), frayed edges indicate the weathering of 10 Å (mica) layers to expandable layers.

mogeneous charge distribution, the transition from monolayer to bilayer, or from bilayer to pseudotrimolecular layer, occurs sharply; whereas, this transition is broad in a mineral with a heterogeneous charge (layer to layer) distribution. The extent of charge heterogeneity measured by alkylammonium ion exchange method followed by XRD analysis is given in Table 1. The charge heterogeneity presented in Table 1 is layer to layer, and thus does not provide the information on charge heterogeneity within a layer (unsymmetrical charge distribution) or a sporadic presence of either very low- or very high-charge layers.

HRTEM allowed direct observation of various types of heterogeneities. As seen in sample 21 (Figure 11), which is a soil vermiculite (treated with dodecylammonium ions), three out of six layers constituting a crystallite remained fully expanded while the others were opened up only at the edge giving a wedge. In sample Imt-1, layers in some crystallites expanded to 24 Å as a result of lower charge compared with unexpanded layers indicating the charge heterogeneity from crystallite to crystallite. Less frequently, expanded 24 Å layers interspersed in a 10 Å matrix indicated the charge heterogeneity within crystallites. In most of the samples, not all expanded layers have the same spacings; and in some cases, the spacings vary even within a layer. All of these structural evolutions appear to be a consequence of charge heterogeneity.

Nanostructure

Generally, it was observed that Na-treated reference clays possessed crystallites with larger number of layers as compared with Na-saturated soil clays. Similar results were also observed by Robert *et al.* (1991) for French soils. The broader XRD peaks observed for soil clays compared to reference clays may be the consequence of fewer number of layers comprising a crystallite in soil clays. It was also evident, in all cases, that the samples treated with alkylammonium chloride solution produced crystallites that were both thinner (c-direction) and shorter (ab-direction) as compared with Na-saturated samples. This indicates that the dodecylammonium chloride solution caused mild degradation of these minerals. Nanostructural feature showing pore systems (indicated by P) originating from an edge-to-edge (E–E), edge-to-face (E–F), or face-to-face (F–F) association of crystallites were also evident in Figures 1, 7b, 9, and 14a. These pore systems may play an important role in water holding capacity of the soils or sediments. Pore structure arising from face-to-face (Ca-smectite) and edge-to-edge (Na-smectite) associations of layers of smectites was also observed and has been described in detail by Ben Rhaiem *et al.* (1987).

In addition to the information obtained on the shape and the size of the crystallite by HRTEM, sample 21,

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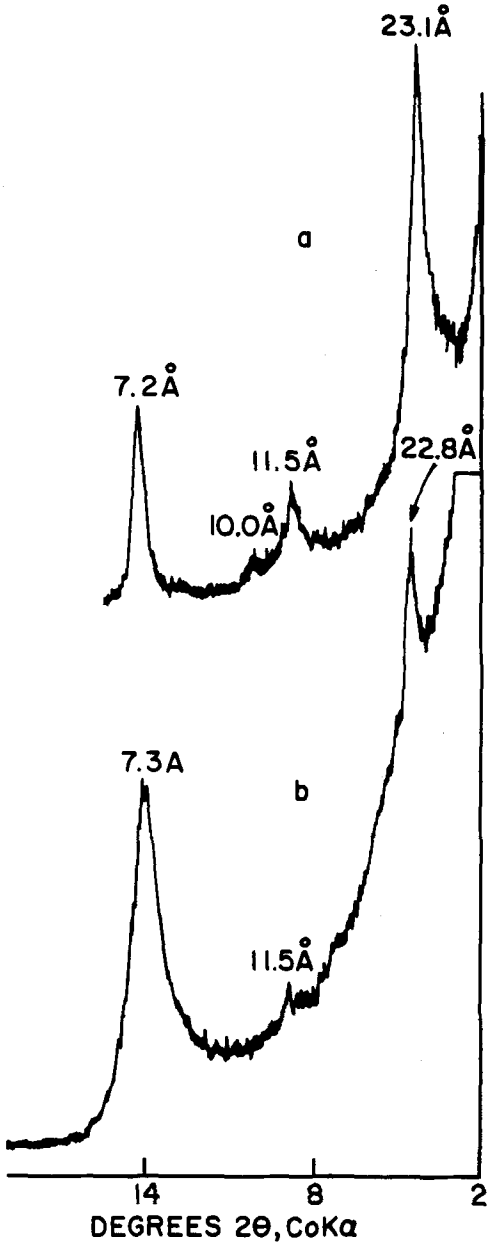


Figure 12. XRD patterns of dodecylammonium ion-exchanged samples: a) 320 and b) 7150.

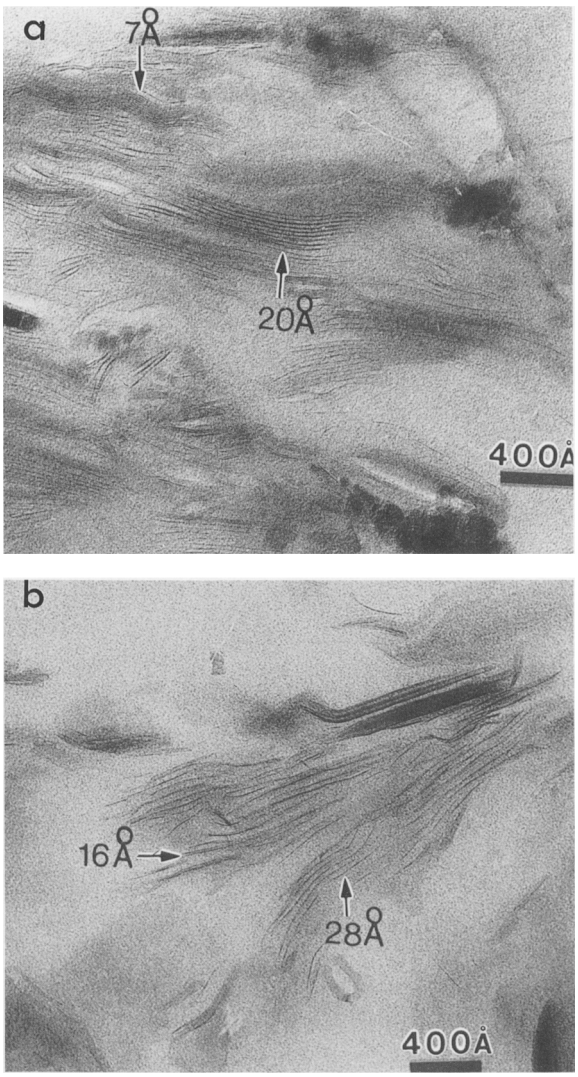


Figure 13. Lattice-fringe images of dodecylammonium ion-exchanged samples: a) 320 and b) 7150.

Transvaal vermiculite, and illite showed additional features. Both expanded and unexpanded layers including frayed edges (wedges) are present in sample 21 confirming that the weathering of mica advances from edge to core (Jackson *et al.,* 1952; Scott and Smith, 1967). In some crystallites, Transvaal vermiculite showed an alternation of expanded (20 Å) and unexpanded (10 Å), i.e., regularly interstratified layers, even after treatment with dodecylammonium chloride. Sample Imt-1 was partially expanded to 24 Å in a manner similar to that observed in high-charge vermiculite with dodecylammonium ions. This treatment also caused partial breakdown of illite, as evidenced by the fewer number of layers per crystallite observed as compared with the NaCl-treated sample. Similar expansion of soil as well as reference illites was also observed by Laird *et al.* (1987). Earlier studies (Malla, 1987) showed that a glauconite (Marlton, New Jersey) sample was also partially expanded within 24 hr; whereas, a muscovite from Madagascar did not expand even after treatment with dodecylammonium chloride solution for at least 3 weeks. Ghabru *et al.* (1989) also observed no expansion of a pure biotite from Bancroft, Ontario, after treatment with alkylammonium cations. This indicates that true biotite and muscovite do not react while illite, glauconite, or repotassified 10 Å vermiculite do react with alkylammonium ions. The above reactions indicate the variations of energies with which the K^+ ions are held in these mica or mica-type min-

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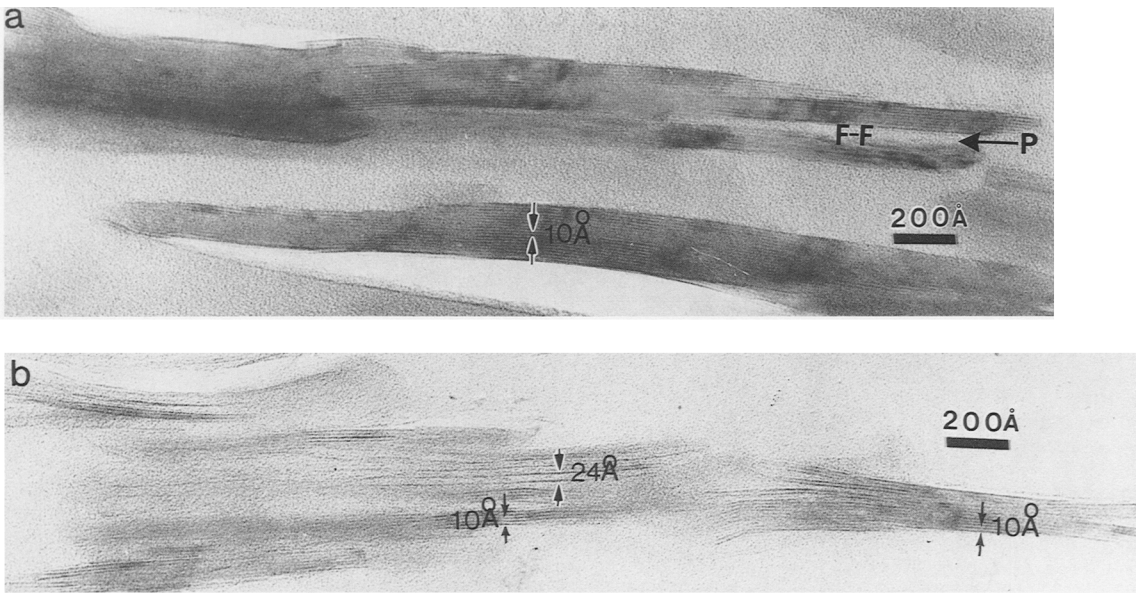


Figure 14. Lattice-fringe images of an illite (IMt-1): a) Na-treated and b) dodecylammonium ion exchanged. In (b), many 10 Å layers have been expanded to 24 Å. Pores (P) associated with layer organization (F–F = face to face) are shown.

erals and their vulnerability to transformation to expandable phases as a result of charge heterogeneity, reduction in magnitude of charge, and/or subtle differences in structural feature. Thus, the study of clays treated with small inorganic as well as large organic cations by HRTEM and XRD is extremely useful in elucidating the charge properties and a variety of the nanostructural features.

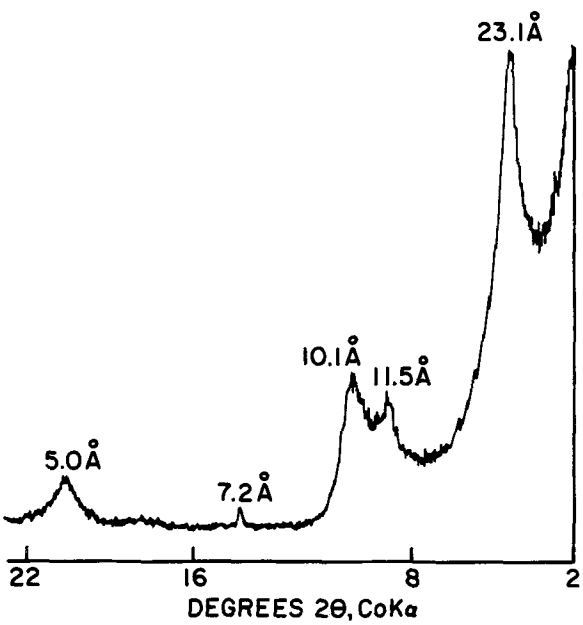


Figure 15. XRD patterns of IMt-1 exchanged with dodecylammonium ions showing expansion of 10 Å layers.

CONCLUSIONS

HRTEM (lattice) imaging of 2:1 clay minerals after treatment with dilute solution of NaCl and alkylammonium ions provided information on layer charge heterogeneity and detailed nanostructure, such as interstratification, layer transformation, number of layers per crystallite, length of the layer in ab-direction, and various pore systems associated with the organization of the layers. In general, the soil clays have thinner (c-direction) and shorter (ab-direction) crystallites compared with the reference clays. Additionally, the alkylammonium-exchanged samples gave more disintegrated layer organization (both numbers of layers per crystallite and the extension of layers in ab-direction) as compared with the Na-saturated samples. In most cases, the d-spacings observed by XRD are in good agreement with those observed by HRTEM; but in a few cases, HRTEM showed d-spacings that were twice as large or larger than those observed by XRD. This approach involving HRTEM and XRD for studying clay texture and charge heterogeneity is very important from the standpoint of predicting physical and chemical properties of soils and sediments. Future work involving the HRTEM study of soil clays having different origins and/or clays having the same origin but at different stages of weathering should prove fruitful to correlating the effect of these factors with the charge heterogeneity and the nanostructure.

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