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"CHLORITIZED" VERMICULITE IN A KOREAN ULTISOL STUDIED BY ULTRAMICROTOMY AND TRANSMISSION ELECTRON MICROSCOPY

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Abstract—"Chloritized" vermiculite coexisting with kaolin-group minerals, vermiculite, mica, and gibbsite in the 0.2–0.5-μm fraction separated from a Korean Ultisol was studied by ultramicrotomy and high-resolution electron microscopy. The (001) lattice images observed from thin sections showed that the "chloritized" vermiculite was composed of particles which differed in their shape and the stacking of silicate layers. On saturation with K^+, the silicate layers had spacings of 14–10 Å, with 14–12-Å layers being dominant. The 8–7-Å layers of a few particles appeared to be segregated close to the basal plane surfaces, but not necessarily close to the edge surfaces. The silicate layers were more or less curved and wavy and were commonly discontinuous. They formed packets (100–500 Å thick) by stacking, which were associated "face-to-face" and/or "edge-to-edge" or stacked parallel or subparallel to form particles of different shapes. The extent of interlayer collapse of the 14-Å layers on heating differed from one particle to the other, but was fairly uniform within a particle. Treatment with hot ⅓ M sodium citrate dissolved the interlayer material and possibly the material present between the packets from the "chloritized" vermiculite and from a few fine plates of kaolin-group minerals. The interlayer material and its chemical composition, therefore, could not be determined.

要約 — 大韓民国のアルテイソルから分離した 0.2-0.5 μm 画分に，カオリン鉱物，パーミキュライト，雲母，ギブサイトと共存していた "緑泥石化した" パーミキュライトを,超薄切片法と高分解能電子顕微鏡観察によって調べた。切片上で観察された (001) 格子像は，"緑泥石化した" パーミキュライトが，形とケイ酸塩層の積み重なりを異にした粒子からできていることを示した。K^+飽和で，粒子内のケイ酸塩層の積み重なり間隔は 14 ないし 10 Å を示し，このうち 14 ないし 12 Å の間隔を有するものが主であった。8 ないし 7 Å ケイ酸塩層もいくつかの粒子で認められ，粒子の端面ではなく，平たん面表面に近い部分に分離して積み重なる傾向を示した。これらのケイ酸塩層は多少とも曲り，ときに波状を呈し，またそのつながりに不連続なところがあった。また，ケイ酸塩層はパケット (100 ないし 500 Å の厚さ) を形成して積み重なり，そのパケットが "面と面" ないしは "端と端" で結合し，平行あるいはこれに近い状態で積み重なって，異なった形の粒子を形成していた。14-Å 層の加熱による層間収縮の程度は，粒子間で差異があったが，一つの粒子内ではかなり一様であった。熱 1／3 M クエン酸ナトリウム溶液による処理は，"緑泥石化した" パーミキュライトから層間物質及び恐らくパケット間に存在していたと推定される物質を溶出するとともに，微細なカオリン鉱物粒子を溶出した。従って，層間物質とその化学組成を決定することはできなかった。

Key Words—Chloritized vermiculite, Stacking arrangement, Transmission electron microscopy, Ultramicrotomy, Vermiculite.

INTRODUCTION

Many soils under leaching conditions in temperate regions contain partly interlayered or "chloritized" vermiculites as major clay mineral species (Rich, 1968; Barnhisel, 1977; Douglas, 1977). Like vermiculite, "chloritized" vermiculite gives a 14-Å reflection on Mg^{2+}-saturation and air-drying, but the shift of this 14-Å reflection to 10 Å on K^+ saturation is incomplete even after heating and occurs only after extraction of "interlayer material" by a hot ⅓ M sodium citrate treatment. Inasmuch as Al is extracted by the treatment, "chloritized" vermiculite has been considered as vermiculite in which the interlayer space is partly filled with polymer hydroxy-Al cations.

On the other hand, studies by Wada and Kakuto (1983a, 1983b) of "chloritized" vermiculites in several red and yellow soils (Ultisols and Alfisols) in Korea showed that (1) the "interlayer material" extracted by the sodium citrate treatment contained not only Al but Si, (2) its molar Si/Al ratio was close to 1.0, and (3) its infrared spectra had features of kaolin-group minerals. Based on these and other analyses, the term intergradient vermiculite-kaolin mineral, in which each 14-Å layer laterally transforms to two 7-Å layers, was proposed for "chloritized" vermiculite.

Douglas (1977) pointed out that vermiculite in acid soils invariably has a hydroxy-Al interlayer, yet virtually no literature exists that describes the actual structure and composition of soil vermiculite. This situation does not seem to have changed since Douglas' report. "Chloritized" vermiculite has been recognized only as clay-size particles, too small for single crystal X-ray diffraction, and only in mixtures with other clay minerals. In the present study, ultramicrotomy and high-resolution transmission electron microscopy (HRTEM) were used to observe stacking of silicate layers in individual clay particles of an Ultisol, in which "chloritized" vermiculite was identified as a major clay mineral.

MATERIALS AND METHODS

Clay samples

The soil selected for the study was the IIB23t(g) horizon of a Typic Hapludult (Wada and Kakuto, 1983a), which is a heavy clay derived from old alluvium associated with granite and gneiss. The soil shows an acid reaction (pH (H_2O) = 5.4; pH (1 M KCl) = 3.80). Clay fractions (<0.2 and 0.2–0.5 μm) were separated from the soil by repeating dispersion at pH 10 (NaOH) with sonic vibration and sedimentation.

Dissolution treatments and X-ray powder diffraction analysis

Treatments with dithionite-citrate (Mehra and Jackson, 1960) and with ⅓ M sodium citrate at 100°C (Tamura, 1958; Wada and Kakuto, 1983a) were used, respectively, to remove iron oxide and "interlayer material" from "chloritized" vermiculite. The treated clays were saturated with Mg^{2+} and K^+ and oriented on glass slides. They were analyzed by X-ray powder diffraction (XRD) after air-drying or heating at 60°, 300°, and 550°C for 1 hr with a Rigaku Geigerflex (CoKα, 30 kV, and 10 mA).

Ultramicrotomy and HRTEM

The 0.2–0.5-μm fractions treated differently and saturated with K^+ (30–60 mg) were washed successively by centrifugation with 5-ml portions of water and 70%, 85%, and 100% ethanol, oxypropyrene, and an oxypropyrene-epoxy resin mixture. Each washed sample was then suspended in 1.5 ml of the epoxy resin plus its hardening reagent. A layer of this suspension, about 1 mm thick, was cast in a flat-bottom plastic vessel, evacuated, and cured at 40°, 50°, and 60°C each for 1 day. A specimen block of appropriate size was removed and trimmed with a razor blade on the specimen holder of LKB 2088V ultramicrotome. The trimmed block was sectioned at a thickness of 900–1500 Å using a diamond knife, and the thin sections were collected on a plastic microgrid. Clay particles sectioned perpendicular to the stacking of silicate layers were examined with a JEOL 100B electron microscope, operating at 100 kV.

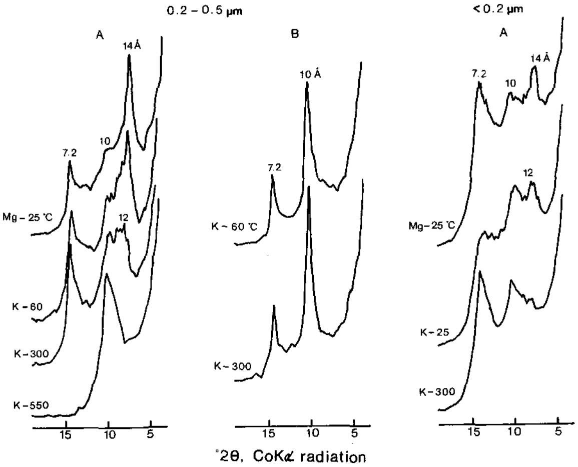

Figure 1. X-ray powder diffraction patterns of parallel oriented clays treated with dithionite-citrate (A) and then with ⅓ M sodium citrate (B).

RESULTS AND DISCUSSION

XRD analyses of the 0.2–0.5-μm fractions before and after the sodium citrate treatment showed that the major mineral component was "chloritized" vermiculite, with lesser kaolin-group minerals, vermiculite, interstratified vermiculite/"chloritized" vermiculite, mica (Figure 1), and gibbsite. The d-values of the 001 reflection used for identification of the layer silicates are shown in Table 1. "Chloritized" vermiculite was also present in the <0.2-μm fraction, but its content was less than that in the 0.2–0.5-μm fraction, and it collapsed more readily on drying and heating. Low-magnification electron micrographs showed that the 0.2–0.5-μm fraction contained not only particles >0.2 μm, but many thin plates <0.2 μm in size (Figure 2a). The thin sections showed that some fine plates coexisted with the large particles on their surfaces, but some were also oriented with each other "face-to-face" and/or "edge-to-edge" to form the larger particles (Figure 3).

Mineral species constituting each particle observed by HRTEM were identified by measuring the spacings of the (001) lattice images that were generated by the thin section and by referring to the XRD patterns of the minerals in the 0.2–0.5- and <0.2-μm fractions. Most of the large particles were identified as "chloritized" vermiculite. They occurred as thin to thick, more or less curved plates (Figures 3a, 3c, 3d, and 4), twisted or crumpled plates (Figures 3b, 5, and 6), and lense- or spindle-shaped particles (Figures 3e, 7, and 8). In all of these particles the silicate layers, as indicated by the lattice images, were more or less curved or wavy and the arrangement of these layers was neither uniform nor continuous throughout the particle. On the other hand, the silicate layers tended to form packets by stacking. The packets were as thick as 500 Å, but most were 100–200 Å thick. The isolated packets may correspond to the fine plates described above (Figure 3). The packets were either associated "face-to-face" and/or "edge-to-edge" or were stacked parallel or subparallel, forming the particles of different shapes. Nonimaged portions between the packets were also noted within the particle (Figures 4–7), suggesting the pres-

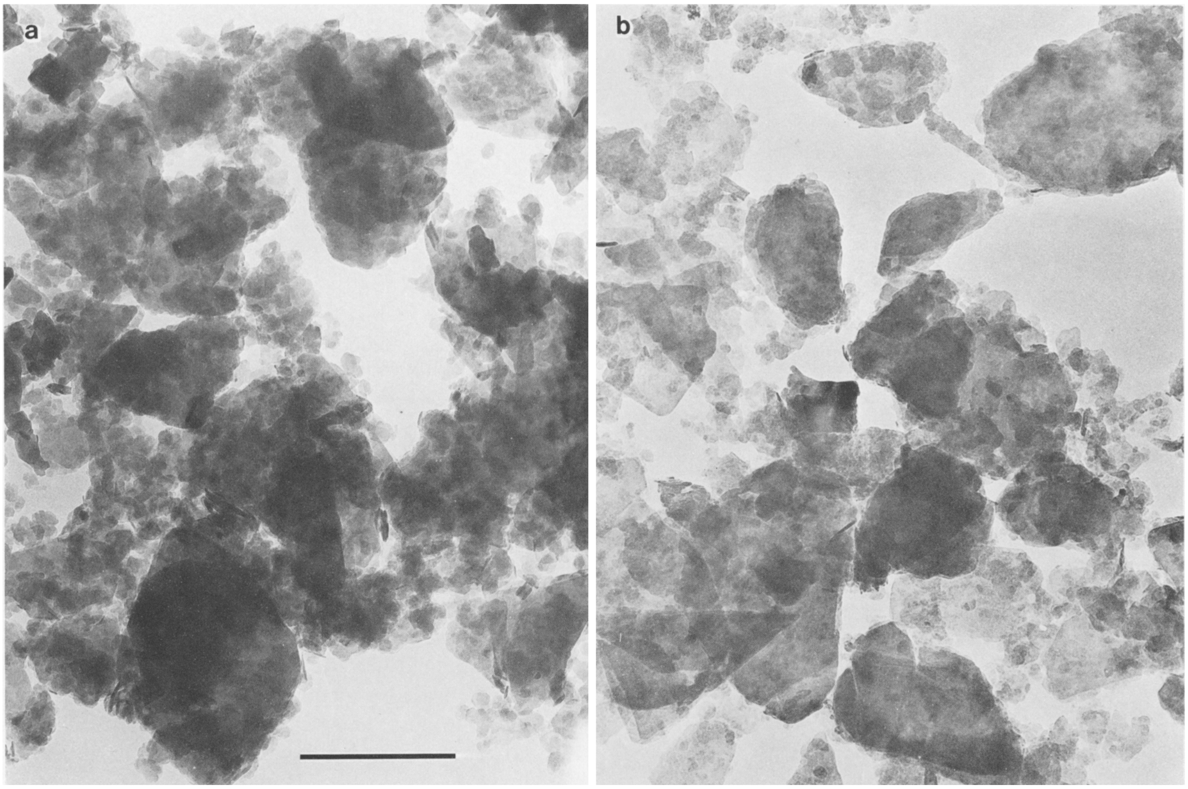

Figure 2. Electron micrographs of the 0.2–0.5-μm fraction; (a) treated with dithionite-citrate and (b) then treated with ⅓M sodium citrate. Marker = 0.5 μm.

ence of poorly crystalline material or the distortion of the packets with respect to the electron beam.

"Chloritized" vermiculite particles were constructed of silicate layers having spacings of 14–10 Å and 8–7 Å (Figures 4–8), the 14–12-Å layers being dominant. These silicate layers were common in K^+-saturated and air-dried clays containing "chloritized" vermiculite by XRD (Figure 1; also see, e.g., Barnhisel, 1977), but layers other than the 14-Å layer were not assigned to "chloritized" vermiculite. The packets were formed by a stacking of the layers having the same spacings (Figures 4–6) and by a random interstratification of the layers having different spacings (Figures 7 and 8). The 7–8-Å layers were noted in a few particles, commonly forming a packet that segregated in a portion close to the basal plane surfaces but not necessarily close to the edge surfaces (Figure 8).

As described in Introduction, the presence of kaolin-group mineral as "interlayer material" in "chloritized" vermiculite was inferred by Wada and Kâkuto (1983a). A partial, lateral transformation of each 14-Å layer to two 7-Å layers, one complete and one incomplete and inverted to each other, was proposed to explain the obtained data. Such 7-Å layers were, however, not detected in the present HRTEM study. No particular indication was found for lateral transformation of a 14-Å layer to a layer or layers having spacings other than 14 Å.

Table 1. The d-values (Å) of the 001 reflection used for identification of layer silicates.

Mineral	Treatment[1]			
	Mg^{2+}—25°C	K—60°C	K—300°C	K—550°C
"Chloritized" vermiculite	14	14	12~10	≥10
Kaolin-group mineral	10~7.2	10~7.2	7.2	not observed
Vermiculite	14	10	10	10
Interstratified vermiculite/ "chloritized" vermiculite	14	14~10	12~10	≥10
Mica	10	10	10	10

[1] See text for details.

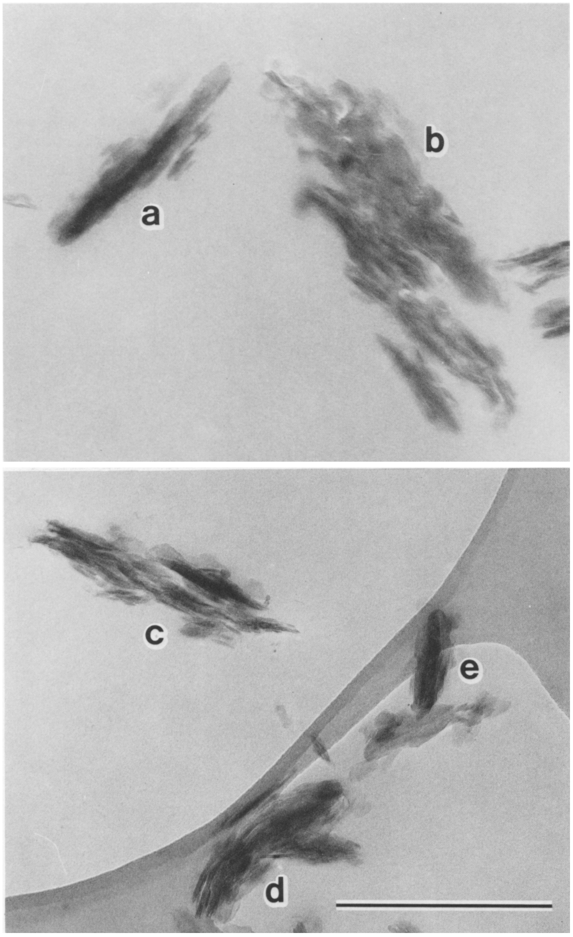

Figure 3. Electron micrographs of thin sections of "chloritized" vermiculite particles of different shapes. Marker = 0.5 μm.

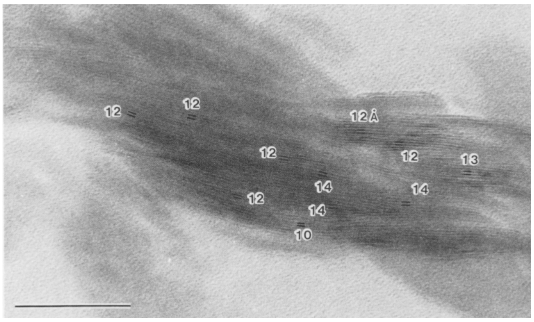

Figure 5. Electron micrograph of thin section of "chloritized" vermiculite showing twisted arrangement of silicate layers. Marker = 500 Å.

A few large plates consisted of a uniform stacking of straight 10-Å or nearly straight 14-Å layers. The plates constructed from the 10-Å layers were identified as vermiculite and those from the 14-Å layers as chlorite, because the plates similar to the latter and constructed from the 14-Å layers alone were found in the sample heated at 300°C. Figure 9 shows a vermiculite plate constructed from straight 10-Å layers in its core, but showing possibly transformation from vermiculite to "chloritized" vermiculite and a kaolin-group mineral at its periphery.

Discrete kaolin particles were noted largely as fine plates (Figure 8), as indicated by the XRD pattern of the <0.2-μm fraction (Figure 1). Large kaolin particles were also noted, but they were fewer than expected from the intensity of the 7-Å XRD reflection of the 0.2–0.5-μm fraction. A common coexistence of a kaolin-group mineral and "chloritized" vermiculite and the existence of 8–7-Å layers in some particles of "chloritized" vermiculite (Figures 8 and 9) suggest a close genetic relation between the two minerals.

XRD analysis showed that K^+-saturation and heating at 300°C resulted in a partial interlayer collapse of "chloritized" vermiculite (Figure 1). HRTEMs of the corresponding thin sections showed that the layer spacings in "chloritized" vermiculite decreased uniformly in each particle to 12.5–11 Å. The interlayer collapse tended to be greater in particles having regular stacking of straight layers (Figure 10a) than in particles having less regular stacking of curved layers (Figure 10b).

As shown in the XRD patterns (Figure 1), the sodium

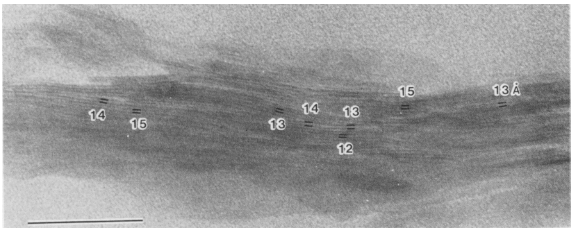

Figure 4. Electron micrograph of thin section of "chloritized" vermiculite showing curved arrangement of silicate layers. Marker = 500 Å.

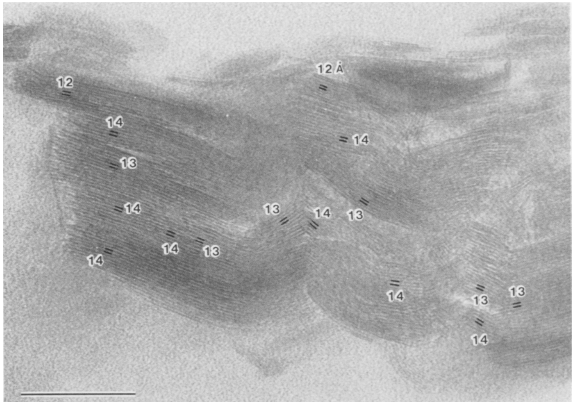

Figure 6. Electron micrograph of thin section of "chloritized" vermiculite showing crumpled arrangement of silicate layers. Marker = 500 Å.

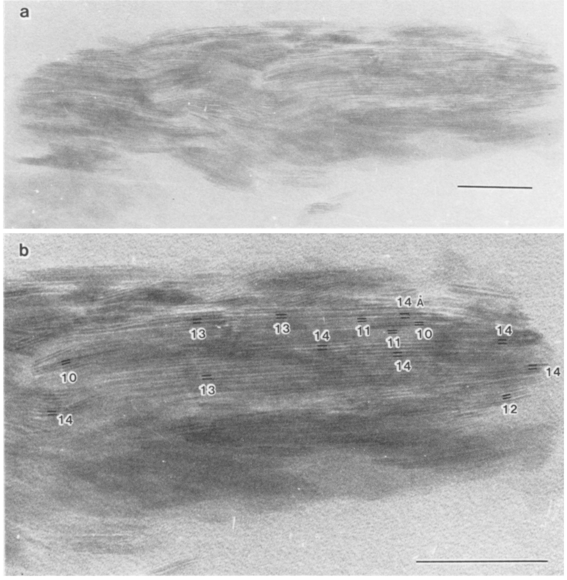

Figure 7. Electron micrograph of spindle-shaped thin section of "chloritized" vermiculite. (a) Whole particle. (b) Stacking of silicate layers in a packet. Marker = 500 Å.

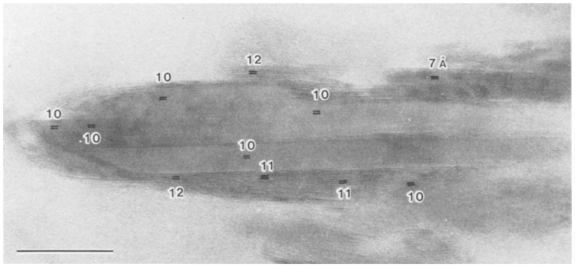

Figure 9. Electron micrograph of thin section of vermiculite showing possible transformation to "chloritized" vermiculite and kaolin-group mineral. Marker = 500 Å.

citrate treatment resulted in the removal of the interlayer material from "chloritized" vermiculite. The low-magnification electron micrographs suggest the thinning of particles as a whole and the dissolution of some finer plates (Figures 2a and 2b). HRTEMs of the thin sections showed that "chloritized" vermiculite from which the "interlayer material" was removed had layer spacings larger and more variable (Figures 11 and 12) than those indicated by XRD analysis (Figure 1). These data suggest that the interlayer collapse on K$^+$-saturation was incomplete in the procedure adopted for embedding in the epoxy resin. The silicate layers, however, became straighter and more extended, and their tendency to form packets and associated non-imaged portions was less noticeable (Figures 11 and 12). On the other hand, the complex interstratification of the layers having different spacings and the portions composed of 8–7-Å layers as well as large kaolin particles remained after the treatment (Figure 12).

The sodium citrate treatment of the 0.2–0.5-μm fraction dissolved interlayer material and possibly material present between the packets from "chloritized" vermiculite and from a few of the fine plates of kaolin-group minerals. The dissolution of the kaolin-group mineral was also indicated by earlier chemical analysis and difference infrared spectroscopy (Wada and Kakuto, 1983a). Si (9.5% SiO_2) and Al (7.8% Al_2O_3) were dissolved by the treatment from the 0.2–2-μm fraction of the same soil. The molar Si/Al ratio of the extracted material was about 1.0. If the dissolution of the kaolin-group mineral and the hydroxy-Al interlayer in "chloritized" vermiculite took place simultaneously, the Si/Al ratio of the extracted material should have been <1.0, unless the amount of Al present as hydroxy-Al interlayer was insignificantly small. The presence of interlayer Al (6.3% Al_2O_3, Barnhisel, 1977; 13.6% Al_2O_3, Frink, 1965), was, however, estimated in clays

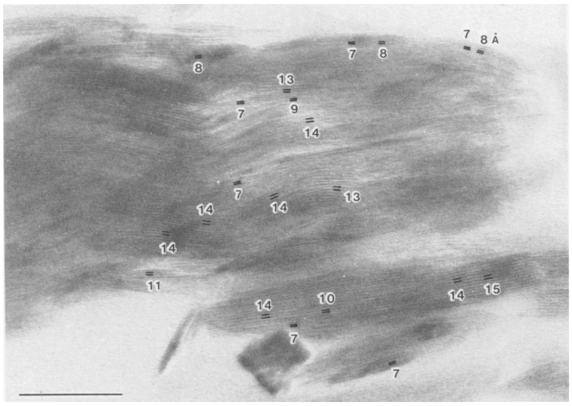

Figure 8. Electron micrographs of thin sections of "chloritized" vermiculite showing segregation of 8–7-Å layers and kaolin-group mineral. Marker = 500 Å.

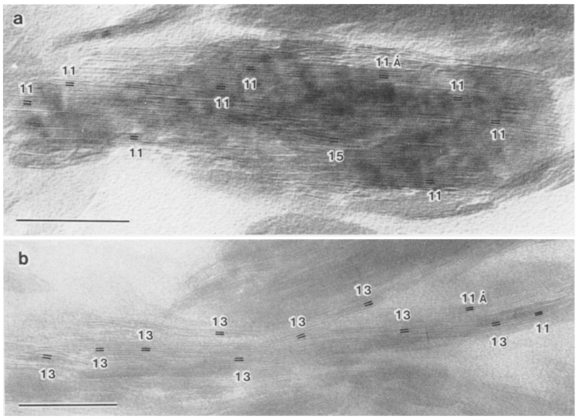

Figure 10. Electron micrographs of thin section of "chloritized" vermiculites heated at 300°C, which differ in regularity of stacking of silicate layers. Marker = 500 Å.

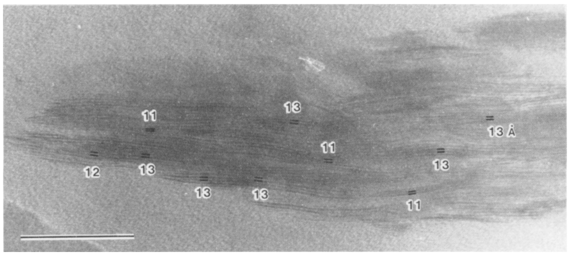

Figure 11. Electron micrographs of thin section of "chloritized" vermiculite treated with ⅓ M sodium citrate. Marker = 500 Å.

in which the cation-exchange capacity of 40 meq/100 g was reduced by blocking due to hydroxy-Al. The interlayer material of studied "chloritized" vermiculite and its chemical composition still remain open to question.

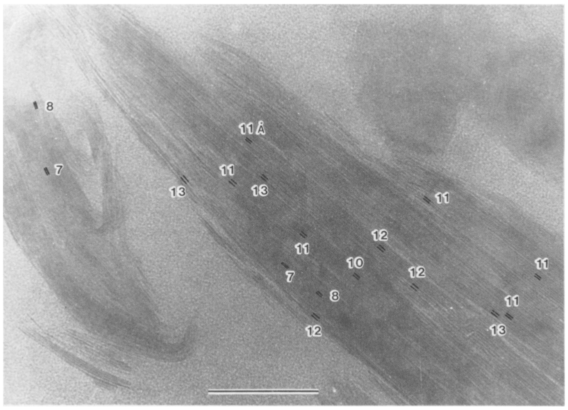

Figure 12. Electron micrographs of thin sections of "chloritized" vermiculite and kaolin-group mineral treated with ⅓ M sodium citrate. Marker = 500 Å.

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