

## INTERGRADIENT VERMICULITE-KAOLIN MINERAL IN A KOREAN ULTISOL

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**Abstract**—A 14-Å mineral coexisting with kaolin minerals, mica, and gibbsite in a Korean Ultisol and showing X-ray powder diffraction features of “chloritized” vermiculite was studied by a combination of methods. The 14-Å mineral collapsed on saturation with K<sup>+</sup> after extraction with hot 1/3 M sodium citrate, but the Si/Al ratio of the extracted material was close to 1.0 and kaolin minerals dissolved, as indicated by difference infrared spectroscopy. The 14-Å mineral was also collapsed by heating at or above 350°C. The difference infrared spectra and the X-ray powder diffraction patterns indicated that two forms of kaolin mineral are present that differ in thermal stability; one decomposed by heating at or below 375°C and the other by heating above 375°C. The former kaolin mineral is probably associated with vermiculite and the latter is present as a discrete form. The 14-Å mineral was inferred to be an intergradient vermiculite-kaolin mineral, in which most vermiculite layers each partially transform into double kaolin layers, and to represent an intermediate phase during the transformation of 2:1 to 1:1 layer silicates in acid soils.

**Key Words**—Chlorite, Difference infrared spectroscopy, Intergradient, Kaolin, Ultisol, Vermiculite.

### INTRODUCTION

Vermiculites and smectites in soils and sediments are commonly partially interlayered or “chloritized” (Rich, 1968; Barnhisel, 1977). As a part of research project on red and yellow soils in temperate and tropical regions, a study was made of active forms of aluminum including interlayer hydroxy-Al in “chloritized” 2:1 layer silicates. In a preliminary experiment one soil containing “chloritized” vermiculite, kaolin minerals, and mica was treated with 1/3 M sodium citrate to extract the interlayer hydroxy-Al from the vermiculite. This treatment was followed by K-saturation and air-drying to collapse the vermiculite. The treatment resulted in a substantial dissolution of Si which paralleled the dissolution of Al. In the present paper, the X-ray powder diffraction, chemical, and infrared spectroscopic analyses for clays separated from the soil before and after dissolution or heat treatment are reported in an attempt to characterize the “interlayer material” in vermiculite. That this “interlayer material” is a kaolin mineral and not hydroxy-Al is discussed, as are the implications of this discovery.

### MATERIALS AND METHODS

#### Soil

The IIB23t(g) horizon (74–130 cm in depth) of a Typic Hapludult (Red-Yellow Podzolic soil), Gwangju series, was collected from a profile located at Samnam, Gyeongdong, Ulju, Gyeongsangnam, Korea. The soil is a friable, red (2.5YR 4/8), heavy clay derived from old alluvium associated with granite and gneiss. The soil is acid (pH (H<sub>2</sub>O) = 5.40; pH (1 M KCl) = 3.80). It is poor in bases (exchangeable Ca = 0.17, Mg = 0.48, K = 0.09, Na = 0.11 meq/100 g soil) and rich in aluminum

(exchangeable Al = 6.81 meq/100 g soil). It contains 65% clay (<2 μm) which consists of “chloritized” vermiculite, kaolin minerals, mica, and gibbsite (Yoshinaga *et al.*, 1981). Clay fractions (<2, <0.2, and 0.2–2 μm) were separated from the soil by repeated dispersion at pH 10 (NaOH), sonic vibration, and sedimentation. The proportion of the <0.2-μm to 0.2–2-μm fractions was 38 to 62. The separated fractions were kept as flocculated suspensions by adding small amounts of NaCl.

#### Dissolution and heat treatments

The clay was treated with dithionite-citrate (Mehra and Jackson, 1960) (4 ml of 0.3 M Na-citrate + 0.5 ml of 1 M NaHCO<sub>3</sub> + 0.1 g of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>/30 mg clay) at 80°C for 15 min and/or with 1/3 M sodium citrate at 100°C for an appropriate period (Tamura, 1958) in a polyethylene flask with a reflux condenser (25 ml of 1/3 M sodium citrate/30 mg clay). The amounts of Fe and/or Al and Si dissolved from the clay were determined by atomic absorption spectroscopy. The clays before and after the treatment with dithionite-citrate were saturated with K<sup>+</sup> and heated at appropriate temperatures between 300° and 550°C in an electric furnace.

#### X-ray powder diffraction analysis and infrared spectroscopy

The clays saturated with Mg<sup>2+</sup> and K<sup>+</sup> were analyzed by X-ray powder diffraction (XRD) and those saturated with K<sup>+</sup> by infrared (IR) spectroscopy after air-drying or heating at different temperatures. IR spectra of material “removed” by the dissolution treatment or the material altered by the heat treatment were obtained by difference IR spectroscopy, wherein the starting clay and the treated product were placed in the sample and reference positions of an IR spectrophotometer.

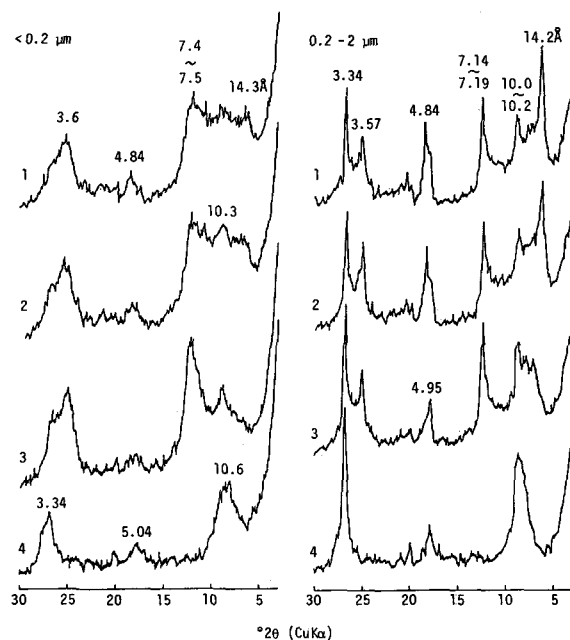


Figure 1. X-ray diffraction patterns of parallel oriented clays separated from a Korean Ultisol IIB23t(g) horizon: 1 = Mg-saturated and air-dried; 2 = K-saturated and air-dried; 3 and 4 = K-saturated and heated at 350° and 550°C, respectively.

#### Differential thermal and thermal gravimetric analyses

Differential thermal (DTA) and thermal gravimetric (TGA) analyses were carried out simultaneously on about 30 mg of clays treated with dithionite-citrate and saturated with  $\text{K}^+$  at a heating rate of 20°C/min in air.

### RESULTS

Figure 1 shows that the 14-Å mineral in the Mg-saturated <math><0.2\text{-}\mu\text{m}</math> and <math>0.2\text{-}2\text{-}\mu\text{m}</math> fractions did not collapse on K-saturation and air-drying. Subsequent heating of K-saturated clays resulted in a gradual shift of the 14-Å reflection toward 10 Å, but the 10-Å reflection showed broadening on its low-angle side even after heating at 550°C. The 14-Å mineral did not expand with Mg-saturation and glycerol solvation.

The collapse of the 14-Å mineral on K-saturation and air-drying was enhanced by the dithionite-citrate treatment (Figure 2A), but the subsequent sodium citrate treatment was much more effective and nearly all interlayer material was removed (Figure 2B). XRD analyses showed that the 14-Å mineral remaining after the sodium citrate treatment did not expand with Mg-saturation and glycerol solvation, indicating that it is vermiculite. Analyses of Si, Al, and Fe dissolved by the successive dithionite-citrate and sodium citrate treatments (Table 1) showed that the materials removed by the respective treatments were different; the main material removed with dithionite-citrate was iron oxide

Table 1. Dissolution of Si, Al, and Fe from <math><0.2\text{-}\mu\text{m}</math> and <math>0.2\text{-}2\text{-}\mu\text{m}</math> fractions by successive treatment with dithionite-citrate and sodium citrate.

Treatment	Constituents dissolved			Si/Al molar ratio of constituents dissolved
	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	
<b>&lt;math&gt;&lt;0.2 \mu\text{m}&lt;/math&gt;</b>				
Dithionite-citrate	—	3.15	12.53	—
Sodium citrate (24 hr)	12.20	10.46	0.04	0.99
<b>&lt;math&gt;0.2\text{-}2 \mu\text{m}&lt;/math&gt;</b>				
Dithionite-citrate	—	2.15	7.56	—
Sodium citrate (24 hr)	9.51	7.79	0.03	1.04
<b>&lt;math&gt;&lt;2 \mu\text{m}&lt;/math&gt;</b>				
Dithionite-citrate	2.12	3.31	10.88	0.54
Sodium citrate (18 hr)	9.48	7.93	0.02	1.02

which possibly incorporated some Al and associated with aluminosilicates, whereas the material removed with sodium citrate was an aluminosilicate with the Si/Al molar ratio of about 1.0, most probably kaolin minerals. On the other hand, the 7-Å reflection was not much affected by the sodium citrate treatment both for the <math><0.2\text{-}\mu\text{m}</math> and <math>0.2\text{-}2\text{-}\mu\text{m}</math> fractions (Figure 2), though a 10-Å reflection probably due to halloysite in the <math>0.2\text{-}\mu\text{m}</math> fraction disappeared.

Dithionite-citrate treated <math><2\text{-}\mu\text{m}</math> fractions were extracted with sodium citrate for various lengths of time and at various ratios of extractant to clay. The dissolution of Si and Al and the associated changes of XRD intensities at 14 Å (on K-saturation and air-drying) and at 10 and 7 Å (on K-saturation and heating at 350°C) are shown in Figure 3. The removal of interlayer material, as indicated by the decrease and increase of the 14- and 10-Å reflection intensities, respectively, was essentially complete when 8% Al (as Al<sub>2</sub>O<sub>3</sub>) was extracted from the clay. Up to this point, equimolar amounts of Si and Al were dissolved. Eight percent alumina corresponds to the dissolution of 20% of a kaolin mineral from the clay, but the 7-Å reflection was not affected. With further extraction, the dissolution of Si and Al continued to increase, though the increase was more marked for Si, and the 7-Å reflection slightly decreased in intensity. The results indicate that the sodium citrate treatment dissolved the kaolin mineral in preference to the vermiculite and mica and that the dissolved kaolin mineral did not contribute to the 7-Å reflection. Probably the latter kaolin mineral is not in a discrete form but is associated with the vermiculite.

The material dissolved by the dithionite-citrate treatment gave a strong and broad IR absorption maximum at 3200–3400 cm<sup>-1</sup> (Figure 4), suggesting iron oxyhydroxides. Substantial amounts of Si and Al were also extracted by the treatment (<math><2\text{-}\mu\text{m}</math> fraction, Table 1),

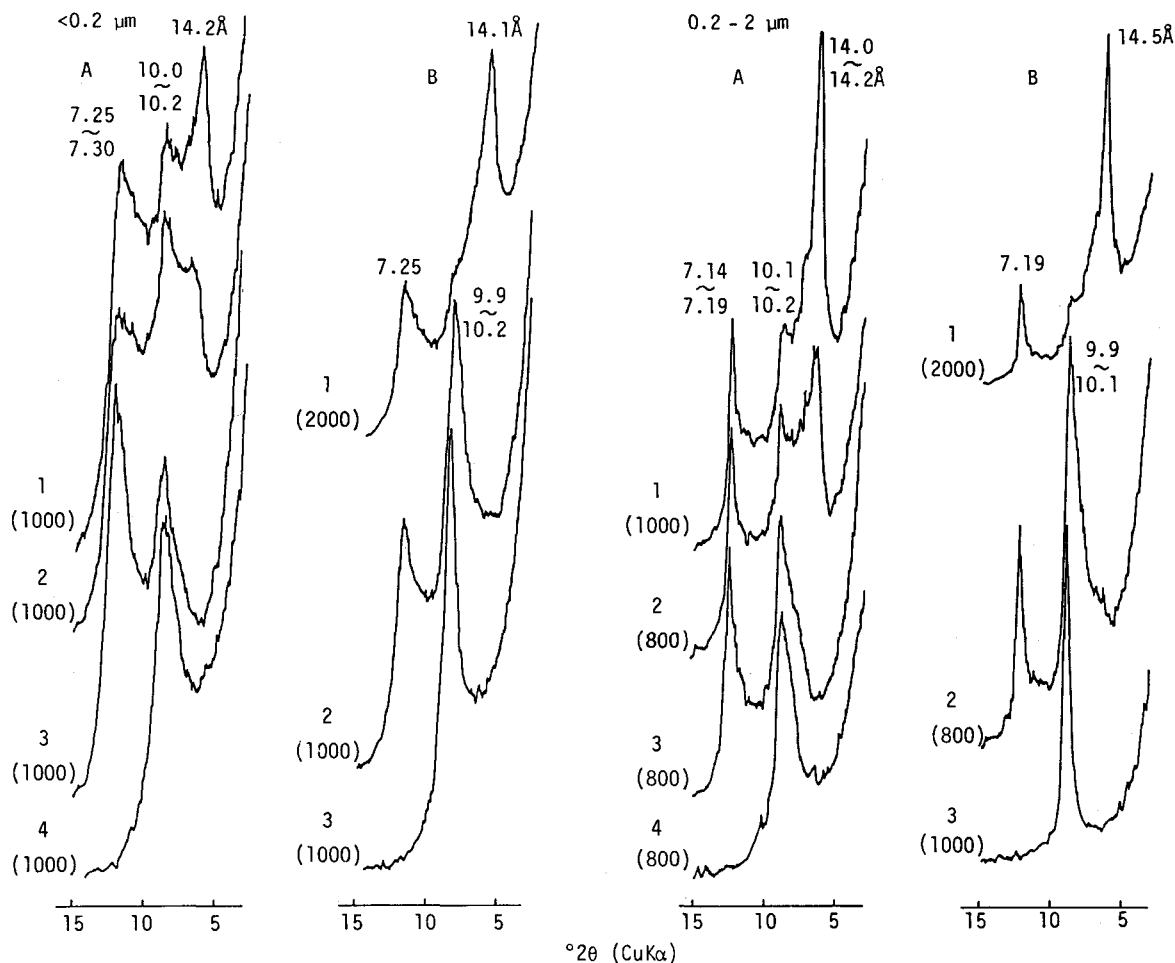


Figure 2. X-ray powder diffraction patterns of parallel oriented clays treated with dithionite-citrate (A) and then with 1/3 M sodium citrate (24 hr) (B): 1 = Mg-saturated and air-dried; 2 = K-saturated and air-dried; 3 and 4 = K-saturated and heated at 375° and 550°C, respectively. The numbers in parentheses show the full scale counting rate in cps.

and the difference IR spectra showed features of a poorly crystallized kaolin mineral whose absorption bands were broad and poorly resolved, particularly at 3600–3700  $\text{cm}^{-1}$ . Such material was possibly partly associated with the iron oxide and partly with the vermiculite as was the material dissolved by the citrate treatment. The difference IR spectra showed no particular absorption at 3690–3700  $\text{cm}^{-1}$ , characteristic of hydroxy-Al produced at interlayers of montmorillonites (Brydon and Kodama, 1966; Ahlrichs, 1968). On the other hand, the dissolution of the kaolin mineral in 1/3 M sodium citrate was indicated by the difference IR spectra (Figure 4). Except for a weak 3695- $\text{cm}^{-1}$  band relative to 3620- $\text{cm}^{-1}$  band, the difference IR spectra are similar to that of kaolinite. The spectra also suggest that the dissolved kaolin mineral and the residual kaolin mineral are similar and that more than half of the kaolin mineral and only a small fraction of the gibbsite were dissolved in 1/3 M sodium citrate. Unlike the XRD analysis, the IR

spectra of the kaolin mineral in the <math><0.2-</math> and <math>0.2-2-\mu\text{m}</math> fractions are similar.

The foregoing results suggest that the kaolin minerals are present in both discrete and associated forms and that the latter is present as “interlayers” of the vermiculite. This suggestion was tested by IR spectroscopy using the clays treated with dithionite-citrate and saturated with  $\text{K}^+$ , and then heated between 300° and 500°C. The difference IR spectra of the clays air-dried and those heated at 375°C showed that about one-third or more of the kaolin mineral and all of the gibbsite appeared to have been decomposed below 375°C (Figure 5). Note that the decomposition of this particular kaolin mineral is associated with the collapse of the vermiculite, but that the decomposition did not reduce the intensity of the 7-Å reflection of the kaolin mineral (Figure 2A). The decomposition of most of the remaining kaolin mineral occurred at 500°C (Figure 5), and resulted in a substantial decrease of the intensity of the

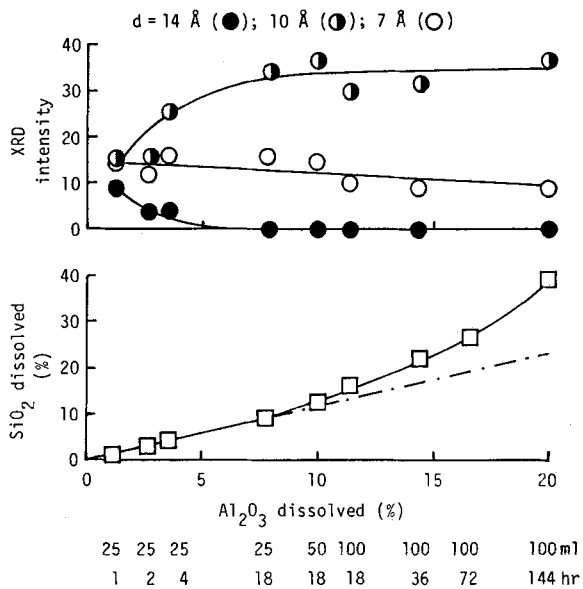


Figure 3. Dissolution of Si and Al from clays (<2 μm) and associated changes of their X-ray powder diffraction intensity at 14, 10, and 7 Å by treatment with 1/3 M sodium citrate. The line (---) indicates the relation between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (%) dissolved from the material with the Si/Al ratio of 1.0. The numbers at the bottom indicate the volume of 1/3 M sodium citrate per 30 mg of clay and the time for treatment.

7-Å reflection. The difference IR spectra of kaolin minerals decomposed at 375°C and 500°C are also different in the region 1100–1200 cm<sup>-1</sup>; only the latter kaolin mineral yielded a negative absorption. The results indicate that two different forms of kaolin minerals are present in both the <0.2- and 0.2–2-μm fractions. One exists in association with the vermiculite and decomposes at lower temperatures, and the other exists as a discrete form and decomposes at higher temperatures.

The XRD patterns of dithionite-citrate treated and randomly oriented clays (Figure 6) show that vermiculite is dioctahedral (d(06,33) = 1.50 Å) and that the vermiculite and kaolin mineral have similar a<sub>0</sub> and b<sub>0</sub> values. Most (hkl) reflections showed features similar to those reported for b-axis disordered kaolinites (Brindley, 1961) and “illites” (Bradley and Grim, 1961), and the stacking of the unit silicate layers was more disordered in the minerals of the <0.2-μm fraction.

Electron micrographs show that thin micrometer-size plates having angular, sometimes hexagonal, outlines predominate in both the <0.2- and 0.2–2-μm fractions (Figure 7). The plates seem to have grown within larger and more rounded particles, possibly of mica-derived vermiculite. Although the presence of halloysite(10Å) is indicated in the <0.2-μm fraction by XRD (Figure 2), only very few curled flakes and no tubes were found.

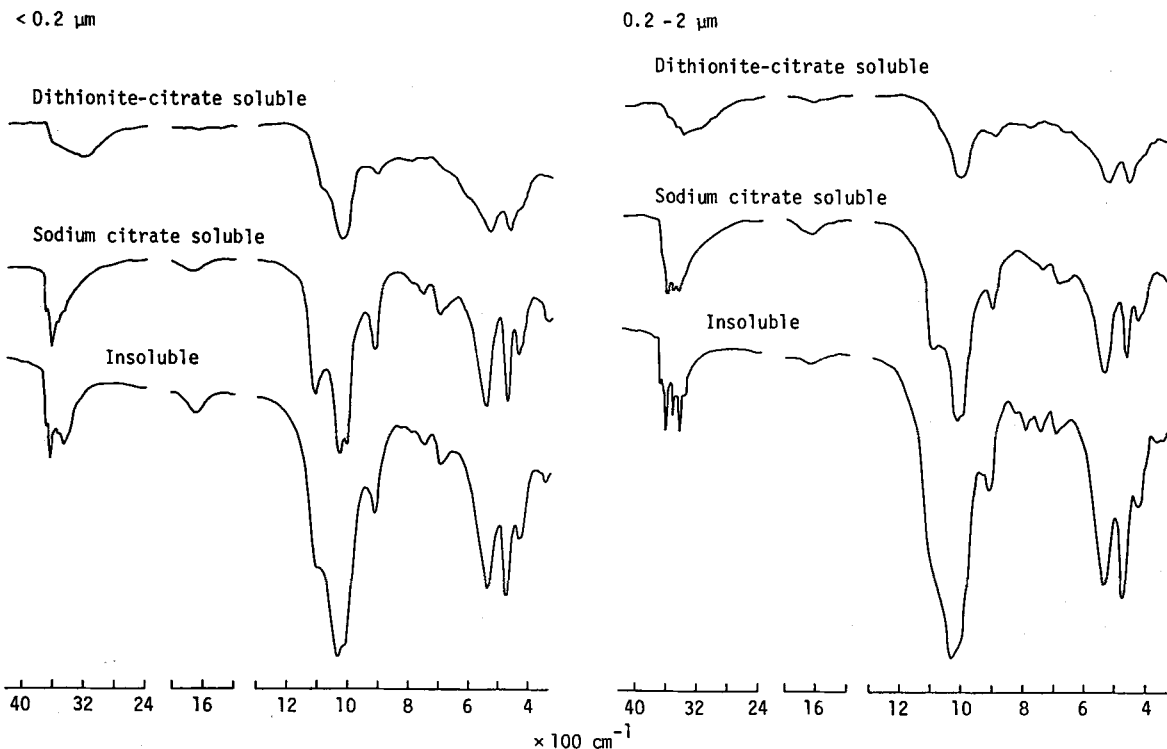


Figure 4. Difference infrared spectra of dithionite-citrate and sodium citrate soluble fractions of clays and infrared spectra of residues remaining after sodium citrate treatment (24 hr).

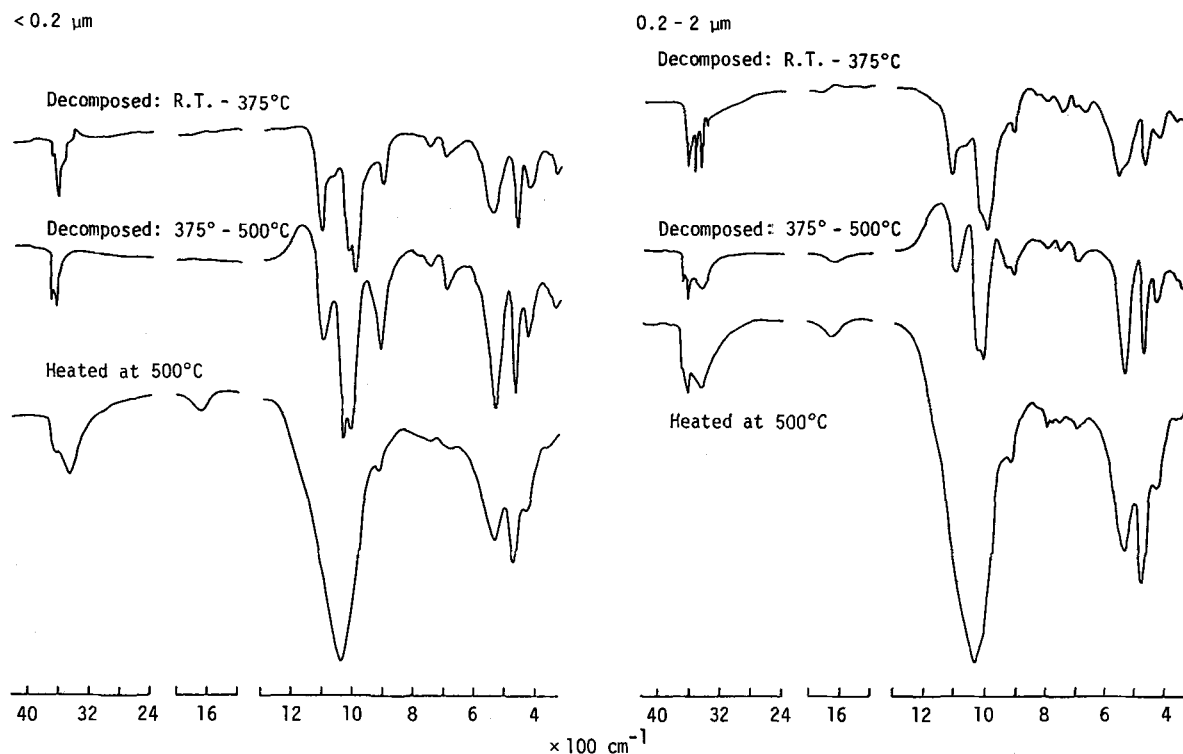


Figure 5. Difference infrared spectra of portions of clay altered by heating between room temperature and 375°C and between 375° and 500°C and infrared spectra of clays heated at 500°C.

DTA curves show two endotherms with maximum at about 300°C and 530°C for the clays treated with dithionite-citrate (Figure 8). The 300°C endotherm is due to decomposition of gibbsite, whereas the 530°C endotherm is due to dehydroxylation of kaolin mineral and vermiculite. The two different forms of kaolin minerals that were indicated by difference IR spectroscopy were

not differentiated by DTA. TGA, however, shows considerable weight losses on heating between 150° and 450°C, in addition to that between 250° and 350°C due to the decomposition of gibbsite (Figure 8). The thermal decomposition of the kaolin mineral associated with the vermiculite did occur, but it did not produce a noticeable thermal effect on the DTA curves. The absence of, or a very weak, high-temperature exotherm may be

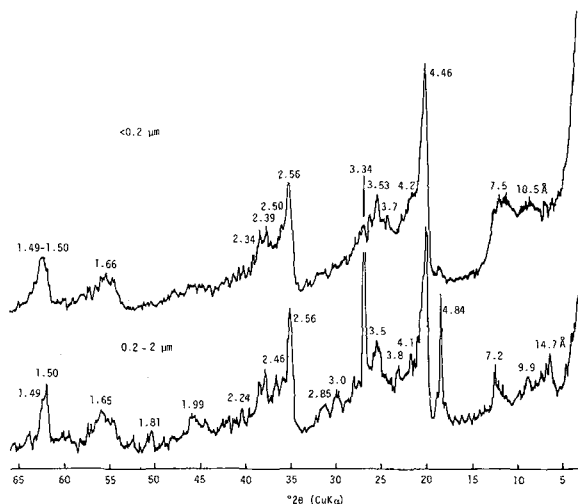


Figure 6. X-ray diffraction patterns of randomly oriented clays treated with dithionite-citrate saturated with  $\text{K}^+$  and air-dried.

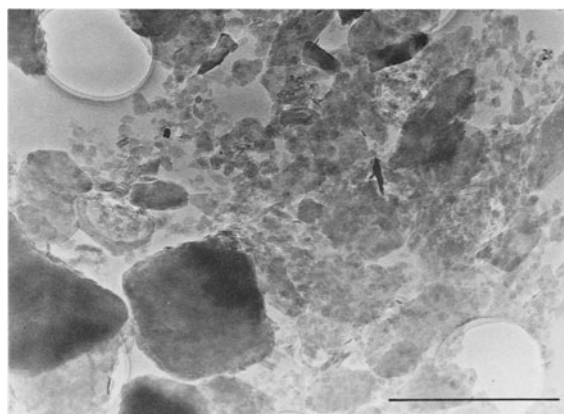


Figure 7. Electron micrograph of the 0.2–2- $\mu\text{m}$  fraction treated with dithionite-citrate and saturated with  $\text{K}^+$ . Marker = 1  $\mu\text{m}$ .

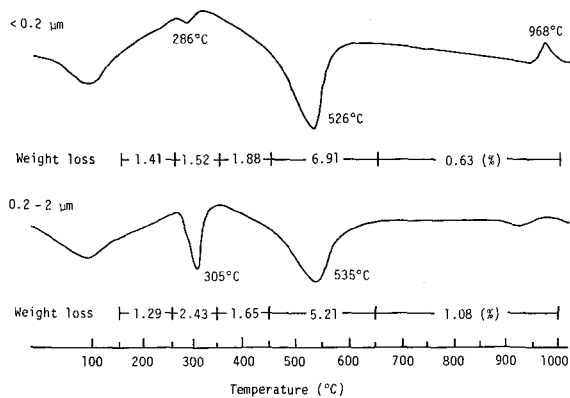


Figure 8. DTA curves of clays treated with dithionite-citrate and saturated with  $\text{K}^+$ . The weight loss (%) is based on the weight of clays heated at  $150^\circ\text{C}$ .

characteristic of the kaolin mineral associated with the vermiculite or it may be related to the use of K-saturated clays.

## DISCUSSION

“Chloritized” vermiculite is commonly identified by XRD. It does not collapse readily when K-saturated, but its sharp  $14\text{-}\text{\AA}$  reflection becomes diffuse and shifts toward  $10\text{ \AA}$  on the heating to  $300^\circ\text{C}$  or  $550^\circ\text{C}$ . When Al is removed by a treatment with reagents such as sodium citrate, it collapses on K-saturation but does not expand with glycerol solvation (Rich, 1968; Barnhisel, 1977). According to these criteria, the  $14\text{-}\text{\AA}$  mineral in question is identified as a “chloritized” vermiculite. The following two observations, however, oppose this identification: (1) The sodium citrate treatment which resulted in the collapse of the  $14\text{-}\text{\AA}$  mineral also resulted in dissolution of not only Al but of Si at the molar Si/Al ratio of about 1.0; (2) the dissolution of kaolin mineral but not any other components, such as gibbsite, quartz, mica, and noncrystalline silica, alumina, and aluminosilicates, are indicated by XRD and difference IR spectroscopy. All observations indicate that the  $14\text{-}\text{\AA}$  mineral is a vermiculite associated with kaolin mineral.

To our knowledge, no such association of vermiculite with kaolin mineral has been reported. It is different from interstratified 2:1/1:1 layer silicates such as montmorillonite/kaolinite reported by Schultz *et al.* (1971) and others. The interstratified kaolinite/Ca-montmorillonite gave a broad reflection at  $7.3\text{--}7.7\text{ \AA}$ , but no well-defined reflection in the  $10\text{--}14\text{-}\text{\AA}$  range for air-dried clay (Cradwick and Wilson, 1972). The mineral in question gave a more or less well-defined  $14\text{-}\text{\AA}$  reflection when saturated with  $\text{Mg}^{2+}$  and air-dried, and this  $14\text{-}\text{\AA}$  reflection became weak and diffuse and shifted toward  $10\text{ \AA}$  when the clay was saturated with  $\text{K}^+$  and air-dried or heated (Figure 2). These XRD features can not be ac-

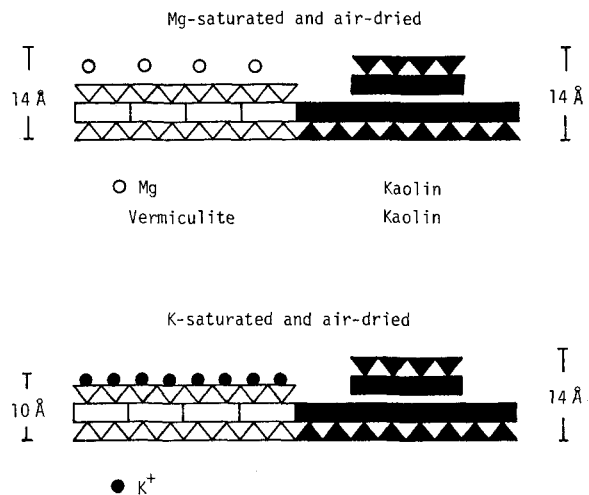
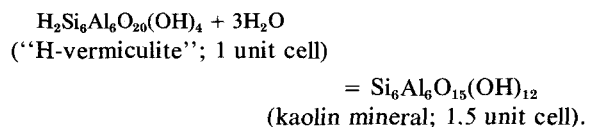


Figure 9. Schematic drawing of a part of unit layer of an intergradient vermiculite-kaolin mineral saturated with  $\text{Mg}^{2+}$  or  $\text{K}^+$ .

counted for by ordinary interstratifications of vermiculite and kaolin layers, either regular or random, but could have resulted from a partial transformation of each vermiculite layer into double kaolin layers (Figure 9), provided it occurs in most layers of each vermiculite particle. The extent of this transformation in the resulting intergradient mineral varies from one layer to another and does not affect the (001) reflection of the  $\text{Mg}^{2+}$ -saturated clay, but affects the (001) reflection of the  $\text{K}^+$ -saturated and air-dried or heated clays (Figures 1 and 2). In the proposed model, every other kaolin layer in the double layer is inverted, because the (001) and (002) reflections from the  $14\text{-}\text{\AA}$  mineral are strong and very weak or absent, respectively (Figure 2). The thickness of the dehydroxylated double kaolin layers is unknown, but the increase of the  $10\text{-}\text{\AA}$  reflection intensity on their dehydroxylation (Figures 1 and 2) suggests that it is nearly equal to or slightly larger than  $10\text{ \AA}$ .

The double kaolin layer as a unit is very thin. The above transformation would proceed from the edge of the vermiculite particle and produce an ample space around one of the double kaolin layers according to the stoichiometry of the reaction; e.g.



These may account for the preferential dissolution of the double kaolin layers in  $1/3\text{ M}$  sodium citrate and their thermal decomposition at lower temperatures.

The extent of transformation from the vermiculite to kaolin mineral in the unit layer of the proposed model was calculated for the  $0.2\text{--}2\text{-}\mu\text{m}$  fraction. Dissolution

analysis showed that kaolin mineral in an amount corresponding to 20% of the clay was dissolved by the sodium citrate treatment; difference IR spectroscopy gave a total kaolin content in the clay of about twice that dissolved. Thus, the vermiculite content is about 50% of the clay by subtracting 10% allocated for gibbsite and mica from the remaining 60%, and the weight ratio of vermiculite to kaolin mineral is 50:20. If the unit-cell compositions of dioctahedral vermiculite and kaolin mineral are approximated by  $\text{Si}_6\text{Al}_6\text{O}_{20}(\text{OH})_4$  and  $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$ , respectively, an average proportion of vermiculite to kaolin mineral unit cell in each layer is 1.8 to 1.

The transformation of vermiculite to kaolin mineral instead of interlayering of hydroxy-Al in vermiculite has bearings on the chemical reactivities of acid soils. It will result in fewer negative and positive charges and smaller surface acidity and specific adsorption of cations and anions.

The formation of the intergradient vermiculite-kaolin mineral has important implications in the transformation of 2:1 to 1:1 minerals during weathering. Such transformations, particularly smectite to kaolinite, have been proposed to explain the inverse concentration relations in weathering profiles through a hydroxy-Al interlayering and a mixed layering between smectite and kaolinite, as reviewed by Altschuler *et al.* (1963) and Rich (1968). Poncelet and Brindley (1967) and Oberlin and Couty (1970) showed that kaolinite could be formed from montmorillonite interstratified with polymer hydroxy-Al ions at or above 170°C. Kittrick (1970) found that kaolinite formed in aqueous suspensions of some montmorillonites acidified with HCl and held for 3–4 yr at room temperature. The natural occurrence of mixed-layer kaolinite/montmorillonite minerals was described by Sudo and Hayashi (1956) and subsequently by other investigators, as reviewed by Sawhney (1977). Lee *et al.* (1975) also observed micaceous occlusions in well-ordered and b-axis-disordered kaolinites by ultramicrotomy and high resolution electron microscopy.

These observations suggest that the hydroxy-Al interlayering in the expandable 2:1 layer silicates and/or the mixed layering between 2:1 and 1:1 layer silicates are the mechanisms by which the 2:1 layer structure converts to the 1:1 layer structure. The present observations suggest, however, that there is a different mechanism operating in soil environments under leaching conditions. It is the direct conversion of a dioctahedral vermiculite layer with exchangeable Al ions to double kaolin layers. To resolve this problem, however, the proposed model must be confirmed by techniques such as ultramicrotomy and high-resolution electron microscopy. Further studies on "chloritized" 2:1 layer silicates in soils and sediments are also necessary to answer the question whether such intergradient vermiculite-kaolin mineral is common or not.

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**Резюме**—При помощи разных методов исследовался 14 Å минерал сосуществующий с минералами каолина, слюды и гиббсита в Корейской кислотной почве и показывающий черты рентгеновской порошковой дифракции как “хлоритизированный” вермикулит. Этот минерал разрушался при насыщении  $K^+$  после экстракции горячим раствором 1/3 М цитрата натрия, но отношение Si/Al для экстрагированного материала было около 1,0 и каолиновые минералы растворялись, что было показано при помощи дифференциальной инфракрасной спектроскопии. Этот 14 Å минерал также разрушался при нагреве до или выше 350°C. Дифференциальные инфракрасные спектры и образцы рентгеновской порошковой дифракции указывали на то, что присутствуют две формы каолиновых минералов, которые различаются термальной стабильностью; одна раскладывается при нагреве до или ниже 375°C, а вторая при нагреве выше 375°C. Первый каолиновый минерал связан вероятно с вермикулитом, а второй присутствует как дискретная форма. 14 Å каолиновый минерал приписывался межградиентному вермикулито-каолиновому минералу, в котором большинство вермикулитовых слоев было частично переведено в двойные каолиновые слои, и представлял промежуточную фазу во время трансформации 2:1 в 1:1 слоистые силикаты в кислотных почвах. [E.G.]

**Resümee**—Ein 14 Å-Mineral, das mit Kaolinmineralen, Glimmer, und Gibbsite in einem koreanischen Ultisol auftritt und im Röntgenpulverdiffraktogramm Kennzeichen eines “chloritisierten” Vermiculites aufweist, wurde mittels einer Kombination von Methoden untersucht. Das 14 Å-Mineral kontrahierte nach einer Extrahierung mit heißer 1/3 molarer Natriumcitratlösung bei einer Sättigung mit  $K^+$ . Das Si/Al-Verhältnis des extrahierten Materials war jedoch nahezu 1,0 und entsprach in etwa gelösten Kaolinmineralen, wie eine Untersuchung mittels Differenzinfrarotspektroskopie zeigte. Das 14 Å-Mineral kontrahierte nach dem Erhitzen auf 350°C oder darüber. Die Differenzinfrarotspektren und die Röntgenpulverdiffraktogramme deuteten darauf hin, daß zwei Arten von Kaolinmineralen vorhanden sind, die sich in ihrer thermischen Stabilität unterscheiden; die eine Art zerfällt beim Erhitzen auf maximal 375°C und die andere beim Erhitzen auf über 375°C. Das erste Kaolinmineral ist wahrscheinlich an Vermiculit gebunden, während das zweite als diskrete Phase vorliegt. Es wird angenommen, daß das 14 Å-Mineral ein Vermiculit-Kaolin-Wechsellagerungsmineral ist, bei dem die meisten Vermiculitlagen teilweise in doppelte Kaolinlagen umgewandelt sind, und somit eine Übergangsphase während der Umwandlung von 2:1 in 1:1 Schichtsilikate in sauren Böden darstellt. [U.W.]

**Résumé**—Un minéral de 14 Å coexistant avec des minéraux kaolins, du mica, et de la gibbsite dans un Ultisol coréen et montrant des traits de diffraction poudrée des rayons-X d’une vermiculite “chloritisée” a été étudiée par une combinaison de méthodes. Le minéral de 14 Å s’est effondré lors de la saturation avec  $K^+$  après extraction par de la citrate de sodium chaude 1/3 M, mais la proportion Si/Al du matériel extrait était proche de 1,0 et les minéraux kaolins dissous, comme l’indique la spectroscopie infrarouge de différence. L’échauffement à ou au dessus de 350°C a aussi causé l’effondrement du minéral de 14 Å. Les spectres infrarouges de différence et les clichés de diffraction poudrée des rayons-X ont indiqué que deux formes du minéral kaolin étaient présents qui diffèrent au point de vue de la stabilité thermique; l’un se décomposait suite à l’échauffement à ou sous 375°C, et l’autre suite à l’échauffement au delà de 375°C. Le premier minéral kaolin est probablement associé à la vermiculite, et le second est présent en tant que forme discrète. On a inféré que le minéral de 14 Å était un minéral vermiculite-kaolin intergradient, dans lequel la plupart des couches vermiculite se transforment chacune partiellement en couches doubles de kaolin, et qu’il représente une phase intermédiaire de 2:1 à 1:1 de silicates à couches dans des sols acides. [D.J.]