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OCCLUDED MICA IN HYDROXY-INTERLAYERED VERMICULITE GRAINS FROM A HIGHLY-WEATHERED SOIL

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Abstract—Hydroxy-interlayered vermiculite (HIV) is a ubiquitous phyllosilicate in the <0.05-mm fraction of sandy soils on the U.S. southeastern coastal plain. Extensive areas of soils with abundant HIV (i.e., peninsular Florida) have no detectable mica; yet the coarseness, platy habit, and nonexchangeable K associated with HIV grains suggest a mica precursor. The objectives of this study were: (1) to probe for mica zones (1.0-nm) within HIV grains, using high-resolution transmission electron microscopy (HRTEM), and (2) to determine intragrain elemental distributions via electron microprobe analysis (EMA). HIV grains from a Quartzipsamment medium-silt fraction, which contained no detectable mica by X-ray diffraction (XRD), were concentrated via high-density liquid separation. EMA transects and X-ray dot maps showed zonation or trends of K depletion near edges of some grains, with K_2O contents ranging from trace levels to >40 g kg^{-1}. Elemental oxide data indicated a dioctahedral phyllosilicate structure, with some octahedral substitution of Fe and Mg for Al. Intermittent 1.0-nm lattice-fringe images obtained by HRTEM supported the presence of mica zones within grains. There were no detectable 1.4-nm fringes, despite the dominance of a 1.4-nm XRD peak, indicating the instability of the HIV specimen under the electron beam. Results support a transformational link between mica and HIV in these soils. Rapid incursion and polymerization of Al following loss of K from mica may limit the extent of the vermiculite intermediate. The latter idea is consistent with the paucity of vermiculite in Florida soils. Traces of occluded mica may be the last remnants of the precursor grain. A sand-sized mica precursor would likely have weathered in place during the period when colloidal components such as kaolinite illuviated to deeper zones. Thus, the transformation product (HIV) would comprise a significant proportion of the <0.05-mm fraction persisting in sandy eluvial horizons.

Key Words—Electron microprobe, High-resolution transmission electron microscopy, Mica transformation, Vermiculite.

INTRODUCTION

Hydroxy-interlayered vermiculite (HIV) is a common mineral in weathering soil environments (Barnhisel and Bertsch, 1989), including soils of the southeastern U.S. (Carlisle *et al.,* 1978, 1981, 1985, 1988; Fiskell and Perkins, 1970). It tends to be particularly abundant in near-surface horizons, rivaling kaolinite as the primary clay component (Bryant and Dixon, 1963; Carlisle and Zelazny, 1973; Harris *et al.,* 1989; Rich, 1968a; Rich and Obenshain, 1955). Its properties are important to consider given its prevalence in the root zone, its reactivity relative to other mineral components present, and its potential for selective cation sorption (Rich and Black, 1964; Rich, 1968b).

The abundance of HIV relative to other secondary phyllosilicates tends to increase with increasing particle size within both the clay-size (Wada and Kakuto, 1989; Weed and Bowen, 1990) and silt-size fractions (Harris *et al.,* 1988; Comerford *et al.,* 1990). In Florida, HIV is often the prevalent phyllosilicate in sandy soil horizons of Quartzipsamments, Paleudults, and Haplaquods (Carlisle and Zelazny, 1973, 1974; Harris and Carlisle, 1987; Harris *et al.,* 1987; Soil Survey Staff, 1975).

Recent studies of HIV from coastal plain soils have indicated that it has the composition of a dioctahedral phyllosilicate (Harris *et al.,* 1988; Weed and Bowen, 1990). Several properties of coastal-plain HIV suggest that it is a mica derivative. These include its prevalence in coarse-clay and silt fractions, its mica-like platy morphology, and its association with nonexchangeable K_2O determined for silt-sized grains by electron microprobe (Harris *et al.,* 1988) and for bulk clay-sized HIV fractions concentrated using high-gradient magnetic separation (Weed and Bowen, 1990). A relationship between mica, vermiculite, and HIV has been documented for soils forming in micaceous parent material (Rich and Obenshain, 1955), but the linkage between the three phases is more tenuous for highly-weathered coastal plain soils (i.e., in peninsular Florida) in which mica and vermiculite are consistently undetectable by X-ray diffraction (XRD) (Carlisle *et al.,* 1978, 1981, 1985, 1988).

The extensive occurrence of HIV in near-surface environments of soils across major physiographic regions such as the coastal plain and piedmont of the southeastern U.S. warrants a more thorough understanding of its origin and properties. The objectives of this study

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were: (1) to probe for mica zones (1.0-nm) within HIV grains, using high-resolution transmission electron microscopy (HRTEM); and (2) to determine intragrain elemental distributions via electron microprobe analysis (EMA). The presence of occluded mica within an HIV matrix would establish a transformational link between the two phases. It would also have implication for extant concepts of mica transformation (*vide infra*), for mechanisms of nonexchangeable K released under the influence of acidifying and complexing root exudates (Comerford *et al.,* 1990), and for lower-than-expected crop response to K fertilization that has been reported for coastal-plain soils (Hutton *et al.,* 1956; Hutton and Robertson, 1961; Yuan *et al.,* 1976).

MATERIALS AND METHODS

The silt fraction analyzed in this study was from the C horizon of an Astatula pedon (Typic Quartzipsamment; Soil Survey Staff, 1975) located in the Ocala National Forest, Florida. The sample had previously been determined to contain appreciable HIV and some nonexchangeable K in clay and silt fractions (Comerford *et al.,* 1990), but no XRD-detectable mica. Chemical and physical properties of the sample were reported by Comerford *et al.,* 1990.

The sample was air-dried and pretreated with Na citrate-dithionite-bicarbonate extraction solution (Mehra and Jackson, 1960) to remove oxide coatings. Sand (2.0–0.05 mm), silt (0.05–0.002 mm), and clay (<0.002 mm) separates were obtained by sieving and centrifugation after adjusting pH to 10 with Na_2CO_3. Silt was further separated by centrifugation and sedimentation into fine (0.002–0.005 mm), medium (0.005–0.020 mm), and coarse (0.020–0.050 mm) fractions. The medium silt was further partitioned into subfractions of density ranges <1.3 g cm^{-3}, 1.3–1.5 g cm^{-3}, and >1.5 g cm^{-3}. Density separates were collected by dispersing the silt in a liquid (Na Polytungstate) adjusted to a selected density, centrifuging the suspension, freezing the heavy fraction by immersing the bottom of the tube in liquid N_2, decanting the light fraction, and collecting each fraction on Millipore filters. Heavy and light fractions were washed repeatedly with distilled water while still on the filter. They were then air-dried, transferred to containers, and examined using petrographic and dissecting microscopes prior to further analyses.

Oriented mounts of medium and fine silt were prepared for XRD analysis by depositing approximately 250 mg from suspension onto ceramic tiles under suction. Also, oriented mounts of density separates were prepared by resuspending them in distilled water, depositing on glass slides, and air-drying. Samples were scanned on a computer-controlled XRD system at 2°2θ per min using CuKα radiation following 2-hr exposure to temperature of 25°, 100°, 200°, 300°, and 550°C.

Electron-optical analyses (EMA and HRTEM) were conducted on the medium-silt density fraction (1.3–1.5 g cm^{-3}) found by XRD to contain the highest proportion of the 1.4-mm (HIV) component (Figure 1). For EMA, a dilute suspension of this fraction was prepared from the same powder used for XRD analysis, deposited on carbon mounts, and dried in a desiccator. Mounts were carbon-coated and examined using an electron microprobe equipped with both an energy-dispersive and wavelength-dispersive X-ray system. Microprobe linescans along the (001) cleavage face were conducted for a total of nine grains, eight of which were selected essentially at random. Random selection was accomplished by stage translation until a grain crossed a central point on the viewing screen and then confirming the presence of Al by wavelength dispersion to screen out quartz. The only deviation from randomness was the exclusion of grains deemed too small for analysis and grains overlying or shadowed by other grains. Analyses were conducted while operating at 15 kV and 20 μA with a focused beam size of 1 μm. X-ray images were obtained for K and Al, with the former requiring longer exposure times due to lower concentrations.

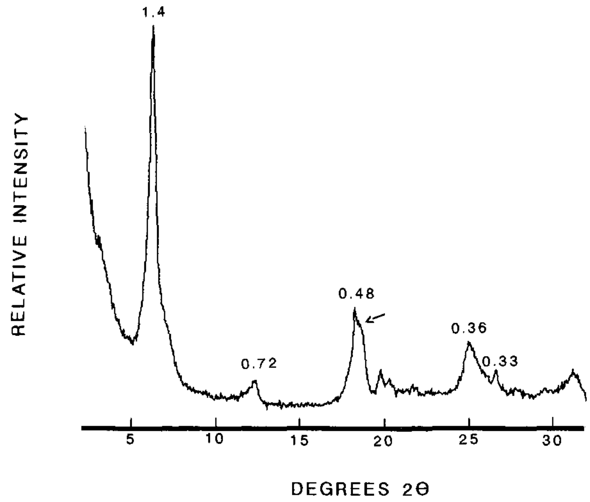

Figure 1. XRD pattern of HIV-dominated medium silt from the Quartzipsamment sample studied, following concentration via density separation (2.3–2.5 g cm^{-3}). Minerals indicated include HIV (1.4-, 0.72-, 0.48-, and 0.36-nm peaks), gibbsite (0.48-nm peak), and quartz (0.33-nm peak). The arrow points to a shoulder inflection attributable to the HIV d_{003} contribution to the 0.48-nm peak.

Mounts for HRTEM were prepared by depositing the 1.3–1.5 g cm^{-3} medium silt fraction in a mold, drying, adding epoxy, and heating at 60°C to cure the epoxy. The molded epoxy-silt blocks were then cut into thin sections (approximately 150 nm in thickness) by ultramicrotome. These sections were mounted on carbon-coated Cu grids and analyzed using a high-resolution transmission electron microscope operating at 400 kV. The instrument was equipped with a light element energy-dispersive X-ray detector.

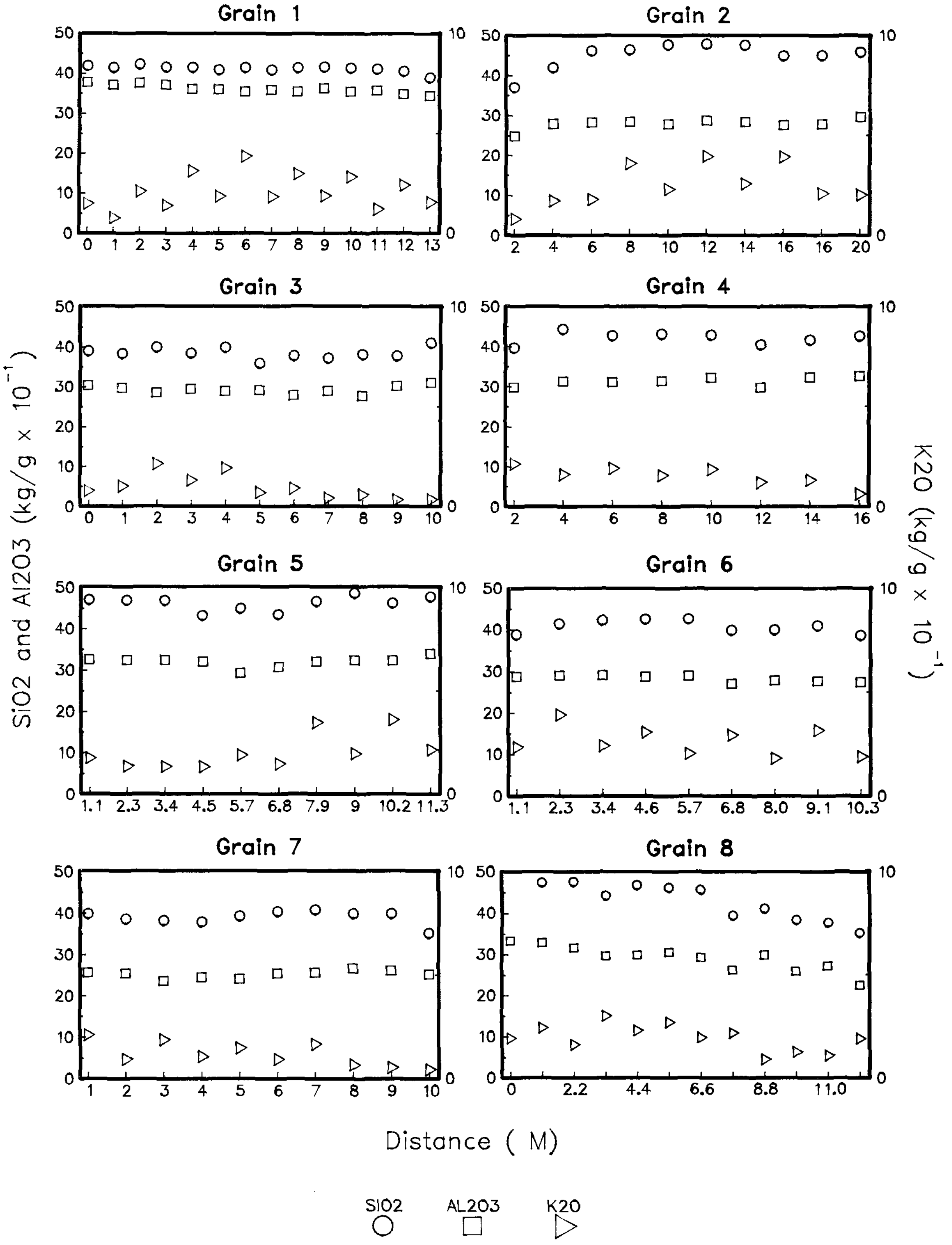

Figure 2. Distribution of SiO_2, Al_2O_3, and K_2O along linescans for eight randomly-selected grains.

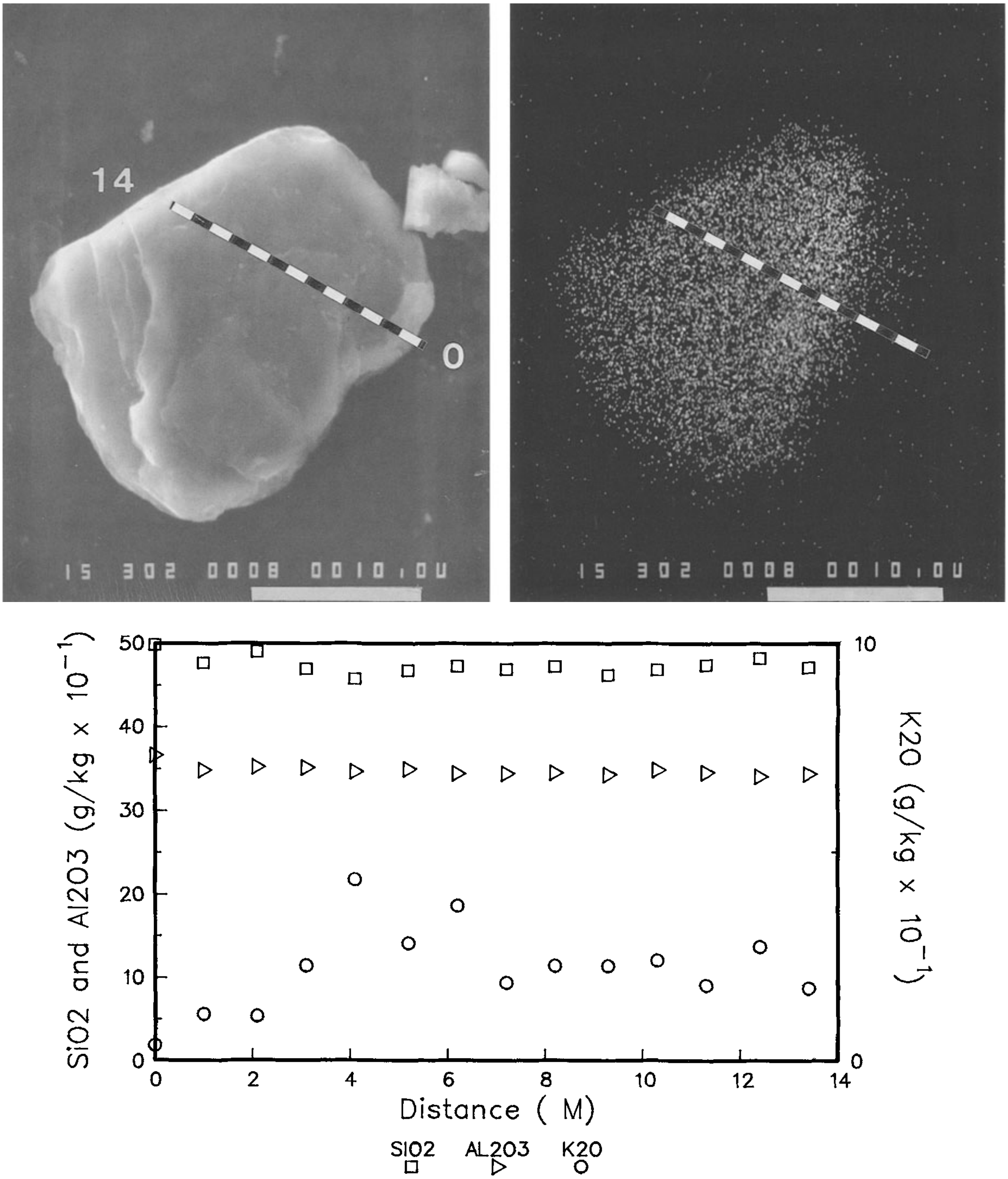

Figure 3. Micrographs and plot illustrating the distribution of SiO_2, Al_2O_3, and K_2O for grain 9, selected as an example of a grain with an abrupt zonation of K_2O content. Linescan path is indicated by black and white dashed line across the secondary electron image (upper right) and K X-ray dot image (upper left) of the grain (scale bar = 10 μm). Linescan data are depicted by plot.

Table 1. Mean oxide percentages and molar ratios for the grains studied, as determined by microprobe.

Grain	n	SiO_2	Al_2O_3	MgO	TiO_2	CaO*	K_2O	FeO	H_2O + Other	Si/Al	Si/(Al + Fe + Mg)
		g kg^{-1}									
1	14	412	361	6	6	1	21	23	171	1.00	0.90
2	12	450	280	25	2	1	24	65	154	1.40	0.97
3	11	385	292	17	4	1	10	24	267	1.15	0.97
4	9	423	313	19	2	1	15	38	190	1.17	0.95
5	11	463	321	19	2	1	20	24	150	1.11	0.92
6	10	408	283	24	1	1	26	21	236	1.26	1.04
7	11	391	253	22	2	1	12	52	267	1.34	0.96
8	12	433	290	22	3	t	19	29	204	1.30	1.06
9	14	471	344	19	4	t	18	36	109	1.19	0.98
Grand mean		428	308	19	3	1	19	34	189	1.22	0.99

* t = trace.

RESULTS AND DISCUSSION

The highest concentrations of HIV were collected within the 1.3–1.5 g cm^{-3} fraction, as indicated by XRD (Figure 1). The only diluents identified in this fraction were minor amounts of gibbsite (0.48 nm) and quartz (0.33 nm). The lighter fraction contained opal plant phytoliths and charcoal (as indicated by light microscopy), and some cristobalite (as indicated by XRD). The heavier fraction was dominated by quartz.

Microprobe linescans across eight randomly-selected, medium silt-sized HIV grains indicate that K_2O contents exceed 10 g kg^{-1} at some location in all grains, and in some grains are >30 g kg^{-1} (Figures 2 and 3). Three of these grains (3, 5, and 8; Figure 2) exhibit locally-elevated levels of K content, with peak contents generally occurring away from the edges. The K contents for grains 1 and 2 gradually increase toward the center of the (001) surface. Other grains show no discernible trend. An additional grain (grain 9; Figure 3) was selected for linescan analysis because of a distinct boundary between high and low K that was evident from X-ray dot maps. The K_2O content of grain 9 drops from a maximum content of 44 g kg^{-1} to 11 g kg^{-1} over a distance of 1 μm. Thus, the K distribution can be very heterogeneous both within and among grains, and there are some indications of K depletion at the grain edges. Unfortunately, the microprobe beam size (1 μm) is too large for precise edge characterization.

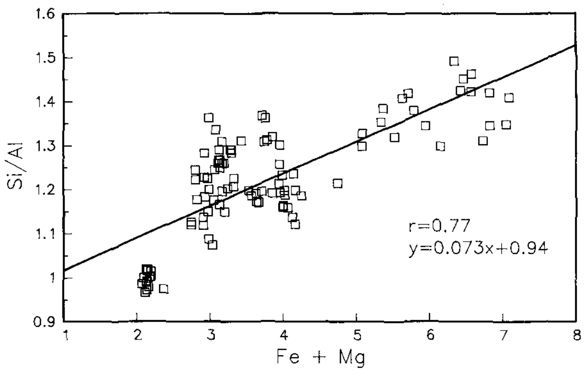

Figure 4. Plot showing relationship between the Si/Al ratio and Fe + Mg content.

The oxide data for the grains studied (Table 1) verify a dioctahedral phyllosilicate composition. These data are similar to those reported for clay-sized HIV concentrated from coastal plain Ultisols (Weed and Bowen, 1990) using high-gradient magnetic separation, as determined by bulk analysis. The latter study indicated higher Fe (47 vs 34 g kg^{-1}) and lower (though appreciable) K_2O (11 vs 19 g kg^{-1}). Real compositional differences would be expected given differences in location (North Carolina vs Florida), particle size (clay vs medium silt), and soil (Ultisol vs Quartzipsamment).

The SiO_2 and Al_2O_3 contents of most grains are relatively stable, but the differences between these components vary among grains (Figures 2, 3; Table 1). The mean Si/Al molar ratios for most linescans are greater than 1.0 (Table 1), with a mean for all grains of 1.22. However, the ratio of Si/(Al + Fe + Mg) is very close to 1 (mean = 0.99). Furthermore, the Si/Al ratio exhibits a trend of linear increase with increasing Fe and Mg content (Figure 4); the "noise" in this plot may arise from variation in the indeterminable amount of interlayer polynuclear Al. These data indicate some substitution of Fe and Mg for Al in the octahedral sheet. The presence of appreciable Fe and Mg in HIV suggests that the precursor could have been an impure muscovite (i.e., phengite-like) with some charge originating from the octahedral sheet, as proposed by Weed and Bowen (1990).

Small zones of 1.0-nm lattice fringes within particles from the concentrated HIV medium silt were documented via HRTEM (Figure 5), despite the fact that a 1.0-nm peak was not detectible by XRD of this material in bulk (Figure 1). These zones were difficult to find, due in part to their intermittent occurrence and in part to analytical constraints. The latter included non-optimal orientation of many particles, excessive thickness, and electron beam destruction. The 1.0-nm fringes, in conjunction with the presence of K within the zones analyzed by HRTEM as indicated by energy-

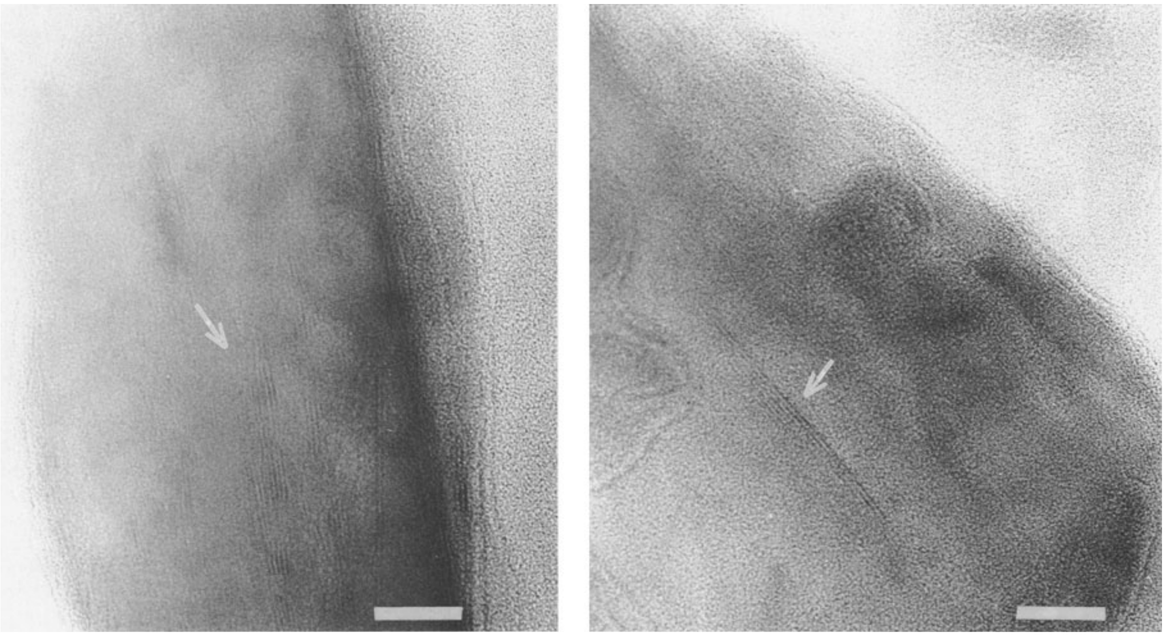

Figure 5. HRTEM images from medium-silt-sized HIV grains, showing zones of 1.0-nm lattice fringes (scale bar = 20 nm).

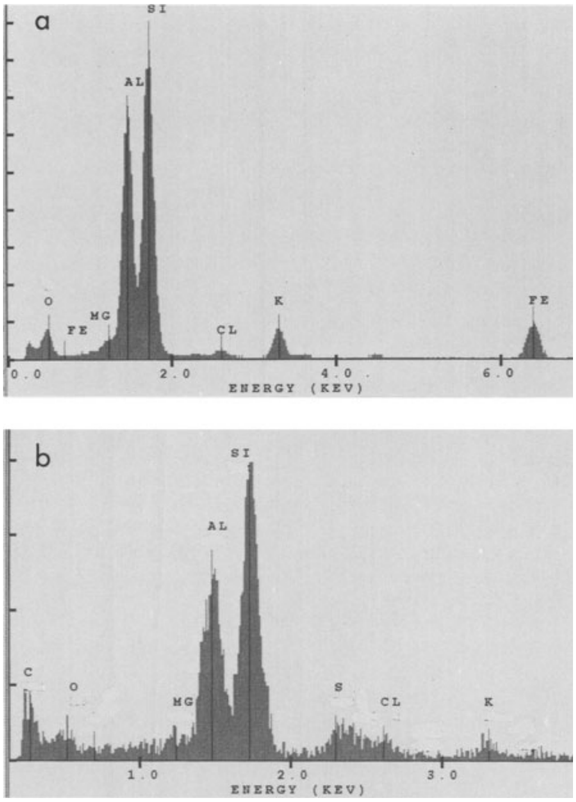

Figure 6. Energy-dispersive X-ray spectra of zones within microtomed sections from which HRTEM images were obtained. (a) Spectrum for a zone with particularly high K count. (b) Spectrum for locale of mount where 1.0-nm fringes were recorded (Figure 5).

dispersive X-ray spectra (Figure 6), verify the presence of occluded mica within grains dominated by HIV.

Where fringes were observed and photographed, they always proved to be 1.0 nm and never 1.4 nm in spacing. The complete absence of 1.4-nm fringes is surprising given the dominance of this phase at 25°C as indicated by XRD. Apparently, the HIV specimen used in this study is very unstable under the electron beam. The specimen markedly loses periodicity at moderately-elevated temperatures, as indicated by irreversible broadening and attenuation of the d_{001} peak (Figure 7). This behavior is typical of HIV in Florida soils (Harris and Hollien, 1988). The d_{001} of this and other Florida HIV specimens does not decrease and re-resolve into a discrete peak between 1.1 and 1.0 nm with increasing temperature, as it does for specimens from other locations (Rich and Obenshain, 1955; Wada and Kakuto, 1989). Rather, it broadens and becomes less resolved, generally centering around 1.2 nm (Figure 7). The absence of 1.4-nm fringes may in part be attributable to the sensitivity of the specimen to heat generated by interactions with the electron beam.

The presence of K (this study; Harris *et al.*, 1988; Weed and Bowen, 1990) in conjunction with occluded mica within HIV grains is strong evidence that the HIV in U.S. southern coastal plain soils is a mica derivative. Close (intragrain) association between HIV and mica has implications for models of mica transformation (Jackson, 1963; Barnhisel and Bertsch, 1989). In effect, application of the simple model:

$$\text{Mica} \rightarrow \text{Vermiculite} \rightarrow \text{HIV}$$

to the natural occurrence of these phases would benefit

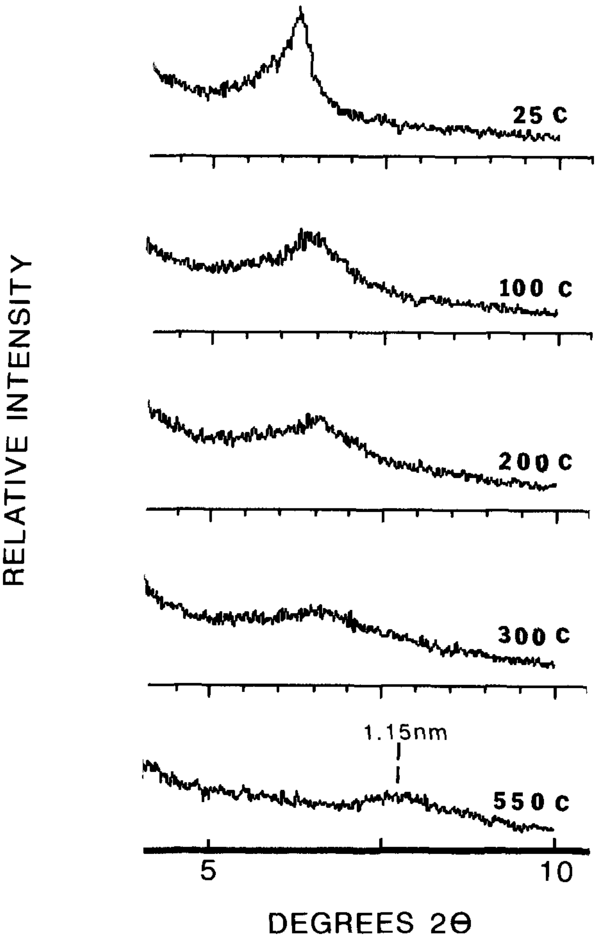

Figure 7. XRD patterns for fine silt from the sample studied, showing slight shift and marked broadening and attenuation in HIV d$_{001}$ with temperature. Samples were heated for 2 hr at each temperature.

from two important qualifications. The first is that mineral boundaries do not necessarily correspond to particle boundaries; in effect, any or all of these phases may occur within the same grain. The second is that the spatial and temporal separation of mica and HIV is dictated by the stability of vermiculite. If the latter mineral is an ephemeral intermediate, then it is more likely that the precursor (mica) and weathering end-product (HIV) would occur in the same grain. For Florida soils, the latter appears to be the case. Vermiculite and interstratified mica/vermiculite are rarely detected, and HIV is ubiquitous (Carlisle *et al.*, 1978, 1981, 1985, 1988). Traces of occluded mica may be the last remnants of the parent (precursor) grain. These remnants could have been protected from further alteration by their surroundings (interlayers bound by hydroxy-Al polynuclear species). Rapid incursion and fixation of Al in these acid soils following loss of K from mica may limit the extent (i.e., duration) of vermiculite.

A mica precursor is consistent with the prevalence of HIV in sandy horizons (Cabrera *et al.*, 1989; Harris *et al.*, 1989). Mica, as a relatively coarse-grained phyllosilicate in sediments, would likely have weathered in place during the period when colloidal components such as kaolinite eluviated to deeper zones. The mica transformation product (HIV) would therefore comprise a significant proportion of the small amount of clay and fine silt persisting in these horizons (largely as grain coatings).

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