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# DEHYDRATION OF HYDROXY-INTERLAYERED VERMICULITE AS A FUNCTION OF TIME AND TEMPERATURE

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**Abstract**—Nonexchangeable polymers in interlayers of expansible phyllosilicates influence thermal dehydration in ways not completely understood. Thermal dehydration of hydroxy-interlayered vermiculite (HIV) from Florida soils, for example, results in irreversible $d_{001}$ shifts. This study was conducted to characterize HIV dehydration as a function of time (t) and temperature (T), and to determine how reversibility of dehydration is affected by elevated T. Clay-sized HIV from 3 soils was heated incrementally and d-spacing shifts ($\Delta d$) were monitored by X-ray diffraction (XRD) at low relative humidity (RH). Samples were then mounted on a metal heating strip in the XRD focal plane and scanned repeatedly at constant T levels to monitor $\Delta d$ with t. Finally, $\Delta d$ in response to RH shifts from <5% to >85% was determined at 25°C and at elevated temperatures. Incremental heating revealed a $\Delta d$ plateau roughly corresponding to the z dimension of hexameric octahedrally coordinated Al. The initial slope of $\Delta d$-*vs*-t curves increased with T. The same maximum $\Delta d$ reached at 200°C was reached at 160°C, but more slowly. All samples exhibited reversible and irreversible dehydration, the former being attributable to sites in equilibrium with external vapor and the latter to sites requiring heat for desorption. Reversible sites were not perturbed by moderate heating, but were apparently eliminated by polymer dehydroxylation. The dehydration behavior of HIV could be explained by steric resistance of water vapor diffusion within a tortuous interlayer polymeric network. Alternatively, new polymer/oxygen-surface bonds exceeding the hydration energy of interlayer components could form via heat-induced re-articulation of polymer/oxygen-surface bonds at smaller basal spacings.

**Key Words**—Dehydroxylation, Hydration, X-ray diffraction.

## INTRODUCTION

Nonexchangeable hydroxy-metal polymers (dominantly Al) in interlayers of soil vermiculite and smectite retard collapse of the basal spacing toward 1.0 nm with heat (MacEwan, 1950; Brown, 1953; Rich and Obenshain, 1955; Barnhisel and Bertsch, 1989). The resultant minerals are commonly referred to as hydroxy-interlayered vermiculite (HIV) or smectite (HIS). Removal of interlayer polymers facilitates collapse and increases CEC (Frink, 1965). Mechanisms and conditions of polymer formation within interlayers of vermiculite (Rich, 1960; Hsu and Bates, 1964) and montmorillonite (Shen and Rich, 1962; Brydon and Kodama, 1966) have been studied via artificial synthesis of polymers within interlayers. Many soils of humid regions (i.e., the southeastern U.S.) contain abundant HIV in clay fractions (Fiskell and Perkins, 1970; Carlisle *et al.*, 1978, 1981, 1985, 1988), particularly in near-surface horizons (Rich and Obenshain, 1955; Bryant and Dixon, 1963; Rich, 1968; Carlisle and Zelazny, 1973; Harris *et al.*, 1989).

Variation in dehydration of HIV from different geographic locations, as monitored by $d_{001}$ shift, is evident from data reported in the literature. For example, the $d_{001}$ of HIV from a Virginia soil shifted with increasing temperature (T) to form a well-resolved peak at a basal spacing slightly greater than 1.0 nm at 550°C (Rich and Obenshain, 1955). In contrast, HIV from silt and clay fractions of Florida soils markedly loses periodicity with increasing T, as evidenced by loss of $d_{001}$ peak resolution (Harris and Hollien, 1988). The $d_{001}$ of Florida HIV is broad and diffuse at 550°C, and generally centers between 1.1 and 1.2 nm. Variations in dehydroxylation T is also indicated from thermal analysis data, with values ranging from 370° to 500°C (Rich and Obenshain, 1955; Dixon and Jackson, 1959; Glenn and Nash, 1964; Harris and Hollien, 1988).

The thermal dehydration of Florida HIV is largely irreversible even at moderately-elevated T (Harris and Hollien, 1988). This irreversibility is an additional distinction between these HIV specimens and standard vermiculites. Vermiculite interlayers will re-hydrate rapidly upon cooling and exposure to water vapor if they are saturated with cations of high hydration energy, and the mineral will return to a basal spacing of approximately 1.4 nm (Walker, 1975). Therefore, vermiculite hydration status is essentially dictated by the hydration energies of interlayer surfaces and cations. Failure of HIV to return to its original basal spacing at sub-dehydroxylation temperatures indicates that polymers significantly influence interlayer access of water, and that hydration energies of interlayer compo-

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nents are a less significant factor for HIV than for vermiculite.

Hydration behavior of macroscopic vermiculite has been studied extensively (Walker, 1975), but little is known of the nature of HIV hydration despite its extensive occurrence in soils. Partial low-temperature irreversibility (Harris and Hollien, 1988) has not been explained, but has implications for the influence of the polymeric network on the interlayer environment. This study was conducted to more thoroughly characterize the dehydration/hydration behavior of HIV as it occurs in the southeastern U.S. Coastal Plain and to interpret the implication of results for prospective mechanisms. The specific objectives were to (1) monitor the d-spacing shift ($\Delta$d) as a function of time (t) and T, and (2) determine how heat-induced dehydration affects the subsequent extent of reversibility at 25°C.

## MATERIALS AND METHODS

### *Soils*

Samples analyzed in this study (samples numbers 1394, 3258, and 3461) were taken from the C horizon of 3 Typic Quartzipsamments (Soil Survey Staff, 1975). These soils had previously been collected and characterized for chemical, physical, and mineralogical properties (Carlisle *et al.,* 1978, 1981, 1985). The sample numbers uniquely designate them within the Florida Cooperative Soil Survey database. Soil sites were located in the central-peninsula, panhandle, and northern-peninsula of Florida (samples 1394, 3258, and 3461, respectively). Subsamples for this study were available from storage. The samples were known to contain appreciable HIV based on the database and subsequent mineralogical analyses (Harris *et al.,* 1987a).

### *Sample preparation*

Stored samples had previously been air-dried, ground, and sieved to remove coarse fragments (>2 mm). Subsamples for mineralogical analyses were pretreated with a Na citrate-dithionite-bicarbonate extraction solution (Mehra and Jackson, 1960) to remove oxide coatings. Sand (2.0–0.05 mm), silt (50–2 $\mu$m), and clay (<2 $\mu$m) were separated by sieving and centrifugation following adjustment to pH 10 with $Na_2CO_3$.

### *Experiment 1: incremental heating*

This experiment was conducted to characterize how the $d_{001}$ changes across a broad T range up to and exceeding dehydroxylation. Oriented mounts of the clay fraction were prepared for X-ray diffraction (XRD) analysis by depositing from suspension onto a ceramic tile under suction, saturating with Mg, and washing free of salts. Mounts were dried for at least 16 hr in an evacuated desiccator containing anhydrous $CaSO_4$. Mineralogical analysis and monitoring of $d_{001}$ shifts were conducted on a computer-controlled XRD system equipped with graphite crystal monochromator and a stepping motor with 0.0025° 2$\Theta$ precision. Samples were scanned at 2° 2$\Theta$ per min using CuK$\alpha$ radiation following 4-hr exposures to temperatures of 25°, 100°, 150°, 200°, 300°, and 500°C in an oven. While being scanned, samples were enclosed in a $N_2$-purged environment with relative humidity (RH) maintained below 5%. Another scan was conducted for the 200°C samples following a subsequent 2 hr exposure to >85% RH attained by placing an open container of water within the enclosure. The enclosure, which surrounded the diffractometer stage, permitted beam passage to and from the sample via a mylar window. A hygrometer probe was positioned within the closure in order to monitor RH. A $\Delta$d value was calculated as the difference between the d-spacing at ≈25°C and the incrementally-elevated T.

### *Experiment 2: effect of t at constant T*

This experiment evaluated the $d_{001}$ shift over time at different levels of T. It required repeated scans at prescribed intervals while the sample was maintained at constant T. A second computer-controlled XRD system was used which was equipped with a metal heating strip positioned in the focal plane of the diffraction circle. Samples were mounted directly on the heating strip from suspension, using calibrated pipets to apply 145 mg of dry clay in an area of approximately 2 cm². The T of the heating strip was rheostat-controlled, and was observed to be stable to within ∓1°C. Target temperatures could be attained within a few seconds.

Samples were heated to an initial T of 40°C for 30 min to promote drying of suspension, and scanned from 5.5 to 7.5° 2$\Theta$ at a rate of 0.4° 2$\Theta$ per min under an $He_2$ purge. Then they were heated to a pre-determined T and repeatedly scanned (5 times) from 5.5 to 7.5° 2$\Theta$ for the first 30 min of heating. Each scan took 6 min, counting the time necessary for the automatic repositioning of the detector between scans. Additional scans were run after 120 and 360 min of isothermal heating. Sample 1394 was scanned at 80°, 120°, 160°, and 200°C, though 80-C $\Delta$d values were small with respect to measurement errors and results are not reported. Samples 3258 and 3461 were scanned at 120° and 160°C only.

### *Experiment 3: documentation of partial reversibility*

The purpose of this experiment was to evaluate the extent to which the $d_{001}$ returned to its original spacing following exposure to elevated T and extremes in RH. The same XRD system used in Experiment 1 was used for Experiment 3. Mounts of Mg-saturated samples were placed in a desiccator overnight. They were then mounted within the XRD enclosure, purged with $N_2$, and scanned at ≈25°C and <5% RH. A second scan was conducted following 2 hr exposure to >85% RH within the enclosure. Samples were then heated for 2

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hr at 110°C, placed immediately in the $N_2$-purged XRD enclosure, and scanned again. A final scan was conducted following exposure of the previously heated sample to >85% RH for 2 hr.

*Data analysis*

Determination of peak position for Experiments 1 and 3 were made using a computer-screen plot of the digitized XRD scan. A cursor was placed over the peak position for an expanded-scale plot, as selected by a laboratory technician, and the exact 2-$\theta$ step corresponding to the cursor position was indicated by the software. Peak determinations for Experiment 2 (involving a different diffractometer) were made manually from expanded-scale plots of the XRD scan using drafting tools to locate the position on the 2-$\theta$ scale. Test replications, made for separate mounts of the same sample at 25°C and <5 and >85% RH (Experiment 3), indicated minimal within-sample variation (0.003 nm maximum). However, peak broadening with increasing T tends to reduce precision in peak determination. For this reason, the study was confined to the 25°–200°C range except where d-spacing shifts were obvious despite the broadening effect.

Results of Experiment 3 were statistically evaluated using a non-parametric test (Kruskal-Wallis; *SAS Institute,* 1985). Experimental error and sample variation were combined, such that the 3 samples were replications in testing d-spacing differences (1) as a function of T (at constant RH) and (2) as a function of RH (for given T treatments).

## RESULTS AND DISCUSSION

*Experiment 1*

The $d_{001}$ peak response to incremental heating for the samples studied was typical for Florida HIV specimens (Figure 1) (Harris *et al.,* 1987b; Harris and Hollien, 1988). In effect, the peaks shifted slightly with increasing T, but broadened considerably. The $\Delta d$ was initially linear with increasing T, but reached a plateau corresponding to the depletion of nonstructural water beginning at approximately 150°C and extending through 300°C (Figure 2). Another major shift occurred between 300° and 500°C, which is attributable to dehydroxylation. Derivative thermogravimetry indicated that HIV dehydroxylation for samples 1394 and 3258 occurred within a range of 400° to 420°C; dehydroxylation of HIV and kaolinite could not be resolved for sample 3461 since the derivative plots revealed no distinct peaks within the temperature range.

The d-spacings corresponding to the $\Delta d$ plateau at sub-dehydroxylation T were 1.378, 1.395, and 1.391 nm for the samples studied. A modal dehydrated interlayer thickness can be estimated as the difference between these plateau $d_{001}$ spacings and an ideal dioctahedral 2:1 phyllosilicate layer dimension of 0.92

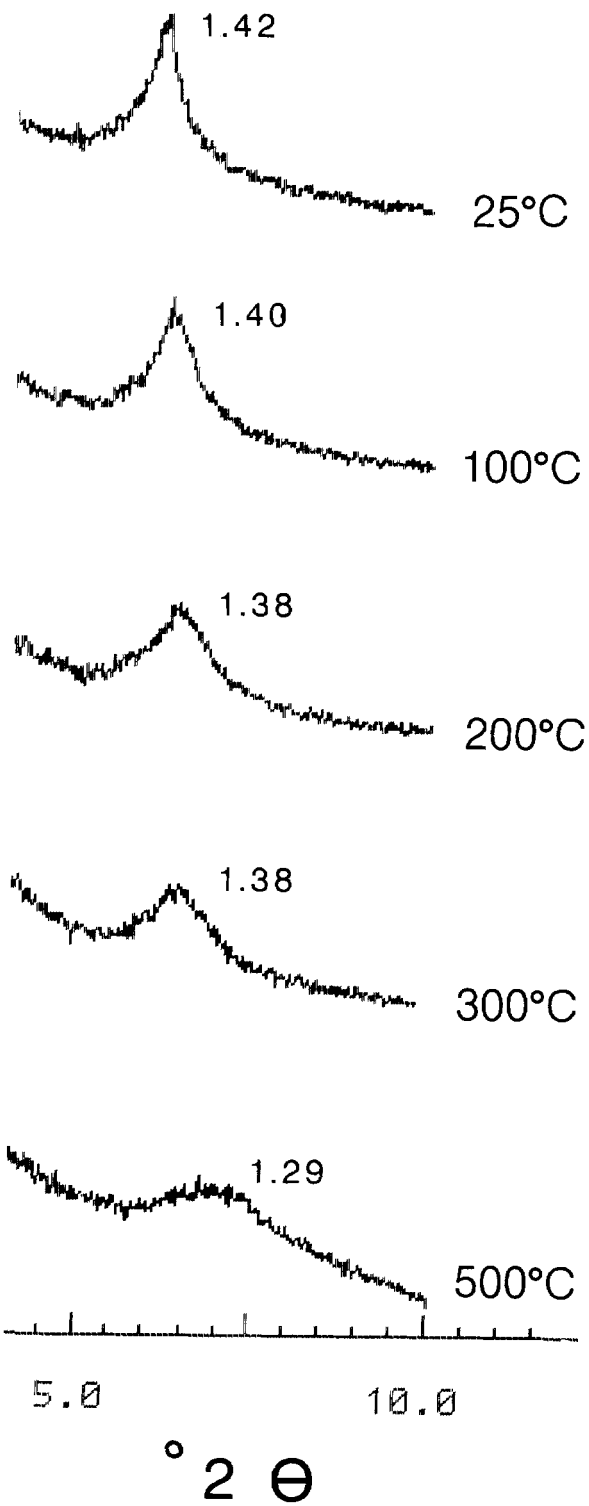



Figure 1. XRD patterns for sample 1394, showing HIV $d_{001}$ peak response to incremental 4-hr heating. Peak position is indicated in nm. All samples exhibited a similar response to incremental heating.

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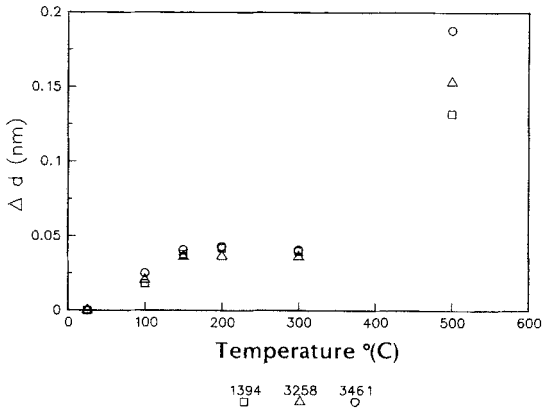



Figure 2. Effect of incremental 4-hr heating on HIV basal d-spacing shift (Δd) from a reference at 25°C and <5% relative humidity for samples studied.

nm. This thickness, in turn, should closely approximate the dimension of the polymeric "pillars." Using this approach, the mean z-axis dimension for the interlayer polymers in these specimens is 0.466 nm. The latter dimension, only slightly less than the $d_{002}$ of gibbsite (0.485 nm), is consistent with hexameric ring structure of octahedrally coordinated Al for the polymers (Weismiller *et al.*, 1967; Barnhisel and Bertsch, 1989).

*Experiment 2*

The d-spacing shift (Δd) with time at 120° and 160°C approximated a power function [$\Delta d = a(t)^b$] for all three samples (Figure 3). The fitted curves indicated a slight slope beyond 360 min, but in fact no change in Δd was evident with longer intervals. There was a greater rate and extent of dehydration at higher T, at least within the 120° to 160°C range. These data are consistent with a higher diffusion rate for water exiting the interlayer at the higher T. They also verify that there are domains of sorbed water which require a higher energy threshold than heating to 120°C to be driven out.

No relationship between Δd and time could be obtained at 200°C, because the maximum shift occurred within the span of one XRD scan (Figure 4). However, the maximum Δd for 200°C was no greater than that for 160°C. The repetitive-scanning experiment was conducted at 200°C for sample 1394 only, but the trend is consistent with a comparable levelling-off for all samples after oven-heating to 150° and 200°C in Experiment 1 (Figure 2). Thus, trends of Experiments 1 and 2 indicate a discreet threshold of energy sufficient to drive out non-structural water. The slower rate of change in Δd at T marginally above the threshold (160°C) than at higher T suggests a diffusion limitation, i.e., slower diffusion at lower energy. A lower threshold is indicated as well, since samples heated to 120°C or lower do not reach the same Δd maxima.

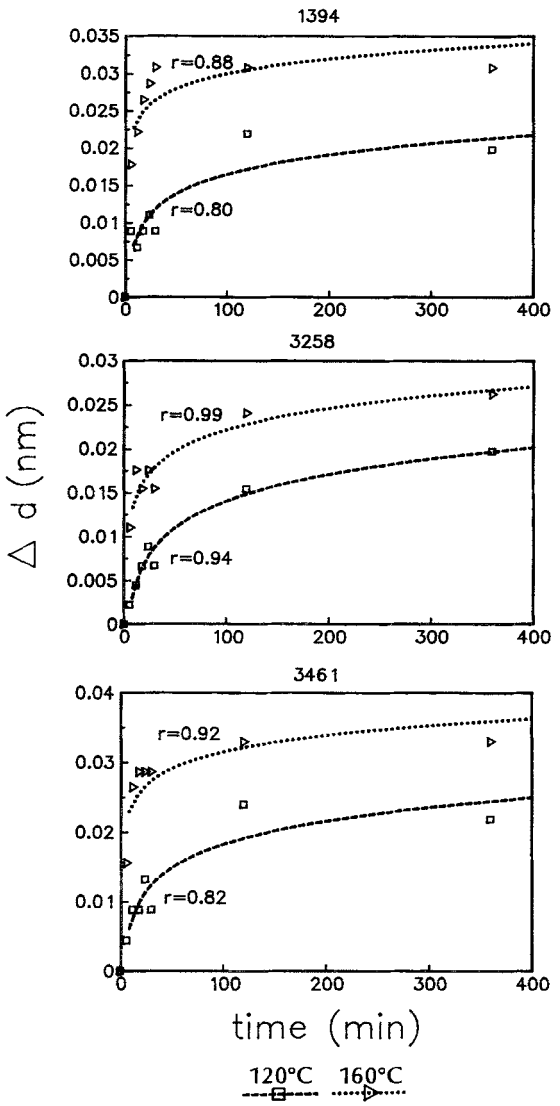



Figure 3. Shifts of HIV basal d-spacing (Δd) at different temperatures with time for samples studied.

*Experiment 3*

All three samples studied exhibited reversible and irreversible dehydration (Figure 5). The $d_{001}$ spacing shifted slightly but elastically in response to isothermal changes in RH, though the difference between means at <5 and >85% RH was statistically significant ($p = 0.046$) only prior to exposure to elevated T. No reversibility was evident following polymer dehydroxylation; the broad XRD peaks following 500°C heating were essentially congruent regardless of RH (data not shown). Shifts induced by even moderate elevations in T (i.e., 25° to 110°C) were of greater magnitude than isothermal shifts and were essentially irreversible, as inferred from the statistically significant differences (p

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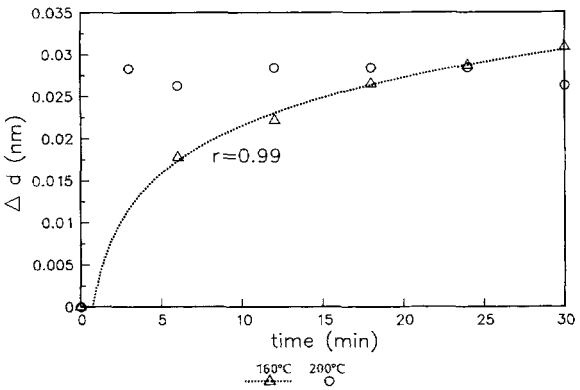



Figure 4. Shifts of HIV basal d-spacing (Δd) at different temperatures over the initial 30 min interval for sample 1394, showing gradual and near-instantaneous shifts to the same maximum value at 160° and 200°C, respectively.

= 0.032) between $d_{001}$ means at 85% RH following exposure to incrementally higher T. These results support the ideas that (1) the reversibly desorbed component is attributable to the relatively small proportion of interlayer water sorption sites in equilibrium with the external vapor phase, (2) the reversibly desorbed sites are not significantly perturbed by moderate heating, but are essentially eliminated by polymer dehydroxylation, and (3) the irreversibly-desorbed component is that which requires heat to overcome steric resistance.

We propose two prospective mechanisms to explain the dehydration properties of HIV in light of experimental results. (1) The tortuosity of the interlayer polymeric network may sterically impede water vapor diffusion. If so, the energy thresholds for dehydration would not be determined by hydration energies of interlayer components but rather by forces required to overcome the steric resistance within the tortuous zone. Increasing T would elevate pressure within the confines of these zones and induce the irreversible outward diffusion of water vapor, since steric resistance of the reentry path would prevent inward diffusion at lower energy states. (2) Alternatively, a re-articulation of polymers and interlayer surfaces may occur with heat and dehydration, resulting in the formation of new bonds at smaller basal spacings which exceed hydration energies of interlayer components. The strong T dependency of dehydration rate favors the former mechanism, which invokes diffusion limitations.

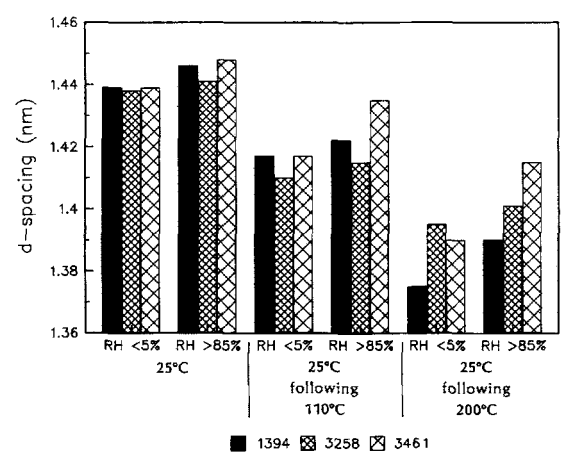



Figure 5. Basal HIV d-spacings for samples studied under specified conditions of relative humidity and temperature, demonstrating both reversible and irreversible components of dehydration.

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