

## THREE-DIMENSIONAL CRYSTAL STRUCTURES OF ILLITE-SMECTITE MINERALS IN PALEOZOIC K-BENTONITES FROM THE APPALACHIAN BASIN

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**Abstract**—The three-dimensional crystal structures of illite-smectite (I-S) in K-bentonite samples from the Appalachian Basin are characterized by rotational disorder in the stacking sequence of 2:1 illite layers, different proportions of  $n60^\circ$  rotations (as opposed to  $n120^\circ$ ) in the rotated layers, and layers with centrosymmetric *trans*-vacant (*tv*) octahedral sites that are randomly interstratified with noncentric *cis*-vacant (*cv*) layers. The proportion of *cv* interstratification in the I-S increases with tetrahedral Al and decreases with octahedral Mg and Fe content. The I-S minerals in the northern Appalachian basin K-bentonites are characterized by high (79% average) proportions of *cv* (P<sub>cv</sub>) layers. In contrast, I-S from equivalent K-bentonites from the southern Appalachian basin has low P<sub>cv</sub> values (38% average). These values do not correlate with expandability or rotational disorder. The geographic distribution of these I-S structural parameters may have resulted from possibly short-term, hot, and advective fluid migrations that differed in Mg concentrations and/or other physical and chemical parameters.

**Key Words**—Bentonite, *Cis*-Vacant Octahedra, Crystal Structure, Illite-Smectite, Polytype, Rotational Disorder, X-ray Diffraction.

### INTRODUCTION

A number of publications describe the calculation of three-dimensional powder X-ray diffraction patterns of phyllosilicates with various kinds and amounts of disorder (e.g., Plançon and Tchoubar, 1977a, 1977b; Plançon, 1981; Plançon *et al.*, 1988; Drits *et al.*, 1984; Sakharov *et al.*, 1990; Drits and Tchoubar, 1990). Reynolds (1993, 1994) developed a computer program (WILDFIRE) similar to those described above for calculating three-dimensional powder diffraction patterns of illite (or mica) and mixed-layer illite-smectite (I-S) with various types and quantities of rotational disorder and composed of two types of randomly interstratified silicate layers. This program was used to define the structural characteristics of 23 K-bentonites from the Appalachian basin that are reported here (Table 1).

The 2:1 layers in the usual dioctahedral mica structure have vacant M1 (*trans*) octahedra (*tv*), whereas both the M2 (*cis*) octahedral sites are occupied. A mirror plane occurs when both symmetrical *cis*-octahedral positions are occupied and the *trans* position is vacant. This situation leads to the ideal centrosymmetric  $C2/m$  space group. The *cis*-vacant (*cv*) unit cell belongs to noncentrosymmetric space group  $C2$ . For this structure, the M1 site and one of the M2 sites are occupied and the dioctahedral cation vacancy occurs in the other M2 site.

The 2:1 phyllosilicates with different distributions of octahedral cations were first reported by Méring and Oberlin (1967) for a sample of Wyoming montmorillonite. Oblique-texture electron diffraction (OTED) work by Tshipursky and Drits (1984) showed that dioc-

tahedral smectites have a wide range of proportions of *cv* and *tv* layers. Reynolds and Thomson (1993) showed that the illite from the Potsdam sandstone of New York has the *cv* structure and Drits *et al.* (1993) described another occurrence. Reynolds (1992), McCarty (1993), McCarty and Reynolds (1995), and Drits *et al.* (1998) demonstrated that *cv* structures exist in I-S exhibiting the  $1M$  and  $1M_d$  stacking sequences, and that *cv* 2:1 layers are commonly interstratified with *tv* layers.

Different distortions of the octahedral sheet about the vacant site cause different monoclinic angles for the *tv* and *cv* structures, producing measurable differences in the positions of some of the X-ray diffraction peaks, and the different octahedral cation positions lead to markedly different diffraction intensities for the diagnostic ( $k \neq 3n$ )  $1M$  diffraction maxima (Tshipursky and Drits, 1984; Drits and McCarty, 1996). Figure 1 shows a comparison between random powder X-ray diffraction patterns for the *cv* Potsdam illite- $1M$  (Reynolds and Thomson, 1993) and a *tv*  $1M$  hydrothermal illite from Silverton Caldera, Colorado (Eberl *et al.*, 1987). The differences in their diffraction patterns between  $2\theta = 20\text{--}35^\circ$  are evident, which demonstrates that these two structures can be confidently identified.

Drits *et al.* (1993) noted that the  $3T$  and *cv*- $1M$  structures produce similar diffraction effects. However, Reynolds and Thomson (1993) found that in determining the structure of the Potsdam illite, the  $d$  values of the Potsdam illite could not be reconciled with a hexagonal structure (e.g.,  $3T$ ) and these values are

Table 1. Sample locations.

Decimal long.	Decimal lat.	Sample and size	#	Bentonite bed, location, and age
-86.00	34.00	9A4 <1.0 $\mu\text{m}$	2	Deicke equivalent, Gadsden, AL, Ord.
-86.00	34.00	AL7-1 <0.5 $\mu\text{m}$	3	Deicke, Gadsden, Etowah Co., AL, Ord.
-85.45	34.92	GA-DD 2-3 <0.5 $\mu\text{m}$	16	Millbrig, Rising Fawn, Dade Co., GA, Ord.
-85.10	34.20	GA-FL 1-1 <0.5 $\mu\text{m}$	17	Deicke, Horseleg Mountain, Floyd Co., GA., Ord
-85.92	33.70	ALCH <0.5 $\mu\text{m}$	41	Millbrig, Alexander Gap, U.S. 431, Calhoun Co., AL, Ord.
-83.47	36.57	TN-CL 1-1 <0.5 $\mu\text{m}$	35	Deicke, Harrogate, Claiborne Co., TN, Ord.
-81.08	37.25	VA-BL 1-15 <0.5 $\mu\text{m}$	37	Deicke, Rocky Gap, Bland Co., VA, Ord.
-83.00	36.70	VA 2-2 <0.5 $\mu\text{m}$	38	Deicke, Hagan, Lee Co., VA, Ord.
-78.50	40.58	DM-PA15 <0.5 $\mu\text{m}$	7	(?) Union Furnace, Blair Co., Tyrone Quad, PA, Ord.
-78.00	39.45	DM-WV3 <0.5 $\mu\text{m}$	8	Deicke(?), Martinsburg, Berkeley Co., W.VA, Ord.
-77.50	40.90	P4-2 <0.5 $\mu\text{m}$	28	(?) Oak Hall, Centre Co., Bellefonte Quad., PA, Ord.
-77.25	41.25	SALONA <2.0 $\mu\text{m}$	31	Deicke equivalent, Salona, Clinton Co., Central AP, Ord.
-76.00	43.00	NY6-3 <0.5 $\mu\text{m}$	27	(?) Crum Creek, Little Falls Quad., NY, Ord.
-76.17	42.97	TD1 <1.0 $\mu\text{m}$	34	Tioga, Onondaga FM, SW of Syracuse, NY, Dev.
-74.42	42.88	CAND <0.5 $\mu\text{m}$	42	Utica FM, Canajoharie Cr., Montgomery Co., NY, Ord.
-75.17	43.17	T01-A <0.5 $\mu\text{m}$	43	Black River, 0.9 Mi S. Middleville, NY, Hwy. 169, Ord.
-74.70	42.78	WT1 <0.5 $\mu\text{m}$	44	Tioga, Onondaga FM, U.S. 20, Cherry Valley, NY, Dev.
-75.92	42.92	WT5-B <0.5 $\mu\text{m}$	45	Tioga, Onondaga FM, Jamesville, NY, Dev.
-76.78	42.85	WT8 <0.5 $\mu\text{m}$	46	Tioga, Onondaga FM, Canoga, NY, Dev.
-77.27	42.93	WT9 <0.5 $\mu\text{m}$	47	Tioga, Onondaga FM, 2 Mi. N. of Canadaigua, NY, Dev.
-78.73	42.88	TD2-A <0.5 $\mu\text{m}$	48	Tioga, Onondaga FM, Cheektowaga, NY, Dev.
-73.83	43.13	ECC-1 <0.5 $\mu\text{m}$	49	Utica FM, E. Canada Creek, Dolgeville, NY, Ord.
-75.67	45.50	CA35 <1.0 $\mu\text{m}$	56	Rosemont Ls FM(?) (below Utica) Ottawa, Canada, Ord.

consistent with the *cis*-vacant unit-cell parameters deduced by Drits *et al.* (1984). Indexing was possible because the Potsdam illite has sharp diffraction maxima. However, the broader reflections from I-S owing to interstratification and rotational disorder preclude the precise location of peak positions. Thus, the possibility exists that some of the *cis*-vacant structures reported here and elsewhere are actually 3*T* polytypes.

The *cis*-vacant structure is assumed here because there are at least two reported *cv* illite occurrences that are well documented (Drits *et al.*, 1993; Reynolds and Thomson, 1993) and because electron diffraction studies have reported the common occurrence of the *cis*-vacant structure in smectites (Tsipursky and Drits, 1984).

The present study developed from efforts to identify the geological parameters that control the occurrence of *tv* and *cv* illite layer types. In the survey of McCarty (1993) of K-bentonites that encompass a wide range in ages and locations, the only convincing correlation noted was between illite layer type and location along the southwest/northeast strike of the Appalachian fold belt. We attempt to explain that correlation in terms of spatially different diagenetic fluid compositions that pervaded and affected the sedimentary rocks during a likely Alleghenian event.

Clay minerals from K-bentonites were chosen for this study because they are better suited to show the diffraction effects produced by different layer types and percentages of stacking disorder and octahedral-cation distributions than I-S from shales and sandstones. The latter almost always have diffraction peak interferences from other fine-grained minerals. In addition, the same K-bentonite beds from different geographic locations initially had the same composition, because they were produced from a short-lived volcanic eruption from a common source. Variations in the three-dimensional structures of I-S in rocks with a uniform starting composition must be products of a particular local geologic history. Note, however, that

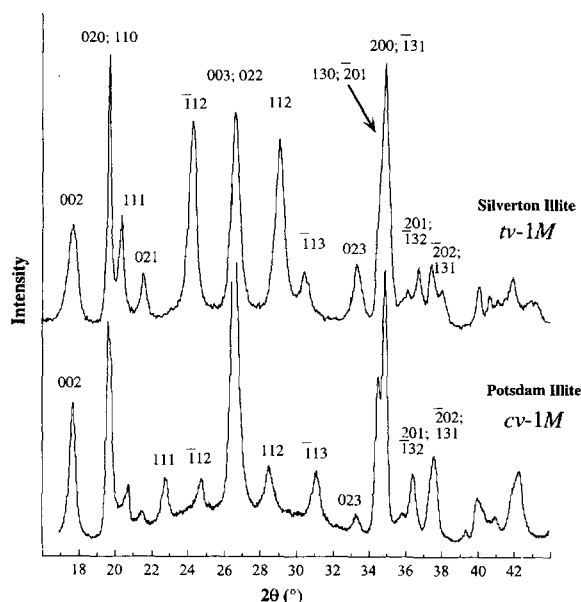


Figure 1. Random powder diffraction scans from Silverton sericite (*tv*-1*M*) and Potsdam illite (*cv*-1*M*) samples.

the systematics of illite-smectite in bentonites might be different from that in shales and mudstones.

### GEOLOGICAL SETTING

Ordovician volcanic ash layers deposited in epeiric seas presently occur over an area of ~1.3 million km<sup>2</sup> of eastern North America and are distributed throughout thick sequences of carbonate and clastic rocks (Kolata *et al.*, 1986). The source volcanoes that produced the original ash beds probably existed in an island arc system in the Appalachian orogenic belt as shown by more numerous and thicker beds in or adjacent to the Appalachian mountains. This is in contrast to more western areas where bentonite beds are thinner and less abundant (Kay, 1935; Kolata *et al.*, 1986). Ordovician K-bentonites reported on here are the Deicke and Milbrig Bentonites or their equivalents.

The Tioga Bentonite is the best known and widespread volcanic ash layer in the middle Devonian rocks of the Appalachian basin and probably covered all of the northeastern United States during Middle Devonian time (Dennison and Textoris, 1970; Droste and Vitaliano, 1973). The volcanic vent or vents that produced the Tioga ash were probably located in central Virginia (Droste and Vitaliano, 1973). The Devonian K-bentonite samples in this study are from the Tioga or Tioga equivalent bentonite beds.

This study and others (*e.g.*, Pytte and Reynolds, 1989; Eberl and Hower, 1976; Huang *et al.*, 1993) demonstrate that the illitization of smectite is a kinetically controlled process that occurs during diagenesis. Huang *et al.* (1993) developed a kinetic scheme based on laboratory synthesis and field studies, and they found that at any specific temperature, the illite reaction rate depends on the activity of K in the pore fluid. The position of a given composition of I-S in the interstratification series thus depends on temperature, K activity in the associated pore fluids, and time.

I-S diagenesis in the distal Appalachian basin, particularly in the north, cannot be explained by the "traditional" model of burial diagenesis because apparent burial depths are too shallow (Harris, 1979). The I-S clays in Appalachian basin K-bentonites are long-range ordered (stacking order) structures (Reichweite > 1) with low to medium expandability similar to those found in deeply buried diagenetic sequences. However, most of these northern Appalachian clays occur in geologic areas that show no evidence of deep burial depths (Huff and Türkmenoglu, 1981; Elliott and Aronson, 1987).

Elliott and Aronson (1987) documented illitic K-bentonites with uniform expandability from middle Ordovician strata throughout the southern Appalachian basin regardless of burial depth. They interpreted the narrowly confined K/Ar ages of illitization between 272–300 Ma (late Pennsylvanian to early Permian) as evidence for a short-lived diagenetic episode caused

by the Alleghanian orogeny. Additional work by Elliott and Aronson (1993) supports the contention that the illite formed during the Alleghanian Orogeny.

Other studies suggest that mineralizing fluids advectively penetrated the rocks of the eastern United States (*e.g.*, Viets *et al.*, 1984; Oliver, 1986; Leach and Rowan, 1986; Hearn *et al.*, 1987; Bethke and Marshak, 1990). Data are much more limited for the northern Appalachians, but Johnsson (1984) reported a partially annealed zircon from the Tioga Bentonite that indicates temperatures (>175°C) much higher than can be explained by most acceptable models for maximum burial depths and a reasonable geothermal gradient. Roden *et al.* (1992, 1993) also found partially annealed zircon fission tracks throughout the southern Appalachian basin indicating temperatures of ~175°C. They suggested that these temperatures were maintained for <1 Ma, but these temperatures are difficult to reach with the estimated burial depth. Siedemann and Isachsen (unpubl. data; personal communication) obtained a K/Ar age of 290 Ma on I-S from a bentonite in the Ordovician Utica formation of New York, thus suggesting an origin similar to that of the much better studied I-S from the southern Appalachians.

There are several possible mechanisms for the migration of hot fluids through basin strata (see review in Bethke and Marshak, 1990). The gravity-driven meteoric-water model is generally the most accepted. Schedl *et al.* (1992) suggested, however, that isotope- and fluid-inclusion evidence indicate that widespread alteration and remagnetization of Paleozoic strata in the Blue Ridge Province in western North Carolina and in the Valley and Ridge Province in Tennessee and Northern Virginia resulted from the expulsion of metamorphic fluids and basinal brines, rather than meteoric waters during the late Paleozoic. For the bentonite beds in this study that are found in carbonate strata, those in the northern Appalachian basin are found in limestone and those in the southern portion of the basin are found in dolomite (Figure 2). The main difference between a basin-brine or metamorphic-fluid model and a meteoric-water model is that in the meteoric-water model the dolomite is the probable source for the higher Mg content in the I-S because meteoric water would presumably migrate through dolomite strata and thus acquire high Mg concentrations. In the basin-brine model, dolomitization and illitization may have been products of the same brine migration event.

### ANALYTICAL METHODS

Sampling, chemical analysis, computer modeling of three-dimensional structures, and diffraction pattern interpretation are explained by McCarty (1993) and McCarty and Reynolds (1995). A complete description of the computer program WILDFIRE is given by Reynolds (1993). All calculated diffraction profiles are

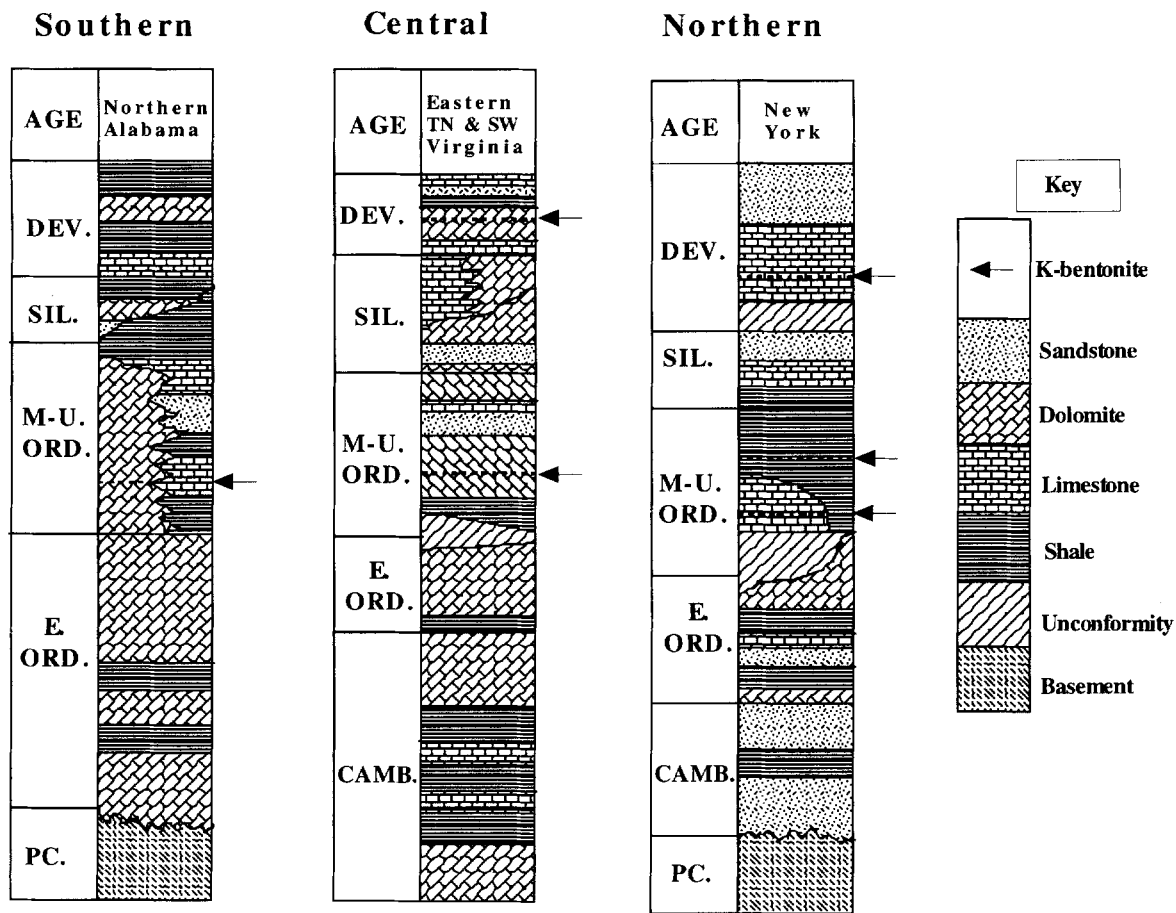


Figure 2. Generalized geologic columns showing lithologies and relative positions of the K-bentonites from the northern, central, and southern Appalachians (adapted from Milici and de Witt, 1988 and Thomas, 1988).

based on atomic coordinates and unit-cell parameters for *cv* and *tv* layers from Drits *et al.* (1984).

Figure 3 compares calculated diffraction data from *cv*-1M and *tv*-1M structures (minus basal reflections for this figure only) and shows the direction the diagnostic reflections (*d* values) migrate when interstratification of *cv* and *tv* layers occurs within illite particles (Drits and McCarty, 1996). Drits and McCarty (1996) analyzed the position and deviation of these reflections in calculated and experimental diffraction patterns based on Méring's principles, and they provide formulae to calculate layer-type content that do not require computer programs.

The X-ray diffraction (XRD) and sample preparation procedures used are described in detail by McCarty and Reynolds (1995). Briefly, the <2, <1, or <0.5- $\mu$ m equivalent spherical-diameter fractions were extracted by centrifugation and saturated with Ca<sup>2+</sup> to provide a common interlayer cation. A particle size was selected that best produced a fraction free from feldspar and/or quartz. Oriented aggregates were produced by the glass slide-pipette or filter-peal transfer

method, and these were analyzed in the air-dried and ethylene glycol-solvated states.

Aliquots of the clay-size dispersion were freeze-dried and then heated for 1 h at 250°C to dehydrate the expandable layers in the I-S. The powder was side-loaded in the holder for diffraction analysis, which was accomplished in an enclosed chamber fitted to the diffractometer. Nitrogen was streamed through the chamber to maintain dehydration during analysis. The data were obtained by step-scanning procedures with a step size of 0.05 °2 $\theta$  and a count time of 20–40 s per step.

The three-dimensional diffraction-simulation procedure requires an analysis of the diffraction pattern from an ethylene glycol-solvated oriented aggregate. Percent expandability and Reichweite, R, were determined by comparison with calculated patterns from NEWMOD (Reynolds, 1985). Where possible, I-S expandability was determined using the delta 2 $\theta$  method of Moore and Reynolds (1997). Mean crystallite thickness was determined from the width at half height of the peak near 26°. Currently, there are no convincing crystal structure models that provide excellent agree-



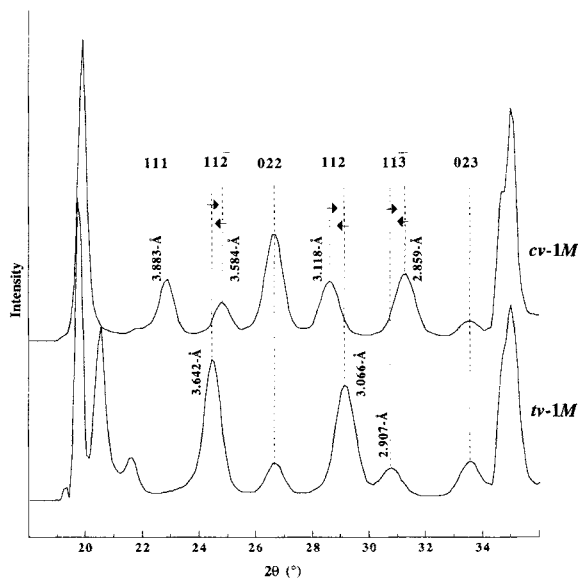


Figure 3. Comparison between calculated *cv-1M* and *tv-1M* structures. Arrows show the migration direction of the indicated reflections (*d* values) where interstratification of the other layer type occurs.

ment between observed and calculated basal XRD patterns for ( $R > 2$ ) I-S. Despite significant discrepancies between theory and experiment, almost all of the samples in this study are clustered near the illite end-member of the compositional range. For such minerals, differences of  $<5\%$  expandability have little or no measurable effect on the accurate determination of the key three-dimensional parameters  $P_0$ ,  $P_{cv}$ , and  $P_{60}$  where these parameters represent the proportions of layers with  $0^\circ$  rotations, *cv* occupancy, or  $60^\circ$  rotations, respectively; see below. Consequently, the failure to deduce the details of I-S layer interstratification does not compromise our results.

Percent expandability, Reichweite, and crystallite thickness are input parameters for WILDFIRE. Basal reflections were calculated using these parameters for an interstratified illite-smectite in which the smectite layers were assumed to be dehydrated with a spacing of  $9.7 \text{ \AA}$ . The expandable interlayers had a fixed composition of  $0.15 \text{ Ca}$  ions, the illite interlayer contained  $0.7 \text{ K}$ , and both layer types had  $\text{Fe}$  fixed at  $0.15$  ions per  $\text{Si}_4\text{O}_{10}$ . The *X* and *Y* crystallite dimensions were 60 and 30 unit cells, respectively.

The three-dimensional diffraction patterns were not computed from the mean crystallite thickness, but instead, a crystallite thickness distribution was used that represents the frequency of occurrence of illite fundamental particles (Nadeau *et al.* 1984). All possible combinations and permutations of illite and smectite interlayers, consistent with the Reichweite, were generated. From these, the thicknesses of the stacks of contiguous illite layers were counted and summed.

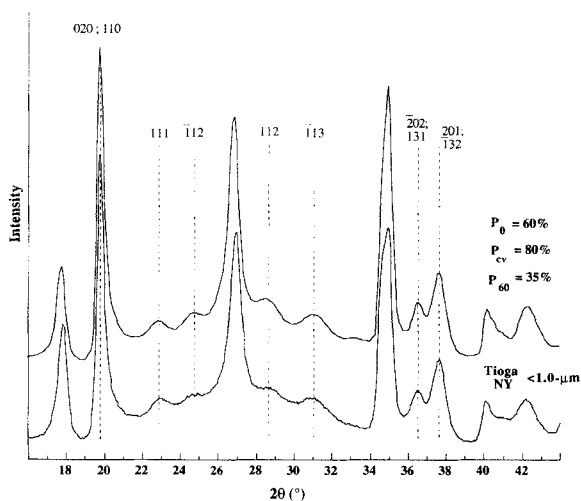


Figure 4. Comparison between calculated (top) and experimental diffraction patterns for Tioga K-bentonite, New York. The parameters are:  $P_0 = 60\%$ ,  $P_{cv} = 80\%$ , and  $P_{60} = 35\%$ .

This procedure is valid if the smectite interlayers are sites of turbostratic disorder that limit coherence to the crystal-volume elements between turbostratic sites. This condition was assumed, and the validity is supported by the successful application to a wide range of expandability and Reichweite in K-bentonites (Reynolds, 1992), and by evidence given by Guthrie and Reynolds (1998).

Each three-dimensional diffraction pattern was modeled with combinations of just three adjustable input parameters  $P_{cv}$ ,  $P_0$ , and  $P_{60}$ .  $P_{cv}$  refers to the percentage of *cv* layers interstratified with *tv* layers in

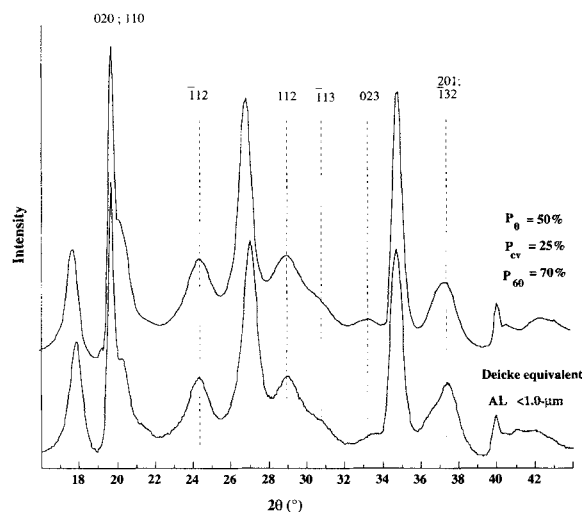


Figure 5. Comparison between calculated (top) and experimental diffraction patterns for Deicke equivalent K-bentonite, Alabama. The parameters are:  $P_0 = 50\%$ ,  $P_{cv} = 25\%$ , and  $P_{60} = 70\%$ .

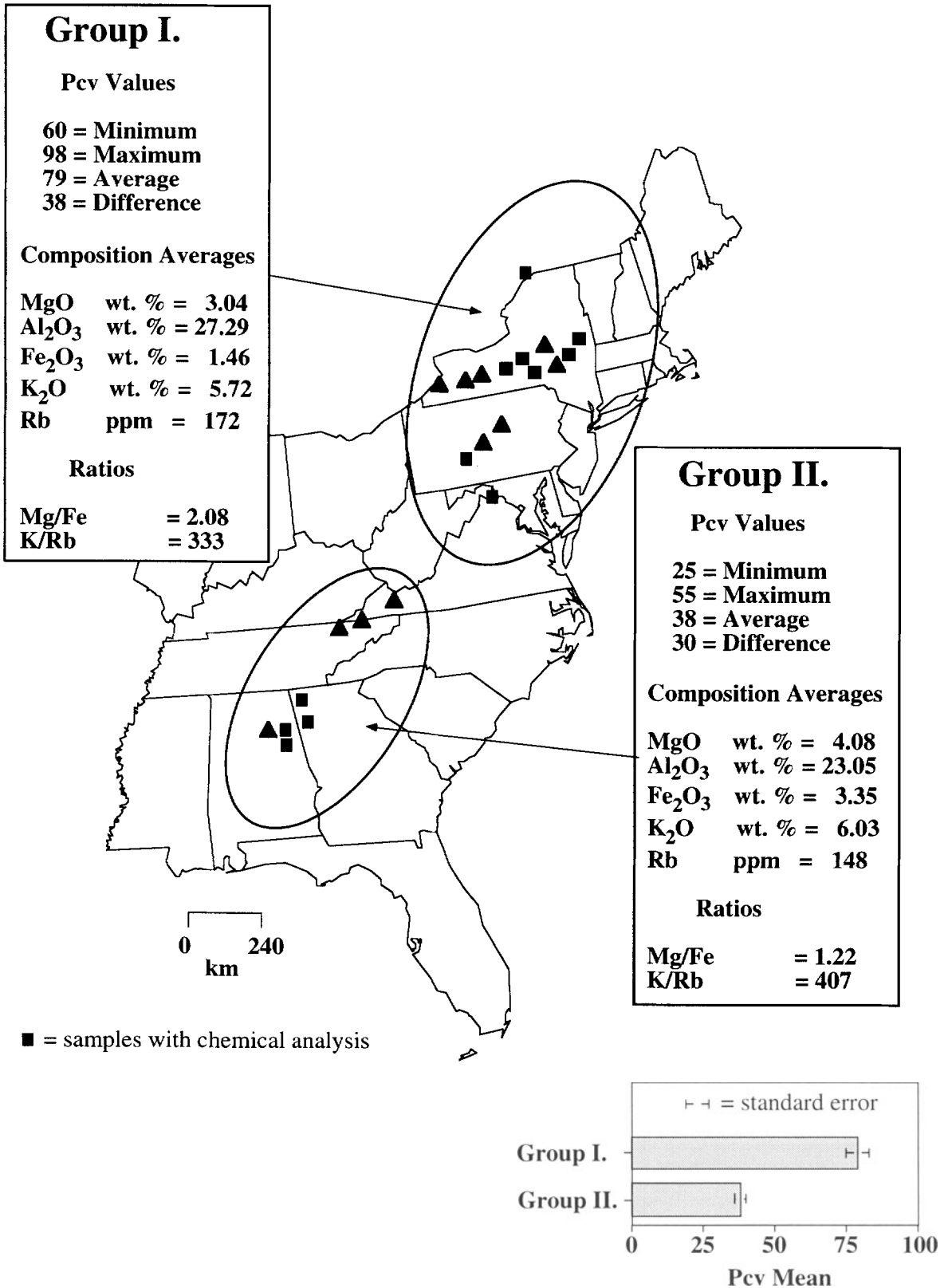


Figure 6. Geographic distribution of the Pcv structures (% cv interstratification) and distinguishing composition values. Group designations are based on value similarity and location.

Table 2. I-S structural parameters.

Sample and size	Sample #	Exp. (%)	Reichweite	P0	Pcv	P60
Group I						
DM-PA15 <0.5 $\mu\text{m}$	7	11	3	70	82	30
DM-WV3 <0.5 $\mu\text{m}$	8	11	3	80	60	30
P4-2 <0.5 $\mu\text{m}$	28	14	2.5	75	60	40
SALONA <2.0 $\mu\text{m}$	31	12	3	60	80	25
NY6-3 <0.5 $\mu\text{m}$	27	18	1.5	62	75	45
TD1 <1.0 $\mu\text{m}$	34	10	3	60	80	35
CAND <0.5 $\mu\text{m}$	42	19	2.5	55	85	30
T01-A <0.5 $\mu\text{m}$	43	11	3	45	65	45
WT1 <0.5 $\mu\text{m}$	44	13	3	55	75	15
WT5-B <0.5 $\mu\text{m}$	45	13	3	50	98	20
WT8 <0.5 $\mu\text{m}$	46	9	3	50	85	10
WT9 <0.5 $\mu\text{m}$	47	12	3	55	97	15
TD2-A <0.5 $\mu\text{m}$	48	21	1.5	55	80	45
ECC-1 <0.5 $\mu\text{m}$	49	18	1.5	55	85	10
CA30 lkt1.0 $\mu\text{m}$	55	13	2.5	70	60	40
CA35 <1.0 $\mu\text{m}$	56	15	2.5	50	95	35
Group II						
9A4 <1.0 $\mu\text{m}$	2	11	3	50	25	70
AL7-1 <0.5 $\mu\text{m}$	3	18	1.5	75	30	85
GA-DD 2-3 <0.5 $\mu\text{m}$	16	14	3	85	55	60
GA-FL 1-1 <0.5 $\mu\text{m}$	17	9	3	65	40	90
ALCH <0.5 $\mu\text{m}$	41	11	3	70	55	60
TN-CL 1-1 <0.5 $\mu\text{m}$	35	10	3	50	30	60
VA-BL 1-15 <0.5 $\mu\text{m}$	37	9	3	50	30	80
VA 2-2 <0.5 $\mu\text{m}$	38	13	2.5	85	35	90

the calculated model crystallite structure, P0 is the percentage of layers rotated zero degrees (the same azimuthal direction as for the  $1M$  setting) with respect to a preceding adjacent layer, and P60 denotes the proportion of rotated layers that are rotated by 60, 180, and 300° with respect to the underlying layer. These latter rotations have been rarely reported in micas, except in  $2M_2$  polytypes. The common rotations that determine polytype and rotational disorder are integral multiples of 120° ( $n120$ ). To extract model Pcv values requires an analysis of the 02 $l$ ; 1 $l$  reflections between  $2\theta = 19\text{--}34^\circ$ .

Figures 4 and 5 show examples of experimental diffraction patterns of dominantly  $cv$  and  $tv$  structures, respectively, together with their model patterns calculated by WILDFIRE. Comparisons between calculated and experimental patterns demonstrate the good agreement that can be obtained between the two, in terms of peak position and reproduction of the essential diffraction features, by adjustments of just three parameters.

## RESULTS

The I-S structures are arranged (Figure 6) according to their Pcv values and geographic location. Figure 6 also shows the calculated mean and standard error for the Pcv values for two (arbitrary) groups and some distinguishing compositional data for nine samples from Group I and four samples from Group II. A sum-

mary of the I-S structural parameters (Pcv, P0, P60) and I-S expandability and Reichweite is presented in Table 2. The diffraction data from the oriented-sample preparations are presented in Figure 7 arranged in order of decreasing  $cv$ -layer content.

Figure 8 shows a plot of Pcv compared to sample location (distance from south to north) after projecting the map sample location to a line along the approximate strike of the basin. Also plotted on Figure 8 is the quantity  $Al/(Fe + Mg)$  (atomic proportions) calculated from chemical analyses of the I-S samples that were analyzed by X-ray fluorescence (McCarty and Reynolds, 1995), and compared with their respective Pcv values. These data show a distinct relationship between Pcv and sample location and between Pcv and the  $Al/(Fe + Mg)$  ratio in the I-S samples. Table 3 analyzes the variance of the correlation between Pcv and the sample locations, which were divided arbitrarily into groups for the northern and southern Appalachians.

## DISCUSSION

Figure 6 and Table 2 show a significant difference in Pcv for the I-S groups I and II. Group I samples from the northern Appalachian basin are dominated by  $cv$  layers, whereas Group II samples from the southern Appalachian basin are richer in  $tv$  layers. These southern Appalachian fold and thrust belt samples are also higher in Mg and Fe and lower in Al (Figures 6 and 8). The data are not sufficiently complete to preclude a continuous trend in Fe + Mg (or Al content) and Pcv with respect to distance north (Figure 8).

If Mg increases in the octahedral sheet, octahedral Al correspondingly decreases and the net negative layer charge increases with Mg,  $Fe^{2+}$  substitution. If tetrahedral Al decreases, such a combination will lead to an end-member celadonite structure with no tetrahedral Al and one octahedral Al per  $O_{10}(OH)_2$ . Thus, the ratio of  $Al/(Mg + Fe)$  will be very sensitive to tetrasilic (1 Al total,  $R^+[Si_4][R^{2+}Al]O_{10}[OH]_2$ ) versus trisilic (3 Al total,  $R^+[Si_3Al][Al_2]O_{10}[OH]_2$ ) compositions for illite samples with equal layer charge.

Figure 9a and 9b illustrates that there are only minor differences in the amounts of rotational disorder (P0) within the sample suite. However, the type of rotational disorder (P60) is distinctly different in the two geographical groups (Figure 9c). Differences in rotational disorder correlate with the octahedral cation composition in the I-S. Rotations by  $n60^\circ$  are favored in Mg and Fe-rich structures that have minimal tetrahedral substitution. In structures with low tetrahedral substitution where layer charge is generated in the octahedral sheet, there is a decrease in the interaction between basal oxygens and the interlayer cation (Güven, 1971; Bailey, 1984). In this case, interlayer cation bonding may be of the "open" prismatic type where basal oxygen atoms from adjacent layers are super-

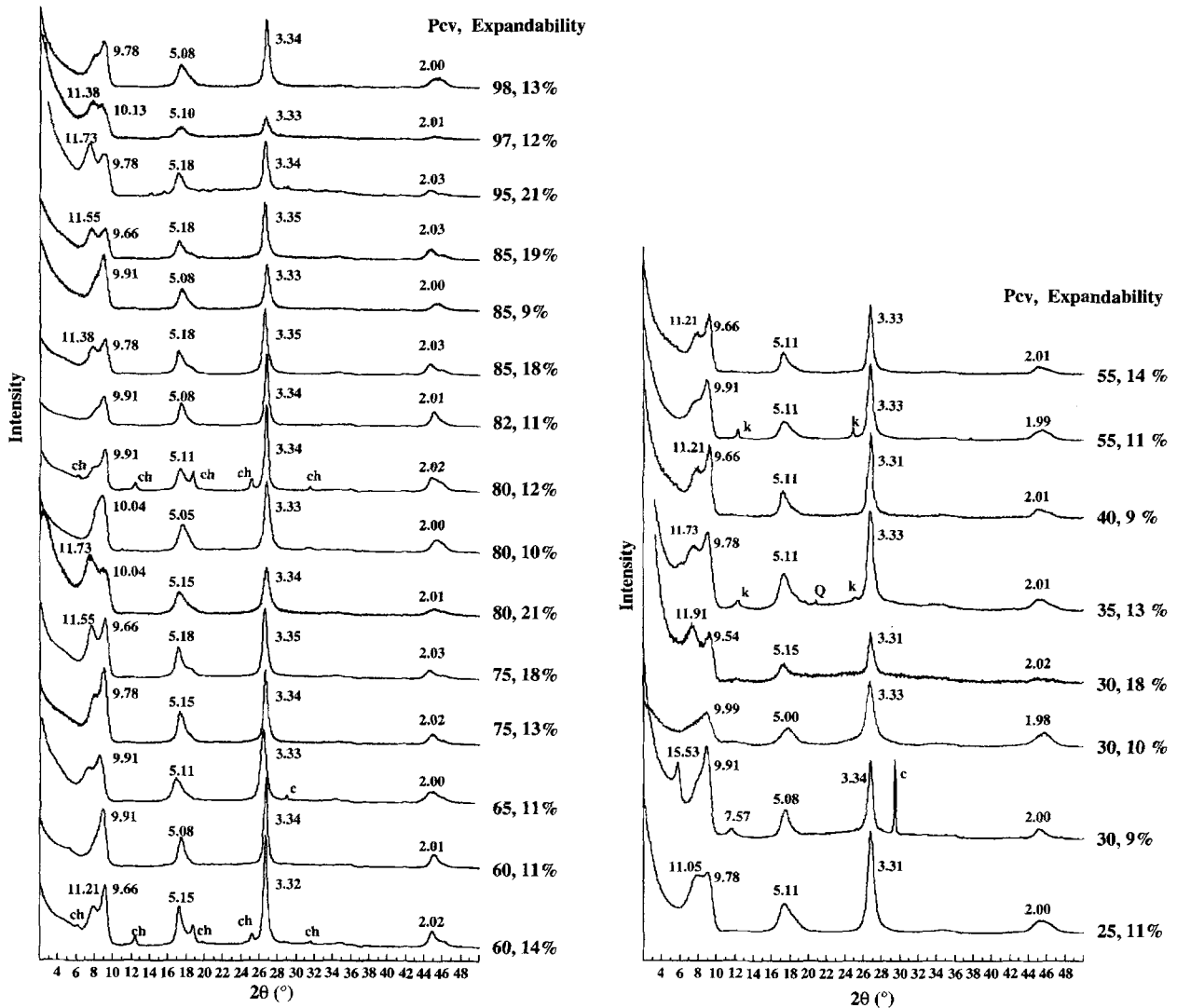


Figure 7. Diffraction data from glycol-solvated oriented-aggregate preparations showing  $d$  values in Å units and estimated % expandability for the studied samples arranged in order of decreasing Pcv. Left contains all Group I samples (Figure 6) and right shows the samples from Group II. ch = chlorite, c = calcite, k = kaolinite, Q = quartz.

imposed. In contrast, trisilic layers have unsatisfied negative charges on the basal oxygens and will tend to repel each other (Bailey, 1984). In this case, the most energetically stable configuration in interlayer cation bonding is by octahedral coordination where the basal oxygen atoms are not superimposed. Therefore, the correlation between  $n60^\circ$  rotations and a tetrasilic composition is related to ionic substitution and the resulting electrostatic forces in the oxygen network in the basal planes adjacent to the interlayers. It is interesting that nearly complete  $n60^\circ$  rotational disorder was reported by Sakharov *et al.* (1990) in a glauconite sample with a tetrahedral Si composition of 3.78 per  $O_{10}(OH)_2$ . Because the southern Appalachian basin

samples are generally higher in Fe and Mg (Figure 6), along with the correspondingly high tetrahedral Si, they have a higher occurrence of  $60^\circ$  rotations.

The distinct populations of  $cv$  structures in I-S samples from bentonites that originally had the same composition and now exist in different geological settings suggest that these structural characteristics are a function of the prevailing geological conditions during the formation of the I-S. Such geological conditions include, but are not limited to thermal maturity. These bentonite beds were not deeply buried, are often contained in carbonate strata, and have ( $R \geq 1$ ) I-S with low expandability, with a narrowly constrained age interval. These results suggest an advective fluid as the



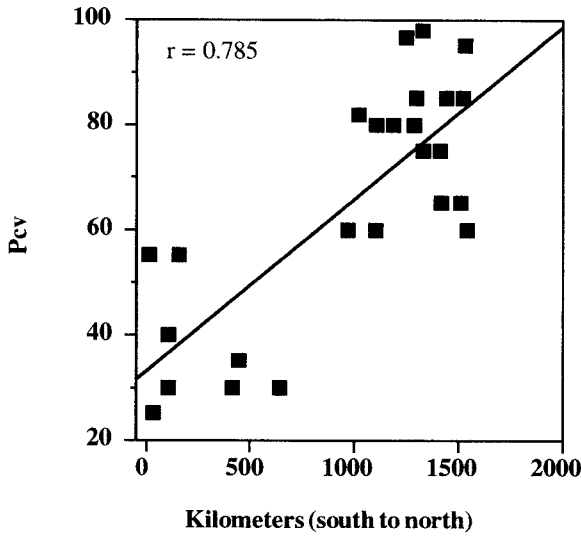


Table 3. Analysis of variance<sup>1</sup> for P<sub>cv</sub> groups shown on Figure 6.

Group	Mean	n	Non-significant ranges Significance Levels	
			5%	1%
I	79	18	<sup>2</sup> a	a
II	38	8	<sup>2</sup> b	b

<sup>1</sup> One-Way ANOVA, Student-Newman-Keuls Test, Error mean square = 170.05, Degrees of freedom = 51.

<sup>2</sup> The distinctions a, and b, indicate unique or non-unique category types at the given significance level.

idence for the existence of Mg-rich brines, then differences in fluid composition may contribute to some mechanism that controls the production of *cv* and *tv* 2:1 illite structures.

Although there is a logical reason (see above) for the correlation between Mg, Fe (*i.e.*, tetrasilicic) composition and  $n60^\circ$  rotations, it is unclear why such compositions result in the *tv* structures that dominate

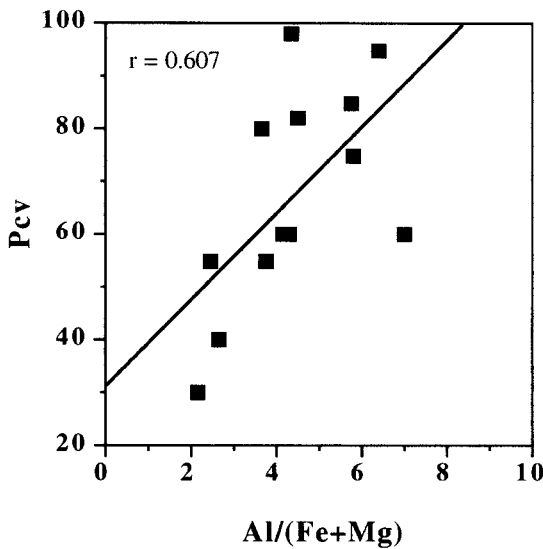


Figure 8. Projected P<sub>cv</sub> values *versus* distance in kilometers from south to north along the approximate strike of the Appalachian basin (Figure 6), and P<sub>cv</sub> values *versus* atom % (Fe + Mg).

source for the requisite K and heat to convert smectite layers to illite layers (*e.g.*, Huff and Türkmenoglu, 1981; Elliott and Aronson, 1987; this study).

Thermal energy and chemical constituents, including the required K, carried by hot fluids migrating through sediments exposed the bentonites to temperatures in excess of the geothermal gradient. Thus, greater progress in the smectite to illite reaction occurs than would be expected from burial depth alone. If the abundant dolomitic rocks in the south are taken as ev-

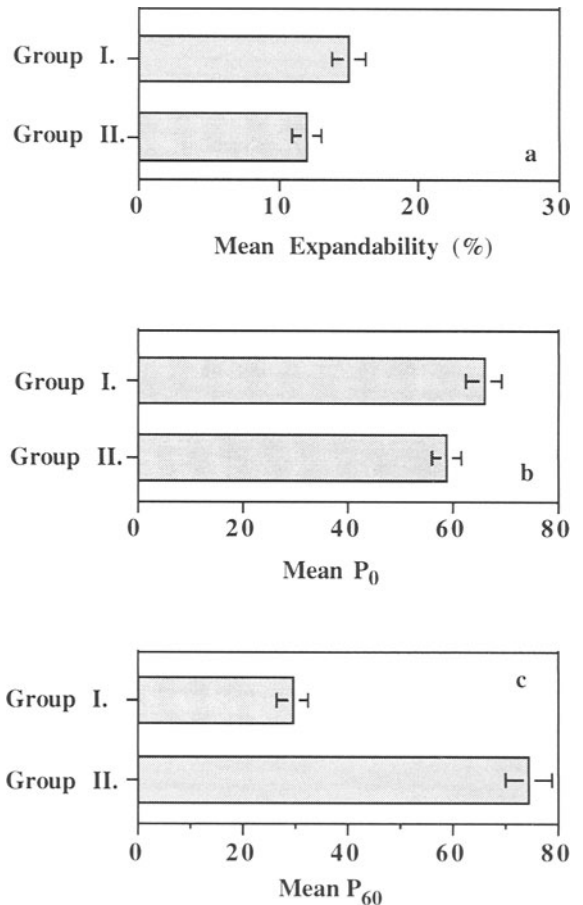


Figure 9. Comparison of mean and standard error among groups shown on Figure 6 for the parameters (a) % expandability, (b) P<sub>0</sub>, and (c) P<sub>60</sub>. Bar interval indicates standard error.

the southern Appalachian Basin samples or why the trisilicic compositions adopt the *cv* structure. McCarty and Reynolds (1995) discuss a possible crystallographic explanation for why trisilicic compositions favor a *cv* structure.

There are major differences in tectonic processes between the *cis*-dominated samples and *trans*-dominated samples going from north to south in the basin (*i.e.*, Groups I and II, Figures 6 and 8). The *tv*-dominated Group II samples are from imbricated overthrust sheets and strongly folded strata. However, the samples from the northern basin were obtained from flat laying and essentially undeformed strata. Such a distinctive tectonic and lithological difference between sample location and the observed differences in the I-S from bentonite that originally had the same bulk composition is intriguing. Unfortunately, the exact physical parameters and crystal chemical mechanisms that controlled the *cv-tv* character in these samples are not known at present.

#### Fluid source

Figure 6 shows that I-S in Group I has average values for Mg, Al, and Fe of 3.04, 27.29, and 1.46 wt. % compared, respectively, to 4.08, 23.05, and 3.35 wt. % for the Group II samples. These data together with the abundance of dolomite suggest that the mineralizing fluids in the southern Appalachian basin were rich in Mg relative to the northern samples.

Reynolds (1963) found that Precambrian and Phanerozoic  $1M_c$  illites and glauconites, as well as crustal igneous rocks have consistent K/Rb ratios between 240–270. The K/Rb ratio in the I-S described in this study ranges from 333 to 407 (Figure 6). These results suggest that illitization of the K-bentonites occurred in the presence of fluids that were depleted in Rb, compared to connate waters that were present during the formation of illite in the shales and limestones as reported on by Reynolds (1963). Such a Rb-depleted source may reflect the drop in K/Rb that occurs if the illitizing fluids migrated over a large distance. Alternatively, admixture of fluids from evaporates may also produce waters with abnormally high K/Rb ratios.

#### CONCLUSIONS

The data obtained in this study and previous studies are consistent with the interpretation that illitization in the Appalachian basin bentonite beds was controlled by heat and K derived from advective fluid flow.

In the Appalachian basin, I-S structure in K-bentonites was controlled by westward fluid migration from the Alleghanian orogeny. I-S structures in the southern Appalachian basin were controlled by fluids richer in Mg than the fluids prevalent in the north. The structural features of the Mg, Fe-rich I-S samples from the southern Appalachian basin K-bentonites are dominated by *tv* layers with 60° rotations. The more Al-rich

samples contain *cv*-layer types with 120° rotations. The physical parameters and crystal-chemical mechanisms controlling the respective *cv-tv* layer content in these samples are not known. At present, differences in bentonite I-S *cv-tv* layer content in this study are only associated in some way with general differences in the tectonic processes and lithology or system composition, because it is likely that the initial composition of these K-bentonites was similar.

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#### REFERENCES

- Bailey, S.W. (1984) Crystal chemistry of the true micas. In *Micas, Reviews in Mineralogy, Volume 13*, S.W. Bailey, ed., Mineralogical Society of America, Washington, D.C., 13–60.
- Bethke, C.M. and Marshak, S. (1990) Brine migrations across North America—the plate tectonics of groundwater. *Annual Review Earth Planetary Science*, **18**, 287–315.
- Dennison, J.M. and Textoris, D.A. (1970) Devonian Tioga tuff in northeastern United States. *Bulletin Volcanologique*, **34**, 289–293.
- Drits, V.A. and McCarty, D.K. (1996) The nature of diffraction effects from illite and illite-smectite consisting of interstratified trans-vacant and cis-vacant 2:1 layers: A semi-quantitative technique for determination of layer-type content. *American Mineralogist*, **81**, 852–863.
- Drits, V.A. and Tchoubar, C. (1990) *X-ray Diffraction by Disordered Lamellar Structures*. Springer-Verlag, New York, 371 pp.
- Drits, V.A., Plançon B.A., Sakharov, B.A., Besson, G., Tsipursky, S.I., and Tchoubar, C. (1984) Diffraction effects calculated for structural models of K-saturated montmorillonite containing different types of defects. *Clay Minerals*, **19**, 541–561.
- Drits, V.A., Weber, F., Salyn, A.L., and Tsipursky, S.I. (1993) X-ray identification of one-layer illite varieties: Application to the study of illites around uranium deposits of Canada. *Clays and Clay Minerals*, **41**, 389–398.
- Drits, V.A., Lindgreen, H., Salyn, A.L., Ylagan, R., and McCarty, D.K. (1998) Semiquantitative determination of trans-vacant and cis-vacant 2:1 layers in illites and illite-smectites by thermal analysis and X-ray diffraction. *American Mineralogist*, **83**, 1188–1198.
- Droste, J.B., and Vituliano, C.J. (1973) Tioga bentonite (Middle Ordovician) of Indiana. *Clays and Clay Minerals*, **21**, 9–13.
- Elliott, W.C. and Aronson, J.L. (1987) Alleghanian episode of K-bentonite illitization in the southern Appalachian Basin. *Geology*, **15**, 735–739.
- Elliott, W.C. and Aronson, J.L. (1993) The timing and extent of illite formation in Ordovician K-bentonites at the Cin-

- cinnati Arch, Nashville Dome and north-eastern Illinois basin. *Basin Research*, **5**, 125–135.
- Eberl, D.D. and Hower, J. (1979) Kinetics of illite formation. *Geological Society of America Bulletin*, **87**, 1326–1330.
- Eberl, D.D., Srodoń, J., Lee, M., Nadeau, P.H., and Northrup, H.R. (1987) Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin, and particle thickness. *American Mineralogist*, **72**, 914–934.
- Guthrie, G.D., Jr. and Reynolds, R.C., Jr. (1998) A coherent TEM- and XRD-description of mixed-layer illite/smectite. *The Canadian Mineralogist*, **36**, 1421–1434.
- Güven, N. (1971) Structural factors controlling stacking sequences in dioctahedral micas. *Clays and Clay Minerals*, **134**, 159–165.
- Harris, A.G. (1979) Conodont color alteration, an organomineral metamorphic index and its application to Appalachian Basin geology. In *Aspects of Diagenesis*, P.A. Scholle and P.R. Schluger, eds., Society of Economic Paleontologists and Mineralogists Special Publication 26, Tulsa, Oklahoma, 3–16.
- Hearn, P.P., Sutter, J.F., and Belkin, H.E. (1987) Evidence for Late-Paleozoic brine migration in Cambrian carbonate rocks of the central and southern Appalachians: Implications for Mississippi Valley-type sulfide mineralization. *Geochimica et Cosmochimica Acta*, **51**, 1323–1334.
- Huang, W.L., Longo, J.M., and Pevear, D.R. (1993) An experimentally derived kinetic model for smectite-to-illite conversion and its use as a geothermometer. *Clays and Clay Minerals*, **41**, 162–177.
- Huff, W.D. and Türkmenoglu, A.G. (1981) Chemical characteristics and origin of Ordovician K-bentonites along the Cincinnati Arch. *Clays and Clay Minerals*, **29**, 113–123.
- Johnson, M.J. (1984) The thermal and burial history of south central New York: Evidence from vitrinite reflectance, clay mineral diagenesis and fission track dating of apatite and zircon. Masters thesis, Dartmouth College, Hanover, New Hampshire.
- Kay, G.M. (1935) Distribution of Ordovician altered volcanic materials and related clays. *Bulletin of the Geological Society of America*, **46**, 225–244.
- Kolata, D.R., Frost, J.K., and Huff, W.D. (1986) *K-Bentonites of the Ordovician Decorah Subgroup, Upper Mississippi Valley: Correlation by Chemical Fingerprinting*. Illinois State Geological Survey, Circular 537, 30 pp.
- Leach, D.L. and Rowan, E.L. (1986) Genetic link between Ouachita foldbelt tectonism and Mississippi Valley-type lead-zinc deposits of the Ozarks. *Geology*, **14**, 931–936.
- McCarty, D.K. (1993) The three-dimensional crystal structure of rotationally disordered illite-smectite from Devonian and Ordovician K-bentonites in and around the Appalachian basin. Ph.D. thesis, Dartmouth College, Hanover, New Hampshire.
- McCarty, D.K. and Reynolds, R.C. (1995) Rotationally disordered illite-smectite in Paleozoic K-bentonites. *Clays and Clay Minerals*, **43**, 271–284.
- Méring, J. and Oberlin, A. (1967) Electron-optical study of smectites. *Clays and Clay Minerals*, 17th National Conference, Pergamon Press, 3–25.
- Milici, R.C. and de Witt, W., Jr. (1988) The Appalachian Basin. In *The Geology of North America, Volume D-2, Sedimentary Cover—North American Craton: U.S.*, The Geological Society of America, Boulder, Colorado, 427–469.
- Moore, D.M. and Reynolds, R.C., Jr. (1997) *X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd edition*. Oxford University Press, New York, 270–276.
- Nadeau, P.H., Wilson, M.J., McHardy, W.J., and Tait, J. (1984) Interparticle diffraction: A new concept for interstratified clays. *Clay Minerals*, **19**, 757–769.
- Oliver, J. (1986) Fluids expelled tectonically from orogenic belts: Their role in hydrocarbon migration and other geologic phenomena. *Geology*, **14**, 99–102.
- Plançon, A. (1981) Diffraction by layer structures containing different kinds of layers and stacking faults. *Journal of Applied Crystallography*, **14**, 300–304.
- Plançon, A. and Tchoubar, C. (1977a) Determination of structural defects in phyllosilicates by X-ray powder diffraction—I. Principle of calculation of the diffraction phenomenon. *Clays and Clay Minerals*, **25**, 430–435.
- Plançon, A. and Tchoubar, C. (1977b) Determination of structural defects in phyllosilicates by X-ray powder diffraction—II. Nature and proportion of defects in natural kaolinite. *Clays and Clay Minerals*, **25**, 436–450.
- Plançon, A., Giese, R.F., and Snyder, R. (1988) The Hinckley index for kaolinites. *Clay Minerals*, **23**, 249–260.
- Pytte, A.M. and Reynolds, R.C., Jr. (1989) The thermal transformation of smectite to illite. In *Thermal History of Sedimentary Basins, Methods and Case Histories*, N.D. Naeser and T.H. McCulloh, eds., Springer-Verlag, New York, 133–140.
- Reynolds, R.C. (1963) Potassium-rubidium ratios and polymorphism in illites and microclines from the clay size fractions of Proterozoic carbonate rocks. *Geochimica et Cosmochimica Acta*, **27**, 1097–1112.
- Reynolds, R.C. (1985) NEWMOD: A Computer Program For The Calculation Of One-dimensional Diffraction Patterns of Mixed-layered Clays. R.C. Reynolds, 8 Brook Rd., Hanover, New Hampshire.
- Reynolds, R.C. (1992) X-ray diffraction studies of illite-smectite from rocks, <1 μm randomly oriented powders, and <1 μm oriented powder aggregates: The absence of laboratory-induced artifacts. *Clays and Clay Minerals*, **40**, 387–396.
- Reynolds, R.C. (1993) Three-dimensional powder X-ray diffraction from disordered illite: Simulation and interpretation of the diffraction patterns. In *CMS Workshop Lectures, Volume 5, Computer Applications to X-ray Powder Diffraction Analysis of Clay Minerals*, R.C. Reynolds, Jr. and J.R. Walker, eds., The Clay Minerals Society, Boulder, Colorado, 43–77.
- Reynolds, R.C. (1994) Wildfire: A Computer Program For The Calculation Of Three-dimensional Powder X-ray Diffraction Patterns for Mica Polytypes and their Disordered Variations. R.C. Reynolds, 8 Brook Rd., Hanover, New Hampshire.
- Reynolds, R.C. and Thomson, C.H. (1993) Illite from the Potsdam Sandstone of New York: A probable noncentrosymmetric mica structure. *Clays and Clay Minerals*, **41**, 66–72.
- Roden, M.K., Miller, D.S., Elliott, W.C., and Aronson, J.L. (1992) The thermal history of the distal margin and interior of the southern Appalachian basin from combined fission-track and K/Ar studies of K-bentonites. *Abstract, 27th Annual Northeastern Section of the Geological Society of America Meeting 24*, no 3, 49.
- Roden, M.K., Elliott, W.C., Aronson, J.L., and Miller, D.S. (1993) A comparison of fission-track ages of apatite and zircon to the K/Ar ages of illite-smectite (I-S) from Ordovician K-bentonites, southern Appalachian basin. *Journal of Geology*, **101**, 633–641.
- Sakharov, B.A., Besson, G., Drits, V.A., Kamenava, M.Yu., Salyn, A.L., and Smoliar, B.B. (1990) X-ray study of the nature of stacking faults in the structure of glauconites. *Clay Minerals*, **25**, 419–435.
- Schedl, A., McCabe, C., Montanez, I.P., Fullagar, P.D., and Valley, J.W. (1992) Alleghanian regional diagenesis: A response to the migration of modified metamorphic fluids

- derived from beneath the Blue Ridge-Piedmont thrust sheet. *Journal of Geology*, **100**, 339–352.
- Thomas, W.A. (1988) The Black Warrior Basin. In *The Geology of North America, Volume D-2, Sedimentary Cover—North American Craton: U.S.*, The Geological Society of America, Boulder, Colorado, 471–492.
- Tsipursky, S.I. and Drits, V.A. (1984) The distribution of octahedral cations in the 2:1 layers of dioctahedral smectites studied by oblique-texture electron diffraction. *Clay Minerals*, **19**, 177–193.
- Viets, J.G., Rowan, E.L., and Leach, D.L. (1984) Composition of fluids extracted from sphalerite, galena, and dolomite in Mississippi Valley-type deposits in the mid-continent: Implications for the origin of the fluid. *Geological Society of America Abstracts with Programs* **16**, 682.

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