TEM OBSERVATIONS OF COHERENT STACKING RELATIONS IN SMECTITE, I/S AND ILLITE OF SHALES:
EVIDENCE FOR MACEWAN CRYSTALLITES AND DOMINANCE OF 2M₁ POLYTPISM

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Abstract—TEM characterization of stacking relations in I/S of expanded shale samples from the Gulf Coast and Michigan Basin was carried out to address the issues of the degree of coherency and the nature of layer stacking sequences in smectite, I/S and illite. The two-dimensional lattice fringe images obtained from this study show that cross fringes are commonly observed to be continuous over at least 3-4 layers for smectite, 6-7 layers for ordered I/S and 9-10 layers for illite-rich I/S. This demonstrates that such sequences are coherent, or at least semi-coherent (in smectite) units (MacEwan crystallites). The observations demonstrate that so-called fundamental particles are fragments of MacEwan crystallites formed primarily as a result of disaggregation along weakly-bonded smectite interlayers. However, both 0k1 and h01 reflections may coexist in selected area electron diffraction (SAED) patterns. The frequency of occurrence of the coexistence in SAED patterns decreases in the order smectite, I/S and illite for Gulf Coast samples. This is consistent with the presence of turbostratically-related interfaces in packets of all of these materials. Therefore, any given layer sequence in smectite, ordered I/S and illite may have both turbostratic and coherent interfaces. The proportion of coherently-related layers increases with increasing proportion of illite-like layers. The concept of fundamental or elementary particles is not related to layer sequences in non-disaggregated, original rocks. Indeed, it implies relations that are not valid.

The observations of this study imply that dissolution-crystallization is a dominant mechanism for the smectite-to-iltite transition. The semi-coherent stacking of smectite-like layers in smectite-rich samples implies that either a dissolution-crystallization process took place subsequent to deposition of detrital smectite or that Gulf Coast smectite is an in-situ alteration product of volcanic ash.

Key Words—2M₁, Polytypism, Coherent, Fundamental Particles, Illite, I/S, MacEwan Crystallites, Optical Diffraction Patterns, SAED, Smectite, Stacking Relations Cross Fringes, Transmission Electron Microscopy (TEM).

INTRODUCTION

The degree of coherency and the nature of layer stacking sequences in smectite, illite and mixed-layer illite/smectite (I/S) constitute two of the most controversial issues in the field of clay mineralogy. The issues in part are concerned with layer sequences as constituting: (1) coherent sequences (MacEwan crystallites); or (2) collections of incoherently-related fundamental particles.

The hypothesis of fundamental particles was proposed by Nadeau et al. (1984b, c), based on measurements of grain thickness in clay separates as obtained from a Pt-shadowing technique. This hypothesis postulated that the smectite, I/S and illite which occur in original rocks are actually aggregates of "fundamental particles." They showed that: (1) Smectite separates consist primarily of aggregates of single 2:1-layer, 10 Å thick particles, called elementary smectite layers (Nadeau et al. 1984a, b, c; Nadeau 1985); (2) Regularly interstratified R1 I/S separates consist primarily of 20 Å particles defined by two 2:1 layers called elementary illite particles (Nadeau et al. 1984a, 1984b, 1984c); and (3) Illite separates consist of 20 Å to 160 Å thick particles with a mean thickness of 70 Å (Nadeau et al. 1984a). They specifically defined a "fundamental particle" as an "individual or free" particle that gives rise to a single-crystal hk0 diffraction pattern, a hexanet. The extended sequences of layers occurring in mudstones or bentonites are thus implied to be collections of fundamental particles separated by interfaces across which the structure is incoherent.

Nadeau et al. (1984b) proposed a process of "interparticle diffraction" as an explanation of the extended one-dimensional coherent scattering units commonly
implied by powder XRD patterns of separates. The
three-dimensionally-incoherent interfaces between
fundamental particles were hypothesized to be capable
of absorbing water or organic molecules and to behave
like smectite interlayers. The interfaces between
stacked fundamental particles were theorized to be
perceived by XRD as smectite interlayers interstrati-
"icated with the non-expandable particles. Since funda-
mental particles are disarticulated in grinding and
reaggregated during sedimentation of samples onto
glass slides, reaggregation must occur randomly. Thus,
if the structural state of I/S obtained from XRD reflects
the original state in natural rocks, this concept implies
that smectite, illite and I/S particles are randomly
stacked with respect to one another as formed in such
rocks. The selected area electron diffraction (SAED)
hk0 patterns of Nadeau et al. (1984c) showed that larger
particles are always aggregates of randomly related
smaller particles in that they invariably consist of
more than one hk0 hexanet related to one another by
random rotations about c*. That is, the individual par-
ticles appeared to be at least in part turbostructurally-
related. They concluded that coherent interstratifica-
tion with crystallographic continuity across layers may
exist only in weathering products like hydrobiotite
(Nadeau et al. 1984).

Reynolds (1992) concluded that there is a direct rela-
tionship between the degree of turbostratic stacking
and proportion of expandable layers in I/S. His con-
clusion was based upon powder XRD data for original
bentonite samples that were not ground. Those data
(Reynolds 1992) suggested that, for those data, inco-
erency occurs across smectite interlayers and that
pure smectite would be completely turbostructurally-
stacked as compatible with the notion of Nadeau and
colleagues. The definition of a “coherent” unit is im-
portant in that regard. Guthrie and Reynolds (personal
communication 1995) have noted that the concept of
a coherent unit is commonly defined relative to the
size of the domain over which coherent diffraction oc-
curs. Such domains are generally much smaller for
XRD than for TEM. They reasoned that coherent XRD
is much more sensitive to the small angular misori-
entations, which are common between layers of clay
minerals. Such misorientations are more common in
low-grade clays (Peacor 1992). The term coherency is
commonly used to differentiate between layers whose
structures are oriented in ordered ways and those in
which they are randomly stacked in terms of rotation
around c*, that is, turbostructurally stacked. Ordered
stacking involves relative positions of layers which
must be related by multiples of 60°. In order for po-
lytypism to be recognized, layers must be so-stacked.
If sequences of layers diffract as units, either by XRD
or ED, then they must be coherently-related. In order
to avoid confusion, we use the term “coherency” to
refer to layers related in an ordered manner in contrast
to turbostratic stacking. This is done with the caveat
that units large enough to “diffract coherently” by ED
may not do so by XRD.

Ahn and Peacor (1986) carried out TEM studies
with clay-rich shale samples that retained original tex-
tures by using ion-milled areas of thin sections. Their
images showed that layer sequences of I/S are very
large when compared with the thickness of so-called
fundamental particles. They coined the term “mega-
crystal” for continuous arrays of 001 layers in smec-
tite-rich I/S. However, such data were insufficient to
show that adjacent layers were coherently related as
001 lattice fringes only show the sequence of layers,
and not the relative orientations of adjacent layers.

Proof of coherency between adjacent 001 layers oc-
curs where 001 lattice fringes are cross-cut by non-
001 fringes (Peacor 1992). If such non-001 fringes oc-
cur for adjacent layers, 020 (d = 4.5 Å) is the most
common due to inclusion of the 020 reflection in the
objective aperture, then those 001 layers must have the
non-001 plane in common and be coherently related.

Several TEM studies of unseparated, ion-milled
samples have shown the following: (1) at least some
sequences of illite-like and smectite-like layers are
continuous; (2) coherently-related, that is, by rotations
of n*(60°), three-dimensional translational-periodic
units, which may be referred to as MacEwan crystal-
lites; and (3) Veblen et al. (1990) observed 4.5 Å cross
fringes in addition to 001 10 Å fringes in images of
R1 I/S and R > 1 I/S of hydrothermal origin. Lind-
green and Hansen (1991) obtained single crystal hk0
SAED patterns of I/S in claystones from the North Sea
that contained individual packets 5 to 20 layers thick.
They also obtained images with 3.6 Å cross-fringes
which were continuous across several 20 Å thick lay-
ers. Ahn and Buseck (1990) obtained structure images
that defined the stacking vectors between individual
interlayers in R1 and R3 I/S of bentonites of hydro-
thermal origin. They demonstrated that the number of
coherently-related layers is consistent with MacEwan
crystallites but not fundamental particles.

As implied by Nadeau et al. (1984c), coherency is
also indicated where hk0 SAED patterns are hexanets
as required of hexagonal or pseudo-hexagonal transla-
tionally-periodic arrays. Such patterns are easily ob-
tained by spreading separates on holey-carbon TEM
mounts. Veblen et al. (1990) pointed out that caution
must be used where individual separated grains ove-

lap, which gave the appearance of a single grain. Freed
and Peacor (1992) observed ring-like hk0 diffraction
patterns in smectite-rich I/S samples from the Gulf
Coast, but with the patterns trending toward single
crystal patterns in R1 or illite-rich I/S. Smectite-rich
material appeared to be at least partially turbo-
structurally stacked, but the thickness of coherent units
increased as the proportion of illite-like layers in-
creased. They also pointed out that where crystals
have hexagonal or pseudohexagonal outlines, coherency is implied.

In summary, some TEM data for separates and all data for ion-milled non-disarticulated samples where cross fringes have been obtained, imply considerable coherency in I/S, including smectite-like interfaces. However, those data supporting MacEwan crystallites have been obtained on only very few samples of sedimentary origin and may not be representative of most I/S in mudstones and shales. Conversely the wealth of data supporting the notion of fundamental particles is based only on separates, and the relation of such grains to those occurring in original rocks is problematic.

Where layer interfaces are coherent, there may be six different relative layer positions, related by rotations of n(60°), and giving rise to polytypism (Smith and Yoder 1956). As reviewed in part by Grubb et al. (1991), numerous XRD studies have documented progressive (diagenesis-metamorphism) changes in polytypism from 1M_0 to 1M to 2M_1 in white micas. However, Grubb et al. (1991) showed that SAED patterns of illite and R1 I/S that have been unmodified since formation, invariably give diffuse, non-periodic and ill-defined reflections having k ≠ 3N. They referred to this material as 1M_a, noting that no true, completely disordered 1M_a material had yet been observed and that the poorly-defined reflections represent local ordering. That is, the poorly-defined reflections must arise from locally ordered 1M, 2M_1 or other polytypes within a largely-disordered stacking sequence. It is those reflections which lead to “cross-fringes” that can be used to specify local stacking sequences.

Ahn and Busseck (1990) observed structure images of ordered R1 I/S showing faulted 1M stacking sequences. Baronnet et al. (1993) observed structure images of biotite showing stacking faults in a 2M_1 matrix. These observations suggested that layer stacking sequences in phyllosilicates may be quite complex. They may be composed of a collection of turbostatically- and coherently-related units. Where coherently-related interfaces occur, they may be related by ordered sequences of stacking vectors, in which case specific polytypic sequences can be locally identified, or stacking vectors may display no local order, that is, 1M_a. It is very likely that there are transitional states in the well-known prograde sequence from 1M_0 to 1M to 2M_1 that consist of polytype mixtures of complex sequences and turbostatic stacking. XRD data are integrated over all sequences and only capable of detecting end members (Bailey 1988) where they occur in extended sequences in volumes large enough to give rise to significant intensity. It is essential to identify individual layers as illite-like or smectite-like. Guthrie and Veblen (1989a, 1990b; 1990) concluded through computer simulations that I/S ordering can only be imaged under overfocus conditions for planes tilted slightly with respect to the electron beam. However, an optimum underfocus condition (Scherzer) is required for imaging of cross-fringes (Veblen et al. 1990). It is very difficult to simultaneously differentiate between smectite-like and illite-like interlayers, while obtaining cross fringes. This is especially true for I/S in shales, for which contrast in I/S is observed only with difficulty (Ahn and Peacor 1989). A relatively new technique for permanent expansion of smectite-like interlayers was originally developed by Tessier (1984) and modified by Kim et al. (1995). That technique allows the identification of individual illite-like and smectite-like interlayers on the basis of differences in layer spacings.

In order to resolve the controversy regarding the contrasting notions of MacEwan crystallites and fundamental particles, it is necessary to obtain direct observations of coherency through cross-fringes using samples of sedimentary origin that are representative of sedimentary sequences. We suspect that actual layer sequences are complex assemblages of both coherent and incoherent interfaces with the proportion of coherent interfaces increasing with increasing diagenetic grade as measured by illite crystallinity. It is essential to obtain such data on samples from different grades. Stacking sequences (polytypism) can also be specified. Illite-like and smectite-like interlayers must be directly correlated with the degree of coherency and polytypism to completely define relations. We have obtained such observations for a sequence of mudstone samples from the Texas Gulf Coast. These samples represent the full range of the smectite-to-illite transition, from 20% to 80% illite from shallow to deep samples as characterized by XRD (Freed 1980, 1982; Freed and Peacor 1989a, 1989b), and that they should be representative of that classic sequence. Also samples from the much older Michigan Basin were included in the study.

**SAMPLE DESCRIPTION**

The Gulf Coast samples used in this study were kindly provided by R. L. Freed. They are mudstones or shales in the form of core cuttings from four depths (4750', 6073', 10,217' and 15,163') from the Pleasant Bayou #1 well, Brazoria County, Texas. These samples were chosen for this study because they have been characterized in detail (Freed 1980, 1982; Freed and Peacor 1989a, 1989b). They represent the “classical” clay mineral transition sequence of smectite-rich I/S to illite-rich I/S that occurs in Texas Gulf Coast shales. Freed (1980) and Freed and Peacor (1989a, 1989b) determined the illite content of the mixed-layer I/S of the four samples to be 20–25, 25, 35 and 80%. The
first two samples are from the pre-transition zone, Anahuauc Formation (Miocene), the third is from the zone in which smectite-to-illite transition occurs, Frio Formation (Oligocene), and the deepest one is from the post-transition zone, Frio Formation. Because of paucity of core cuttings from the Pleasant Bayou #1 well, we were unable to obtain enough separates for XRD studies for these samples. However, numerous XRD and TEM studies (Freed and Peacor, 1992; 1989a, 1989b) have shown that shale samples from the Zula Boyd well, DeWitt County, Texas are equivalent to those from the Pleasant Bayou #1 well in terms of overall mineralogy, smectite-to-illite transition sequence and illite percent in I/S. Because Freed made <0.2 μm separates from the Zula Boyd well available to us, one smectite-rich (40% illite, 7000', Eocene) and one illite-rich (80% illite, 12,000', Paleocene) sample from the Zula Boyd well were used for XRD. The main geologic unit is the Eocene Wilcox group. The fact that samples from two different wells were used for XRD and TEM provides legitimate reason to question the comparison. However, we emphasize that a plethora of both XRD and TEM results for Gulf Coast mudstones implies that such comparisons are valid and all TEM and XRD results on both series of samples used in this study are entirely consistent with such equality. It is precisely because both the Zula Boyd and Pleasant Bayou samples have been so completely characterized in other studies that they serve as standard materials on which further work of the type presented here is based. Nevertheless, we recognize that the use of samples from two wells calls for caution in data interpretation. One sample from the Antrim Formation (370 Ma) from the Michigan Basin was also included in this study for comparison, as representative of older, cratonic sediments. It was provided by V. Hover and it has been studied in depth by powder XRD and TEM (Hover et al. personal communication 1995) and found to be representative of cratonic Paleozoic shales in Michigan, Ohio and New York.

EXPERIMENTAL METHODS

XRD

Because of the paucity of clay separates and difficulty in preparing totally random specimens for powder XRD characterization, the Gandolfi method was used to obtain XRD patterns of randomly oriented clay minerals in order to detect the non-001 reflections that can be used to characterize polytypism. Gandolfi XRD photographs were obtained for Gulf Coast smectite-rich (7000') and illite-rich (12,000') samples from the Zula Boyd well and illite-rich material from the Antrim Formation. However, because the weak non-001 reflections could be observed only with difficulty, patterns of all samples were also obtained with the camera under vacuum in order to improve peak-to-background ratio. The two kinds of photographs taken at atmospheric pressure and vacuum (10−3 torr) respectively were identical, demonstrating that such a low vacuum did not change the structural state of smectite, I/S and illite.

TEM Sample Preparation and TEM Procedures

The five samples were expanded with L. R. White resin following the procedure of Kim et al. (1995). The three shallowest Gulf Coast samples are smectite-rich and water-sensitive. Great care was taken to avoid direct contact with water during sample expansion. Lack of reaction (spalling) to water, subsequent to expansion, is a test of the success of the expansion technique. Sticky wax-backed thin sections were prepared with surfaces normal to bedding and examined with optical microscopy and SEM. Typical areas were removed for TEM observations via attached Al washers, thinned in an ion mill and carbon coated. TEM observations were made with a Philips CM 12 scanning-transmission electron microscope (STEM) fitted with a Kevex Quantum solid-state detector and computer system. The STEM was operated at 120 kV and a beam current of 20 μA. Most images were obtained at 100,000× magnification. For one-dimensional lattice fringe imaging, an objective aperture 20 μm in diameter was used to improve the contrast and to exclude non-001 reflections. For two-dimensional lattice fringe imaging, an objective aperture 80 μm in diameter was used to include the non-001 reflections with d-values >2.5 Å. Because focus conditions are different for imaging 001 fringes and cross fringes, through-focus series of images were obtained from 100 nm underfocus to 100 nm overfocus. The through-focus technique was also necessary to obtain both images with optimum contrast in I/S ordering (overfocus) and cross-fringes (underfocus). However, because initial focus was controlled manually by minimizing contrast, small deviations from exact underfocus or overfocus numbers were inevitable. Samples were not easily degraded by the electron beam as evidenced in part by through-focus images which were all of high quality. A camera length of 770 mm and a selected-area aperture 10 μm in diameter were used to obtain SAED patterns. Since selected-area apertures are not small enough to obtain an SAED pattern from only one crystallite, optical diffraction patterns (Jiang and Peacor 1991) were derived from specific areas of TEM images where two-dimensional lattice fringe images were obtained in order to relate specific areas of TEM images to their diffraction patterns. Quantitative EDX chemical analyses were obtained in STEM mode by using a beam diameter of 50 Å and a scanning area of 300 × 300 Å. Standards and other conditions for chemical analysis were used as defined by Jiang et al. (1990).

The HRTEM observations were made with a JEOL
Table 1. Crystallographic data for identification of stacking sequences.

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1 These space group and cell parameter data arc from Bailey (1988).
2 The values in brackets are those for expanded smectite layers.

Identification of Stacking Sequences

Where layers are coherently related, that is by rotations of n(60°), it is possible to place limits on stacking vectors and to differentiate 2M1 and 1M polytypes based on two-dimensional lattice fringe images. The non-001 cross fringes have d-values and make angles with (001) that are different for some planes that are related by rotations of the n(60°), and those values can be measured. Some crystallographic relations that permit characterization of stacking vectors were developed here for 2M1 and 1M polytypes.

The SAED pattern must include c*, an orientation that is promoted by preparation of TEM samples as thin sections normal to bedding, that is, with (001) planes parallel to the electron beam. A second vector of the SAED pattern must then lie in the a*-b* plane and the rotation around c* may be caused to be a*, b* or one of their pseudosymmetrically-related, n(60°) rotation-equivalents. Although a*(b*) and its 60° rotation-equivalents have identical or nearly equal d-values, the angle between c* and 60°-rotation equivalents is different from c*/a*(b*). The d-values of vectors in the a*-b* plane and the angles between c* and such vectors, for example, c*/\(110^\circ\), are different for 1M and 2M1 polytypes.

The (020) 60° rotation-equivalents are (110), (110), (020), and (110). However, only two unique vectors exist, as (110) and (110) are related by reflection, and inversion relates (020), (110) and (110) to the remaining three. The (200) 60° rotation equivalents are (200), (130), (130), and (130). As for (020) and equivalents, only two distinct vectors exist because (130) and (130) are related by reflection. Table 1 lists d-values and the corresponding angles to c* for unique vectors for both 1M and 2M1 polytypes. The space group and cell parameter data are from 1M and 2M1 muscovites, based on Bailey’s assignments (Bailey 1988). For calculation of d-values of smectite, the c cell parameter used was 12 Å for 1M polytypes and 24 Å for 2M1 polytypes, since most smectite layers observed in this study were expanded by the resin to 12 Å. The large c value does not affect the d-values of hk0 reflections, but does affect d-values of hkl reflections. The d-values and the corresponding angles to c* for smectite layers are given in brackets for non-hk0 reflections.

Because intensities of pseudosymmetrically-related reflections differ in characteristic ways, identification of polytypes was augmented by standard 0-level diffraction patterns for orientations defined above. These included SAED patterns of 2M1 muscovite and the
XRD patterns for 1M mica given by Bailey (1988). Although intensities of the latter are not strictly analogous to intensities in SAED patterns, they provide an adequate qualitative basis for comparison.

Before describing the experimental results, it is first necessary to clarify general diffraction relations, as diagrammed for three conditions in Figure 1: (1) Single crystal diffraction pattern. Phyllosilicates are indexable on an orthohexagonal unit cell with translations $a$ and $b$ in the layers and with $a^* = \sqrt{3}b^*$. The translation $c$ defines the periodicity of layers (Figure 1a) and where the layers are coherently-related by rotations of $\pi(60^\circ)$ in a periodic fashion, a well-ordered polytype results. The diffraction pattern in Figure 1a corresponds to the 1M polytype; (2) Diffraction pattern of disordered 1Md polytypism with coherently-related layers (Figure 1b). The upper tetrahedral sheet in the mica 2:1 layer structure is staggered by $-a/3$ relative to the lower tetrahedral sheet in order to accommodate octahedral coordination. This stagger may occur randomly with respect to the three pseudohexagonal axes, leading to loss of periodicity along $c$ for the basal oxygen atoms and consequent diffuseness along $c^*$ of all reflections for which $k \neq 3N$. The periodicity of all octahedral atoms (repeating at the interval $b/3$) is not affected, and therefore the reflections for which $k = 3N$ remain sharp (Bailey 1988). However, diffuseness is also generally present in 001 reflections of SAED patterns as a result of multiple diffraction with respect to the diffuse non-001 reflections; and (3) Diffraction pattern of turbostratically-stacked layers (Figure 1c). In this case, layers are randomly stacked with respect to one another leading to loss of periodicity not only of the basal oxygen atoms but also of the octahedral atoms, with resulting diffuseness of both reflections with $k \neq 3N$ and $k = 3N$. However, the 001 reflections are affected only by $z$ atom coordinates, which remain periodic. Complete turbostratic stacking gives rise to an SAED pattern in which $hk0$ reflections occur as powder-diffraction-like circles if the electron beam is normal to the layers. Thus, diffraction patterns that include $c^*$ are cross-sections...
through cylinders and include diffuse lines parallel to \(c^*\) for both \(a^*\) and \(b^*\). Such streaks parallel to \(c^*\) are separated from the line of discrete 001 reflections by \(2a^*\) and \(2b^*\).

**EXPERIMENTAL RESULTS**

**XRD data**

Figure 2 shows Gandolfi photographs for Gulf Coast smectite-rich and illite-rich I/S from the Zula Boyd well, Texas and for Antrim Fm. illite-rich I/S. The corresponding \(d\)-values and intensities are listed in Table 2. All three materials have similar patterns. The indexing of reflections is based on Bayliss et al. (1986) and Bailey (1988). Not all reflections characteristic only of 2M\(_1\) and none of the reflections characteristic only of 1M were observed. Two out of six reflections observed for all three materials are characteristic only of 2M\(_1\), and the others are assigned to 2M\(_1\) and underlined in Table 2. The other two reflections (\(d = 4.48-4.50, 2.57-2.58 \text{ Å}\)) have \(d\)-values in common with both polytypes and their intensities are too large for 2M\(_1\) alone. We infer that there is some contribution from the strongest two reflections of the 1M polytype (Bayliss et al. 1986). These two reflections are assigned to a mixture of 2M\(_1\) and 1M in Table 2. The reason for the lack of complete sets of reflections having predictable \(d\)-values and intensities for either 1M or 2M\(_1\) polytypes is not clear on the basis only of XRD data. We give a tentative explanation below based upon the non-existence of sequences of layers sufficient to give rise to coherent diffraction patterns as observed by TEM. We also note that characteristic reflections for Antrim Fm. illite-rich I/S (\(d = 3.70\) and 2.85 Å) differ from those for Gulf Coast illite-rich I/S (\(d = 3.53\) Å and 2.85 Å). Characteristic reflections for Gulf Coast illite-rich I/S are similar to those for Gulf Coast smectite-rich I/S (\(d = 3.57\) Å and 2.84 Å). Data in Table 2 show that the 2M\(_1\) polytype may be
### Table 2. X-ray diffraction data and assignment of polytypes.

<table>
<thead>
<tr>
<th>Int.</th>
<th>d(Å)</th>
<th>hkl</th>
<th>Assign.</th>
<th>Int.</th>
<th>d(Å)</th>
<th>hkl</th>
<th>Assign.</th>
<th>Int.</th>
<th>d(Å)</th>
<th>hkl</th>
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<tbody>
<tr>
<td>35</td>
<td>4.97</td>
<td>002</td>
<td>$2M_1$</td>
<td>30</td>
<td>4.96</td>
<td>002</td>
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<td>002</td>
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</tr>
<tr>
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<td>4.49</td>
<td>020</td>
<td>$2M_1$</td>
<td>100</td>
<td>4.50</td>
<td>020</td>
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<td>020</td>
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<td>023</td>
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<td>80</td>
<td>2.58</td>
<td>130</td>
<td>$2M_1/1M$</td>
</tr>
</tbody>
</table>

1. The intensities are estimates from Gandolfi photographs.
2. The indices are based on $2M\_1$ or 1M muscovite (Bailey 1988). One reflection of Gulf Coast illite-rich I/S (d = 3.53 Å) and one reflection of Gulf Coast smectite-rich I/S (d = 3.57 Å) are indexed based on $2M\_1$ muscovite given by Grim (1968, 142).
3. The polytype assignments are based on both d-values and intensities. The characteristic reflections based on both d-values and intensities for $2M\_1$ and 1M are listed in bold (Bailey 1988; Grim 1968). The reflections with common d-values for both $2M\_1$ and 1M but with characteristic intensities for $2M\_1$ are underlined (Bayliss et al. 1986). The reflections with neither characteristic d-values nor characteristic intensities are assigned both polytypes.

The clays in the Antrim Formation and the Gulf Coast illite-rich I/S and smectite-rich I/S are dominated in all three materials with perhaps a small proportion of 1M. Since identification of the 1M polytype is based on the absence of all characteristic polytype reflections, it was not possible to determine the relative proportion of 1M based on XRD data.

**TEM Observations**

All five samples have been fully characterized by TEM. They fall into one of three categories: that is, (1) smectite-rich I/S (Gulf Coast, 4750', 6073' and 10,217'); (2) illite-rich I/S with some R1 and R2 I/S (Gulf Coast 15,163'); and (3) more highly ordered illite-rich I/S with R1, R2 I/S (Antrim Fm.). Only TEM observations for the 4,750' and 15,163' Gulf Coast and Antrim samples are described below, as representative of all samples. The other two samples from the Gulf Coast (6,073' and 10,217') are not described here because they represent intermediate states of coherency between the first (4,750') and the last (15,163') sample. The TEM data are representative of several hundred SAED patterns and TEM images taken from all five samples.

**SMECTITE-RICH I/S, I/S (4,750', GULF COAST, 20–25 ILLITE %).** Figures 3a and 4a are typical lattice fringe images of smectite-rich material. The 001 fringes have variable spacing, typically 12–13 Å. This indicates differential layer expansion by L. R. White resin that may be caused by compositional or structural heterogeneity among layers. The 001 fringes are anastomosing and wavy. The orientations of fringes change a few degrees over distances of several nanometers, resulting in difficulty in obtaining lattice fringe images over large areas. Layer terminations (dislocations) are common and subparallel packets intersect at small-angle-like boundaries. These general features duplicate the observations of Ahn and Peacor (1986) for smectite-rich I/S that had dehydrated and collapsed to layer spacings of 10 Å. However, no fringes with 10-Å spacings were observed in the smectite-rich sample of this study, suggesting the absence of illite-like layers. This observation is apparently inconsistent with XRD data that indicate the presence of 20–25% illite. Similar observations were made by Kim et al. (1995) for smectite-rich I/S. One possible reason for this inconsistency between XRD and TEM results may be caused by the different chemicals used for expansion in the two techniques, that is, ethylene glycol vs. L. R. White resin. Thus, L. R. White resin may cause expansion of high-charge smectite layers, as opposed to ethylene glycol which may not cause expansion of the same material. Similar differences were noted for low- and high-charge smectites by Vali et al. (1994). The results of this study support the idea that the illite component of such smectite-rich material is not illite.
Figure 4. Lattice fringe image and diffraction patterns of smectite-rich I/S. (a) Two-dimensional lattice fringe image of smectite showing 12- to 13-Å smectite basal fringes (near horizontal) and non-001 cross fringes (near vertical). Smectite layer terminations are common (long arrow) and subparallel packets intersect at small-angle-like boundaries (short arrow). The cross fringes are continuous over 8–9 smectite layers. The spacings of these cross fringes vary from 4.0 to 4.5 Å, and the angles between these cross fringes and 001 basal fringes vary from 62 to 90°, that is, orientations of these cross fringes are highly variable. (b) The corresponding SAED pattern shows both 0kl and h01 reflections which are diffuse both parallel and normal to c*, with a superimposed discrete 020 reflection (arrowed) corresponding to either 2M₀ or 1M; (c) Optical diffraction pattern obtained from area A of Figure 4a showing the presence of only 001 and 0kl reflections. The 001 reflections have a periodicity of 12 Å and 0kl reflections have a periodicity of 24 Å, showing that these 12-to-13-Å smectite layers are 2M polytypically-related. The indexing shows that the 0kl reflections have k = 2, that is, (020, 021) etc.; and (d) Optical diffraction pattern obtained from area B of Figure 4a showing relatively ill-defined reflections with some degree of streaking parallel to c* in both 001 and non-001 reflections.
at all. The corresponding 001 SAED patterns (Figures 3b and 4b) show 12 to 13 Å periodicity with diffuseness both parallel and normal to \( c^* \). The streaking normal to \( c^* \) was caused by variable orientation of smectite layers or packets whereas those parallel to \( c^* \) resulted from variable layer spacings.

Two-dimensional lattice fringe images were commonly obtained, as shown in Figures 3a and 4a. Figure 3a shows that cross fringes are continuous over three 12 Å smectite layers, demonstrating that the layers are related by lattice translations, that is, coherently related. The spacing of the cross fringes is 4.5 Å and the angle between these cross fringes and 001 smectite basal fringes is 90°. Since these cross fringes are perpendicular to 001 fringes, it was not possible to determine a unique stacking sequence (Table 1). Figure 4a shows that cross fringes are continuous over as many as 8 to 9 12 Å smectite layers, demonstrating that coherency may extend over a considerable number of layers. The spacings of these cross fringes vary from 4.0 to 4.5 Å, and the angles between them and 001 basal fringes vary from 62 to 90°. The 4.5 Å spacing and the 90° angle between some cross fringes and 001 basal fringes correspond to 020 of both 2M1 and 1M (Figure 4a). The spacing of 4 Å and the angle of 62° between other cross fringes and 001 basal fringes correspond to the 2M, 112 reflection (Figure 4a). The cross fringes shown in Figure 4a typically have a wavy, variable appearance, reflecting different orientations as caused by changes in stacking sequences. The variable orientations of the cross fringes in Figure 4a resulted from a coherent polytypic relationship in which 020 cross fringes change to 112 fringes over 3–4 smectite layers. The highly variable orientation of the cross fringes (Figure 4a, area B), suggests that the dominant 2M1 stacking sequence in these smectite layers is interrupted by many stacking faults. The wavy aspect of 001 fringes relates to variable orientation of layers, which affects continuity of cross fringes. The corresponding SAED pattern (Figure 4b) has both 0kl and h01 reflections, as consistent with diffraction from turbostratic interfaces in the layer stacking sequence included within the selected area aperture, in addition to diffraction leading to the coherently-related smectite fringes cross-cut by cross fringes in Figure 4a. The non-001 reflections are ill-defined, diffuse and non-periodic, and superimposed on diffuseness parallel to \( c^* \). The diffuseness parallel to \( c^* \) is attributable to random stacking, whereas the discrete reflections are produced by local 1M or 2M1 stacking. An attempt was made to index those discrete reflections on the basis of 1M or 2M1 polytypes by superimposing standard diffraction patterns over them. The correlations between standards and unknowns verified, for example, that the discrete reflection in the 0k1 row of Figure 4b (arrowed) may be indexed as the 020 reflection from either 1M or 2M1 (\( d_{020} = 4.5 \text{ Å} \), \( c^* \wedge 020 = 90° \)).

However, the positions and intensities of the discrete reflections vary significantly from one pattern to another, for example, the 020 reflection is present in one pattern and 112 is present in another for 0kl reflections. Whether or not a particular discrete reflection is present in the SAED pattern is determined by the presence or absence of a corresponding coherent diffracting unit within the selected area aperture. The coherent diffracting unit must be large enough to yield the corresponding distinct reflection in the SAED pattern, which invariably displays diffuseness parallel to \( c^* \). Ideally, the dimensions of such units can be directly measured in two-dimensional lattice fringe images by counting the number of layers cross-cut by corresponding continuous cross fringes. However, the number of coherently-related layers is not limited by the extension of cross fringes because variable layer orientation can cause absence of cross fringes (Guthrie and Veblen 1990). Therefore, the layers cross-cut by cross fringes give only the minimum number in the coherent diffracting unit that gives rise to a particular discrete reflection in an SAED pattern. Figure 4b shows the presence of an 020 reflection, and Figure 4a shows that the corresponding 020 cross fringes are continuous over 4 to 5 layers. Therefore, this number of layers represents the minimum number of coherent diffracting layers. However, other cross fringes, for example, 112, do not extend across regions sufficiently large to give rise to a corresponding distinct 112 reflection in the SAED pattern.

The SAED patterns are actually composite transforms of complex layer sequences, including different proportions of turbostratic and coherent interfaces (polytypes). The diffraction patterns of any unit is the sum of the diffraction patterns of subunits. Full interpretation of SAED patterns requires that specific diffraction relations be correlated directly with specific image characteristics. This is difficult because SAED patterns originate from areas that are large relative to the entire TEM image. That is, SAED patterns may include diffractions from several packets with slightly different orientations. Correlation was accomplished by obtaining optical diffraction patterns of those small areas of images with well-constrained features such as cross fringes, and comparison of such diffraction features with those in the SAED pattern, and especially where individual distinct reflections in SAED patterns had already been correlated with specific polytypes. The optical diffraction obtained from the relatively well-defined area A of Figure 4a displays well-defined 001 reflections showing 12 Å periodicity and relatively strong 2M, 0k reflections having \( k = 2 \) (Figure 4c), which were included in the objective aperture to give rise to the 021, cross fringes for example, \( d_{021} = 4.50 \text{ Å}, c^* \wedge 020 = 90° \) etc. Figure 4c clearly shows 24 Å periodicity in 0kl reflections (arrowed), suggesting that these smectite layers are 2M1 polytically-related.
The 020 cross fringes are of constant orientation over only four to five 12 Å smectite layers with changed orientation leading to other reflections in diffraction condition, for example, 112 etc. However, these four or five coherent layers form a packet that is sufficiently large to produce three-dimensional reflections in optical diffraction patterns. The optical diffraction pattern obtained from the ill-defined area B of Figure 4a displays relatively ill-defined reflections with some degree of streaking parallel to c* in both 001 and non-001 reflections (Figure 4d). The streaking is probably due to both random stacking and variable spacing along c* of smectite layers in area B.

The collective observations of many TEM images, of which the above-described relations are typical examples, demonstrate that lattice fringe images of smectite may have cross fringes that are continuous over 3 to 9 layers, with a mean of 3 to 4 layers. SAED patterns commonly display coexistence of both turbostratic and coherent interfaces in stacks of subparallel layers. In all cases, the lattice fringe images and SAED and optical diffraction patterns suggest that where the interfaces are coherent, the stacking vector defines a layer stacking sequence of the 2M1 polytype. However, stacking faults occur so frequently that 2M1 units are limited to 2 to 5 layers, as shown by highly variable orientations of cross fringes in lattice fringe images and diffuseness in both SAED and optical diffraction patterns. The random stacking relations give rise to the diffuse, ill-defined non-001 reflections commonly observed in SAED patterns.

ILLITE-RICH I/S (GULF COAST, 15,163’ AND ANTRIM FM., MICHIGAN). Figures 5a (Gulf Coast 15,163’) and 6a (Antrim Fm.) are typical lattice fringe images of illite-rich I/S samples. The 001 fringes are straight and have a constant spacing of 10 Å, indicating that these are 001 fringes corresponding to illite layers that were unaffected by L.R. White resin. These illite layers occur as well-defined packets with a mean packet thickness of ≈10 layers in both Gulf Coast and Antrim illite-rich I/S. The contrast in TEM images is relatively uniform. This indicates constant layer orientation of illite 10 Å layers with respect to the electron beam. Layer terminations (dislocations) are rare, but subparallel packets commonly intersect along small-angle boundaries. The corresponding SAED patterns of Figures 5a and 6a show well-defined 001 reflections with periodicities of 10 Å. Some packets of layers of both Gulf Coast and Antrim illite-rich I/S show periodic contrast differences with alternate fringes having darker and lighter contrast defining periodicities of ≈ 21 to 22 and ≈ 31 to 32 Å (Figure 7a). Such images correspond to mixed-layering of illite- and smectite-like layers. The 21-to-22 Å periodicity corresponds to R1(ISIS) and 31-to-32 Å periodicity corresponds to R2 (ISIS) I/S. The individual smectite- and illite-like layers in R1 and R2 I/S are thus unambiguously distinguished. However, the images are dominated by fringes with 10 Å periodicity and uniform contrast that are inferred to correspond only to illite-like layers. The corresponding SAED pattern of image 7a (Figure 7c) shows only 10, but not 21 or 32 Å periodicity, because most fringes in the image are illite layers and R1 and R2 I/S occur in only rather limited regions. However, the optical diffraction patterns obtained from the regions where R1 and R2 I/S were observed clearly show 21-to-22 and 31-to-32 Å periodicities (Figure 7d).

Two-dimensional lattice fringe images were also commonly obtained in both illite packets and regions with ordered I/S. Figure 5a (Gulf Coast, 15,163’) shows cross-fringes that are continuous across 12 to 13 10 Å illite layers, whereas Figure 6a (Antrim illite) shows cross-fringes across 4 to 7 10 Å illite layers. In contrast to those in smectite layers, the cross fringes in illite layers have relatively constant orientation, suggesting that polytypic stacking sequences extend over much larger areas without being interrupted by stacking faults. The spacings of cross fringes in both Figures 5a and 6a are 4.5 Å. The angles between these cross fringes and 001 basal fringes are 90°. Thus, it was not possible to determine a unique polytype. The corresponding SAED pattern of Figure 5a (Figure 5b) also shows the presence of both 0kl and h01 reflections, indicating the presence of turbostratically-related interfaces in a single stack of layers of Gulf Coast illite-rich I/S. Since the illite layers have constant orientation, there is very little diffuseness of reflections perpendicular to c*. Diffuseness parallel to c* is also much diminished relative to smectite SAED patterns, implying that polytypic stacking sequences are more extended than in smectite. Discrete non-001 reflections are also superimposed on diffuse streaks (Figure 5b). Correlation of such observed reflections with those of standard patterns shows, for example, that the discrete 0kl reflection of Figure 5b is 020. It was included in the objective aperture, giving rise to the 020 cross fringes of Figure 5a.

The corresponding SAED pattern of Figure 6a (Figure 6b) is that of a single crystal pattern with only 001 and 0kl reflections present, as consistent with the absence of turbostratic interfaces in stacking sequences of this Antrim illite-rich I/S. However, diffuseness both parallel and normal to c* is present in both 001 and non-001 reflections. The diffuseness normal to c* is caused by small variations in orientation of illite packets (Figure 6a), whereas that parallel to c* is caused by a small proportion of random stacking, with discrete reflections resulting from superimposed contributions of many different packets. The correlation of this SAED pattern with standard patterns shows that it is the c*-021 section with the 020 reflection as the strongest. It therefore gives rise to the 020 cross fringes in Figure 6a. It is difficult to determine a unique
polytype from this pattern because diffuseness parallel to $c^*$ obscures individual reflections.

Figure 5c is an optical diffraction pattern obtained from an area of Figure 5a showing that illite layers in that sample of Gulf Coast shale are 2M$_1$-polytypically stacked, as shown by 20 Å periodicity in 001 reflections. Figure 6c is an optical diffraction pattern obtained from an area of Figure 6a showing that illite layers in Antrim shale are also 2M$_1$ polytypically-re related through 20 Å periodicity in 0kl reflections. The indexing results showed that the 0kl reflections have $k = 2$, that is, they are 021 reflections.

The relations described above for Figures 5 and 6 are typical of those for illite-rich I/S in Gulf Coast and Antrim shales as demonstrated by large numbers of TEM images and SAED patterns. The lattice fringe images show that cross fringes are continuous over 4 to 13 layers with a mean of 9 to 10 layers. SAED patterns typically show that turbostratic interfaces are present in Gulf Coast illite-rich I/S, but occur much less frequently than in smectite-rich I/S. However, they are absent in Antrim illite-rich I/S. The optical diffraction patterns of all samples uniformly show that

where interfaces are coherent, illite layers are 2M$_1$ polytypically-stacked. The constant orientation of cross fringes extending over large areas, typically 9 to 10 illite layers, and diminished diffuseness parallel to $c^*$ in SAED patterns relative to those of smectite, suggest that the 2M$_1$ stacking for illite layers is much less limited by stacking faults than for smectite layers.

Cross fringes were obtained not only for smectite layers in smectite-rich I/S and illite layers in packets of only illite, but also for R1 and R2 I/S. For example, Figure 7b (Antrim Fm.) shows cross fringes transecting a sequence with R1 and R2 components. The cross fringes are continuous over at least one R1 and three R2 I/S layers. Because of variations in layer orientation relative to the electron beam, some areas where cross fringes were observed do not show contrast differences in 001 fringes typical of R1 and R2 I/S. The I/S ordering was best observed near 100 nm overfocus (Figure 7a), whereas the cross fringes were best observed near 100 nm underfocus (Figure 7b). The spacing of cross fringes in Figure 7b is 4.5 Å and the angle between these cross fringes and 001 fringes is in the range of 84 to 86°. The variation of the angle between
Figure 6. Lattice fringe image and diffraction patterns of Antrim Fm. illite. (a) Two-dimensional lattice fringe image of illite showing cross fringes (near vertical) which are continuous over 4-to-7 10-Å illite layers (near horizontal). The spacing of these cross fringes is 4.5 Å and the angle between the cross fringes and the 001 basal fringes is 90°. Illite layer terminations are rare, but subparallel packets commonly intersect along small-angle boundaries (arrowed); (b) The SAED pattern corresponding to Figure 6a as a single crystal diffraction pattern. The correlation of this pattern with standard patterns shows that this is the c*-021 section; and (c) Optical diffraction pattern obtained from Figure 6a showing illite 10-Å periodicity in 001 reflections and 20-Å periodicity in non-001 reflections, as a measure of 2M1 polytypism. The indexing showed that the 0kl reflections have k = 2, that is, 021 etc.

HRTEM Data

Although smectite layers with spacings of 12 to 13 Å were routinely observed in expanded smectite-rich samples with the CM12 TEM, they were only rarely observed with the JEOL 4000 FX HRTEM. Lattice fringe spacings observed in images of the smectite-rich sample generally ranged between 10 Å and 11 Å. The expanded smectite apparently partially collapsed in the HRTEM electron column due to beam damage consistent with the occurrence of extremely rapid deterioration of I/S, as evidenced by loss of diffraction patterns and lattice fringes. Nevertheless, it was possible to obtain two-dimensional lattice fringe images and structure images for both smectite and illite. Figure 8 is a typical two-dimensional lattice fringe image of smectite obtained at near-Scherzer focus conditions, in which cross fringes extend across three, 11 Å expanded smectite layers. It was possible to measure both the spacing of these cross fringes and the angle between the 001 basal fringes and the cross fringes. The values of \(d_{111} = 3.8\) Å, \(c^*/\gamma_{111} = 58^\circ\) are consistent with 1M polytypism. Figure 9 is a typical two-dimensional lattice fringe image of Antrim illite, in which cross fringes are continuous over 6 to 7 10 Å illite layers. The values of \(d_{300} = 2.6\) Å and \(c^*/\gamma_{200} = 85^\circ\) are consistent with 2M1 polytypism. Although rapid beam damage prevented more detailed interpre-
tation of relations, those images that were obtained displayed relations that were in agreement with those observed using the CM12 TEM.

**DISCUSSION**

**Layer Stacking Sequence**

**TURBOSTRATIC (FUNDAMENTAL PARTICLES) VS. COHERENT STACKING (MACEWAN CRYSTALITES).** The coexistence of both 0kl and h01 reflections in all SAED patterns of Gulf Coast smectite, I/S and illite suggest that there are turbostratically-related interfaces in packets of all of these materials. The question is one of frequency of such interlayers within a given layer sequence. The fundamental particle theory (Nadeau et al., 1984a, 1984b, 1984c; Nadeau 1985) implies that such turbostratic interfaces are present at all smectite-like interlayers. Thus, pure smectite is hypothesized to consist of turbostratically-related 10 Å elementary particles (corresponding to an unexpanded smectite layer); R1 I/S (50% illite) of 20 Å “illite” particles (two, 10 Å, 2:1 layers separated by an interlayer with K); and illite of fundamental particles several 10’s of angstroms in thickness. All such units are seen as “fundamental particles” as they were shown to give single-crystal hk0 SAED patterns. However, the two-dimensional lattice fringe images obtained in this study clearly show that cross fringes are commonly observed to be continuous over at least 3 to 4 layers in smectite, 6 to 7 layers in I/S and 9 to 10 layers in illite. This demonstrates that such sequences are coherent units with no turbostratic interfaces. These results, especially for smectite, are at variance with the XRD results by Reynolds (1992). He demonstrated that the incoherency occurs across smectite interlayers. Guthrie (personal communication) suggested that if adjacent smectite patterns are stacked so as to be misoriented relative to one another by a very small amount (1 degree or so), these layers appear turbostratic to X-rays, whereas they would probably still produce cross-fringes in TEM. In this sense, the cross-fringes observed in the smectite would only indicate a semi-coherent boundary with many defects. Nonetheless, the occurrence of cross fringes is still consistent with structural coherency and the degree of coherency perhaps differs for smectite and illite interlayers. The coherent units occur within much thicker stacks of layers, for which no cross-fringes may be observed. However, the numbers of coherently-related layers are minimum numbers because the absence of cross fringes does not necessarily indicate incoherent interfaces for the reasons discussed above. Furthermore, the absence of h0l reflections in SAED patterns of Antrim illite suggests, but does not prove, that whole packets are coherent units. Incoherent interfaces must be present at some expandable interfaces of smectite, as shown by the coexistence of 0kl and h01 reflections in SAED patterns, but such specific interfaces cannot be identified. The SAED patterns for Gulf Coast illite layers also suggest the presence of some turbostratic displacements in I/S and illite but with much lower frequency than in smectite. More importantly, the direct observation of continuous cross fringes across R1 and R2 units also definitively shows that the smectite-like interfaces can be coherent or semi-coherent.

The different numbers of coherently-related layers in smectite, I/S and illite imply that the frequency of occurrence of turbostratic interfaces in any given layer sequence decreases with increasing frequency of illite-like layers, with an absence of turbostratic stacking in some packets of Antrim illite (>95% illite, Hover et al. personal communication 1995). This conclusion is consistent with the observations of Freed and Peacor (1992). They showed that hk0 reflections for Gulf Coast smectite-rich I/S give hk0 ring-like SAED patterns, whereas the illite-rich I/S generally gives single crystal patterns. Such coherent units are defined as MacEwan crystallites. Their dimensions are large enough to give rise to single crystal diffraction patterns if they occur as isolated units, as shown by the optical diffraction patterns in this study.

The observed minimum thicknesses of semi-coherent or coherent units (3 to 4, 6 to 7 and 9 to 10 layers) in smectite, I/S and illite are much larger than those proposed by fundamental particle theory. This discrepancy may be reconciled if semi-coherent smectite interlayers are easily disaggregated during sample preparation. That is, units may be separated as semi-coherent smectite interlayers and may, upon reconstitution in XRD samples, be related by turbostratic interfaces. That is, coherent MacEwan crystallites may be disaggregated into separate units, as suggested by Ahn and Peacor (1986) and Ahn and Buseck (1990). The number of layers in illite MacEwan crystallites observed in this study is close to that observed by Nadeau et al. (1984a, 1984b, 1984c) and Nadeau (1985) for separates, suggesting that the illite interlayers are relatively strongly-bonded and tend not to cleave due to high interlayer charges. A potential for strong bonds is generally consistent with a higher degree of order (coherency).

Thus, the TEM data collectively demonstrate that at least the smectite, I/S and illite of this study, which
to Figure 7a, showing the pattern similar to those for illite as discussed in the text; and (d) Optical diffraction pattern obtained from the area where the R1 and R2 I/S and cross fringes were observed showing 31 to 32 Å periodicity in 001 reflections. The 001 reflection of R2 and 002 reflection of R3 are almost superimposed (arrowed).
are representative of Gulf Coast and cratonic Paleozoic illite, do not consist of elementary particles. Neither are the thick stacks of smectite-rich layers observed for mudstone samples and dubbed “megacrystals” by Ahn and Peacor (1986) only coherently-related. Rather, any given layer sequence may have both coherent and incoherent interfaces. The proportion of coherently-related layers increases with increasing proportion of illite-like layers. This is consistent with the general increase in structural order that was summarized for prograde pelite sequences by Peacor (1992). The nature of stacking sequences is not a matter of one end member vs. another (fundamental particles vs. MacEwan crystallites), but of the relative proportion and sequences of each in any given layer sequence and as a function of grade. Future studies should define the way in which sequences change and thus ultimately define their relation to significant geological variables.

We emphasize that these relations do not affect measures of the relative proportions of smectite-like and illite-like layers by XRD. The excellent correlation between XRD measures of I/S ratios and even of modes of ordering of I/S that has been observed through comparison of TEM observations and XRD data for 001 reflections (Veblen et al. 1990; Srodon et al. 1990; Jiang et al. 1990) is easily rationalized on the basis of reconstitution of layers in XRD samples at the same smectite-like interfaces that occur in original, non-disaggregated samples. Because turbostratically- and coherently-related layers differ only in x and y atomic coordinates, 001 reflections are not affected significantly.

STACKING SEQUENCES IN I/S AND THEIR DIFFRACTION PATTERNS. Where layer interfaces are coherent, the layer stacking sequence was almost invariably identified as 2M1 polytypism in smectite, I/S and illite, as defined by stacking vectors. The TEM observations are qualitatively consistent with the XRD results for all three materials, which are consistent with 2M1 as the dominant polytype. The 2M1 stacking sequence in smectite is frequently interrupted by stacking faults, as suggested by the highly variable orientation of cross fringes in TEM images and diffuseness in SAED patterns. True 2M1 stacking occurs in only 2 to 5 smectite layers. Because the nomenclature 2M1 implies a periodic array, that label cannot be applied to the stacking sequence only of two layers. However, when applied to two layers it simply implies a relative rotation of 180°. The result of such stacking sequences is an SAED pattern with non-001 (k ≠ 3N) reflections that are extremely diffuse parallel to c*, approaching the appearance of patterns of ideal 1M1 polytypism, but with some broad, diffuse reflections that are non-periodic and are the source of the cross fringes. The number of layers over which 2M1 polytypism was observed to occur without faulting increases with increasing proportion of illite-like layers. Gulf Coast illite-rich material consists of packets of two types, those that have no expandable component and those that have an expandable component and consist of variable sequences of dominant R1 and some R2 I/S and illite. Thus, such material gives rise to SAED patterns in which diffuseness is much reduced relative to that in SAED patterns of smectite and in which discrete reflections are much better defined than for smectite, but still largely non-periodic. The inferred non-periodicity in reflections is caused by the small number of layers defining coherent diffracting units. It was such diffraction patterns that were referred to as “1M0,” by Grubb et al. (1991) as they represented the maximum degree of disorder observed for illite in the earliest stages of formation, even though complete disorder was not indicated as theoretically should be the case for 1M0 polytypism, sensu strictu.

Antrim Fm. illite also occurs as two kinds of packets, with illite having no expandable component being dominant. However, packets of I/S also occur infre-
quently, and always with a relatively high degree of R1 and R2 order, that is, highly disordered sequences intermediate to those of ordered I/S and illite are rare. The larger number (9 to 10) of layers over which ordered 2M1 periodicity was observed results in sharper reflections characteristic of 2M1 polytypism are commonly observed, usually superimposed on diffuseness and other non-periodic reflections.

The general sequence is thus one in which the proportion of turbostratically-related interfaces decreases, as the proportion of illite-like layers increases. There is a concomitant increase in proportion of coherently-related layers, with such layers defining periodic 2M1 sequences of increasing length. The SAED patterns evolved from those with virtually complete diffuseness in smectite to those having discernible 2M1 periodicity in illite. With further maturation of illite to muscovite in higher grade rocks, such patterns would presumably be those of a well-ordered 2M1 polytype in most cases.

The observations of this study are at variance with powder XRD results in two significant ways: (1) 1M polytypes have been commonly reported to occur in prograde white mica sequences (Velde and Hower 1963; Maxwell and Hower 1967; Hoffman and Hower 1979; Lee et al. 1985). However, although discrete non-001 reflections were observed in XRD patterns of this study, they were not completely consistent with either 2M1 or 1M polytypism; (2) Reynolds (1992) found, using non-disaggregated samples of K-bentonite, that turbostratic stacking ubiquitously occurred at smectite interlayers. Although turbostratic stacking was observed in this study to occur with increasing frequency at lower grades, some degree of coherency was commonly observed at smectite interlayers. Thus the XRD data and TEM data appear to be irreconcilable. In addition to the reason described above, there may be another factor to consider. That is, the TEM observations are directly obtained from individual layer sequences for which ordering of coherent sequences occurs only over a few layers, and therefore coherent interference for X-radiation is limited. That is, a few coherent layers that are 2M1 polytypically-related are not sufficient to produce characteristic reflections in XRD patterns. On the other hand, XRD patterns represent the transform of a large volume of material and such transforms are the sum of the highly variable individual transforms of each sequence. Therefore, we tentatively note that the XRD patterns observed for Gulf Coast and Antrim samples in this study display 2M1-like characteristics, but without full likeness, as an expression of the tendency for 2M1 polytypism. The XRD and TEM results are thus compatible.

There is an apparent tendency to infer that illite must occur as 1Md, 1M or 2M1 polytypes in extended layer sequences and therefore, that XRD patterns must display all of the discrete reflections of one polytype or another. However, the TEM observations of this study show that layer sequences are not discrete and well-ordered. The diffraction patterns are thus complex composites of infinitely variable sequences, but sequences that have local ordering. The XRD patterns have neither the full characteristics of 1M nor 2M1 polytypism.

Prograde Sequences of Polytypes: 1M,, to 2M,, with No 1M

White mica polytypes have been thought to progress from 1M to 1M to 2M1 polytypes ever since the pioneering work of Yoder and Eugster (1955). Much research has demonstrated, on the basis largely of identification of polytypes by powder XRD, that the 1M polytype occurs intermediate to 1Md and 2M1 polytypes in prograde sequences (Velde and Hower 1963; Maxwell and Hower 1967; Hoffman and Hower 1979; Lee et al. 1985). The rarity of observation of 1M polytype sequences in this study, as compared with common 2M1 polytypism, is at variance with the idea that 1M polytypism occurs commonly in transitional white micas. However, Grubb et al. (1991) noted that, based on a survey of all SAED patterns from a wide variety of dioctahedral clays obtained in the TEM laboratory at the University of Michigan, no SAED patterns showing well-defined 1M reflections could be found. That is consistent with the results of this study.

The occurrence of the 1M ordered polytype as an Ostwald-step-rule-like intermediate transitional phase from the 1Md polytype to the stable 2M1 polytype requires that the 1M polytype structure be transitional. However, the ubiquitous occurrence of 1M as the stable polytype in trioctahedral micas is a reflection of polytype stability as a function of composition, and therefore in minor variations in structure, but not as an intermediate stage en route to the 2M1 polytype. There is no clear crystal chemical rationalization for such an intermediate state. Prograde sequences of polytypes may generally involve increasing perfection of stable 2M1 sequences, rather than transition from 1M to 2M1 polytypism. However, full resolution of this question must rely on research on full sequences for which both XRD and TEM data are fully available.

S-I Transition Mechanism

The observations of this study have important implications for the mechanism of the transition of smectite to illite. Several models have been proposed that differ in one way or another, but they generally can be classified as one of two types: (1) Successive replacement of individual layers of smectite by illite layers, a reaction that may be referred to as solid-state, even though H2O is a component and perhaps mediates the reaction locally. Such a mechanism was implied by the study of Hower et al. (1976); and (2) Dissolution of smectite, transport of reactants via fluids and precipi-
tation of neoformed illite. Such a process is generally associated with hydrothermal fluids, as in Salton Sea sediments (Yau et al. 1987). Various "hybrid" mechanisms involving local dissolution and precipitation have been presented by Nadeau et al. (1985) and Ahn and Peacor (1986).

Reactions that occur by solid state mechanisms involve local bond breaking, diffusion and bond formation in which the reactant and product 2:1 layers are virtually identical structurally, but with slight differences in composition (and thus in atom positions). Thus, there is an implied memory for orientation of structure of individual layers. However, the data of this study show that relative orientations of layers change with progressive diagenetic grade, both with respect to increasing proportion of coherent layers and with increasing order in polytypic stacking sequences within coherent units (stacks of coherently-related layers). Although not all layers need change orientation, such relations require that the relative orientations of a large proportion of layers must change significantly with increasing grade toward translationally-periodic coherent sequences. Even changes in stacking vectors, in the absence of high stress, must involve major changes in structure which can be accommodated by dissolution, transport and neocrystallization. Although the mechanism of Ahn and Peacor (1986), which hypothesized progressive growth in illite within a smectite matrix, is also consistent with such relations. Such processes are clearly consistent with the formation of neoformed MacEwan crystallites. Conversely, it has not been proven that random, progressive replacement of illite layers within a smectite framework, or even replacement of two smectite layers by IS, must occur with a "memory" for structure orientation of the replaced layer(s). Although lack of mutual orientation seems unlikely, it cannot be dismissed. In any event, the relations described in this study establish constraints with respect to which models of the smectite-to-illite transition in shales must be consistent.

Origin of smectite coherent interfaces

Smectite that originates by direct replacement through alteration of some primary silicate may have layers that are coherently related. For example, Banfield et al. (1991) observed cross fringes in lattice fringe images of smectite that was a weathering product of pyroxene and plagioclase. Such coherency would be normal where atoms are progressively added in low energy states during initial crystallization. Smectite commonly forms through alteration of volcanic glass during diagenesis. The coherent layer sequences for smectite are thus consistent with such an in-situ origin.

Conversely, smectite may originate through terrestrial weathering and be subsequently transported, probably as separates, as implied by observations of "elementary" particles. Flocculation and sedimentation of such layers would presumably give rise to turbostatically-related layers. Such relations would seem to be at variance with the degree of coherency observed in this study. However, that is not necessarily the case because Clauer et al. (1990) showed, based on a stable isotope study of smectite occurring in near-surface marine sediments, that detrital smectite had evolved to smectite occurring as lath-like grains through dissolution and crystallization. Likewise, Buatier et al. (1989) demonstrated that dissolution of smectite and precipitation of glauconite occurred near the water/sediment interface. It is therefore possible that randomly-oriented detrital smectite may have undergone post-sedimentation modification, as is consistent with the high proportions of interlayer K found by Freed and Peacor (1992). Thus, the coherency observed for smectite does not unequivocally point to a single origin, although it does provide constraints.

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