

A COHERENT TEM- AND XRD-DESCRIPTION OF MIXED-LAYER ILLITE/SMECTITE

GEORGE D. GUTHRIE, JR.¹

Department of Geology, Western Michigan University, Kalamazoo, Michigan 49008, U.S.A., and Geology and Geochemistry Group, Los Alamos National Laboratory, P.O. Box 1663, MS D462, Los Alamos, New Mexico 87545, U.S.A.

ROBERT C. REYNOLDS, JR.¹

Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755, U.S.A.

ABSTRACT

We present a model for the low-charge (smectite?) layers in mixed-layer illite/smectite based on an integration of observations from transmission electron microscopy (TEM) and powder X-ray diffraction (XRD). This model is an attempt to account for the apparent discrepancies in the structural descriptions based solely on one technique or the other, in which the low-charge interlayers appear to be coherent interfaces by TEM but incoherent interfaces by XRD. In our model, the low-charge boundaries between adjacent 2:1 layers are semicoherent owing to rotational disorder (*i.e.*, they are turbostratically stacked), but the degree of rotational disorder is limited. Such a model is consistent with both TEM and XRD observations and with an intuitive model of the interlayer-site occupancy: if a low-charge interlayer must have approximately $1/4$ to $1/3$ of the total sites occupied to satisfy charge balance, then the rotational disorder must be less than $\sim 10\text{--}15^\circ$.

Keywords: illite, smectite, X-ray diffraction, transmission electron microscopy, mixed-layer I/S.

SOMMAIRE

Nous présentons un modèle pour expliquer la présence de couches de faible charge électrostatique (à aspect smectitique?) dans des interstratifiés de type illite-smectite, fondé sur une intégration d'observations provenant de microscopie électronique par transmission et de diffraction X. Il s'agit d'expliquer les discordances apparentes dans les descriptions de la structure utilisant seulement les données de l'une ou l'autre de ces techniques; les interfaces à faible charge semblent être cohérentes selon l'évidence en microscopie électronique par transmission, mais incohérentes en diffraction X. Selon notre modèle, les interfaces à faible charge entre couches 2:1 adjacentes seraient semi-cohérentes à cause d'un désordre d'empilement dû à une rotation (empilement dit turbostratique), mais le degré de rotation serait limité. Un tel modèle rend compte des données obtenues par les deux méthodes, et concorde avec un modèle intuitif de l'occupation des sites inter-feuillets. Si le site inter-feuillet a une occupation d'environ $1/4$ à $1/3$ du total des sites disponibles pour satisfaire l'électronneutralité, le désordre de rotation doit être inférieur à $\sim 10\text{--}15^\circ$.

(Traduit par la Rédaction)

Mots-clés: illite, smectite, diffraction X, microscopie électronique par transmission, interstratifié I-S.

INTRODUCTION

Transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) are both ideally suited for the characterization of fine-grained materials. Where the two techniques are used together, they offer unique insights into both specific structural features of individual unit cells and the average structural state of millions of unit cells. Consequently, XRD and TEM have been used extensively to investigate the structural state of smectite and mixed-layer illite/smectite (I/S).

For some aspects of mixed-layer I/S, observations based on the two techniques have led to a consistent

model: 1) the number of 2:1 layers per crystallite in the c^* direction is small for pure smectite and larger for illite; 2) the size of 2:1 layers in directions normal to c^* for both minerals is large; 3) after sample preparation, the 2:1 layers in mixed-layer I/S are parallel, with at least two types of interlayer (high charge and low charge) in sequences ranging from random to ordered, and 4) different types of stacking sequences are present for 2:1 layers within illite packets (*i.e.*, within sequences of high-charge interlayers).

One aspect of the structure, however, remains poorly understood: what is the structure of the low-charge-interlayer region? In this paper, we present a model for

¹ E-mail addresses: gguthrie@lanl.gov, robert.c.reynolds@dartmouth.edu

mixed-layer I/S that is based on an integration of observations made by XRD and TEM. This model assumes that some interlayers in mixed-layer I/S are expandable in water and ethylene glycol (so-called low-charge interlayers), whereas others are not (so-called high-charge interlayers). It also assumes that the structure of mixed-layer I/S is largely determined by the spatial relationship of 2:1 layers (the structure of which is similar, at least to a first order, to the structure of 2:1 layers in micas). The spatial arrangement of the 2:1 layers exerts a strong control on the distribution of cations, water, and other molecules within the interlayer region.

In this model, both expandable and non-expandable layers are centered at the midpoint of the interlayers. In other words, a layer consists of 0.5 octahedral sheet – tetrahedral sheet – interlayer – tetrahedral sheet – 0.5 octahedral sheet. We refer to the interlayer regions of expandable and non-expandable layers as *low-charge interlayer regions* and *high-charge interlayer regions*, respectively. We resort to this description in order to avoid the debate initiated by the classic papers by Nadeau and coworkers (1984a, b, c): are the low-charge interlayers in mixed-layer I/S to be considered smectite or grain boundaries between fundamental particles of illite crystals? In our model, we develop a geometrical description that is applicable to either point of view. In addition, we treat these interlayer regions as interfaces between two adjacent 2:1 layers. Both low-charge and high-charge interlayer regions are interfaces, *i.e.*, the term *interface* is not meant to imply a boundary between different phases or minerals.

Our main goal is to begin a description of the structure of the low-charge interlayer region by describing the separation and the translational or rotational relationship of the adjacent 2:1 layers. In this paper, we discuss the information that XRD and TEM can provide with respect to the structural state of mixed-layer I/S, with an emphasis on the ability of each technique to address these two aspects of the relationship between 2:1 layers adjacent to a low-charge interlayer region (a smectite interlayer?).

SEPARATION OF 2:1 LAYERS

Most XRD and TEM studies of mixed-layer I/S have focused on the detection of low-charge layers, *i.e.*, on the stacking sequence of I and S layers. XRD characterization of mixed-layer I/S is widely practiced and is discussed in detail in a large number of sources (Reynolds 1967, 1980, Moore & Reynolds 1989). In short, low-charge layers can be readily detected by XRD because of their expandability, and XRD studies have extensively documented that XRD samples of mixed-layer I/S contain sequences of expandable and non-expandable layers. Because of its high vacuum, TEM examination causes the dehydration and, hence, the collapse of expanded (low-charge) layers, making them more difficult to detect. Nevertheless, sequences of low-

and high-charge layers have been documented by TEM using either a vacuum-resistant expanding agent (*e.g.*, Vali *et al.* 1994, Dong *et al.* 1997) or phase-contrast imaging (Guthrie & Veblen, 1989b, Ahn & Peacor 1989, Veblen *et al.* 1990) combined with novel focusing techniques (Guthrie & Veblen 1989a, 1990). These studies are consistent with XRD observations and show that the I/S layer sequence inferred by XRD is present in bulk samples as prepared for TEM.

TEM and XRD studies of the layer sequence in mixed-layer I/S provide important constraints on the structure of the low-charge layers: the spacing between octahedral sheets is 0.95–1.00 nm for dehydrated samples and expands as H₂O enters the interlayer region [*e.g.*, to ~1.25 nm at low to intermediate P(H₂O)]. This simple observation constrains the structure of these low-charge interlayer regions, provided one assumes that the topology of the 2:1 layers remains unchanged (to a first order) by hydration state, and is similar to the topology of the 2:1 layers in talc–pyrophyllite and phlogopite–muscovite. The remaining uncertainty in the structure of this region, then, relates to the translational or rotational relationship between the 2:1 layers and the arrangement of atoms within the interlayer region.

ORIENTATION RELATIONSHIP OF 2:1 LAYERS ACROSS A LOW-CHARGE INTERLAYER REGION

Interfaces between crystals are often described with respect to the degree of coherency of the structures on either side. A coherent interface is one along which the structures of both materials are sufficiently alike and properly oriented to allow a perfect fit. Typically, the coherency of structures is discussed at the level of lattices; hence, a coherent interface occurs where the lattices on either side of the interface have identical dimensions and appropriate orientations (*i.e.*, they match up; Fig. 1a) (see Putnis 1992, p. 333–338). A coherent interface contains no lattice defects, and it possesses two-dimensional symmetry. In addition, the strain energy associated with the interface is low or zero. In contrast, an incoherent interface occurs where the lattices on either side have very dissimilar dimensions or orientations (or both). The intermediate case is a semicoherent boundary, in which there is partial match of the lattices on either side (Fig. 1b). A semicoherent boundary contains defects that accommodate excessive stress associated with the mismatch between the lattices (which, in turn, implies a mismatch between the structures). (Strain energy in a structure results where atoms are displaced from their normal equilibrium positions, so a stressed structure has a higher strain energy than an unstressed one. Lattices cannot have strain energy because a lattice is an imaginary array of points. But if two lattices are mismatched, their associated structures also must be mismatched.)

To relate this discussion of the coherency of boundaries to mixed-layer I/S, one must simply consider the

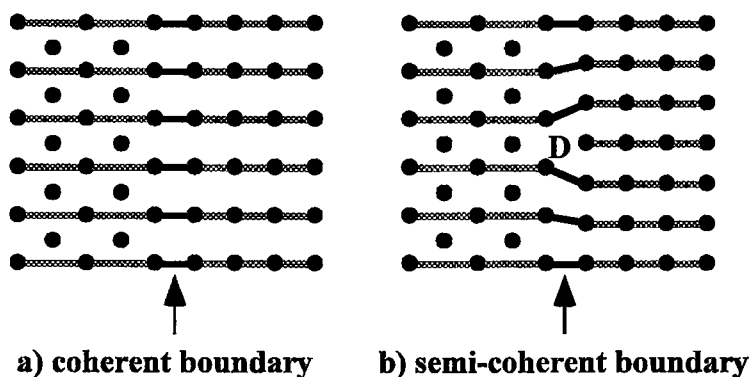


FIG. 1. Schematic diagram of an interface between two lattices illustrating the difference between coherent and semicoherent boundaries. Dislocations (D) are required along the semicoherent boundary owing to lattice mismatch.

interlayer sites (I-sites) formed by the juxtaposed hexagonal or ditrigonal rings (hereafter referred to as ditrigonal rings) in the basal plane of oxygen atoms of the 2:1 layers (Fig. 2). If two adjacent 2:1 layers are oriented such that all of the ditrigonal rings are perfectly juxtaposed across the interlayer, then all of the I-sites would be present (occupiable), and the interface between the 2:1 layers would be coherent.

Pure translation (without rotation) of one 2:1 layer relative to the other can result in a loss of coherency between the two layers. As one of the 2:1 layers is shifted relative to the other, the I-sites between the two sheets of basal oxygen atoms become smaller until,

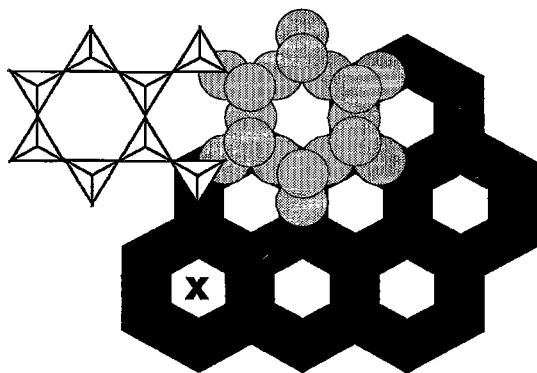


FIG. 2. Schematic diagram of a tetrahedral sheet from a 2:1 layer, showing space filling and polyhedral representations and a generalized black-and-white schematic (as used in Fig. 3 in a reduced form). "X" marks the center of the open ditrigonal ring that, when juxtaposed with a ring from the tetrahedral sheet on an adjacent 2:1 layer, forms an interlayer site.

eventually, cations no longer fit. This will be particularly true for large cations, such as K^+ , for which entry accompanied by even small shifts of the 2:1 layers from the equilibrium relationship will be energetically unfavorable. Where the samples are expanded by a polar molecule, the larger separation of the charged 2:1 layers reduces the electrostatic forces holding the 2:1 layers in their equilibrium position, potentially allowing random translations of 2:1 layers. Occupation of the I-sites by molecules lacking spherical symmetry (*e.g.*, linear molecules) might also cause shifting of 2:1 layers such that the ditrigonal rings are no longer juxtaposed. These two factors are not significant for the dehydrated and collapsed samples observed by TEM. Finally, cations of different size (*e.g.*, K^+ and Na^+) will result in different amounts of layer offsets (Bailey 1984), but the impact on coherency due to this shift is likely to be minor relative to the impact due to rotation. Hence, pure translation (without any rotation) is not addressed in the model below.

Rotation (which also, of course, inherently involves translation) can result in a loss of coherency between two adjacent 2:1 layers. As one of the 2:1 layers is rotated about c^* relative to the other, some of the ditrigonal rings will remain juxtaposed whereas others will not (*i.e.*, some I-sites can be occupied by large cations, but some cannot) (Figs. 3a–c). At rotations of 0° or multiples of 60° , the mismatch between the ditrigonal rings is zero. At small degrees of rotation, there are large areas containing I-sites that can be occupied by cations (*e.g.*, white region in Fig. 3b) separated by areas that cannot be occupied by cations. Within regions of occupiable I-sites, the 2:1 layers would have a coherent boundary, but within regions of unoccupiable I-sites, the 2:1 layers would have an incoherent boundary; taken as a whole, the interface would be semi-coherent.

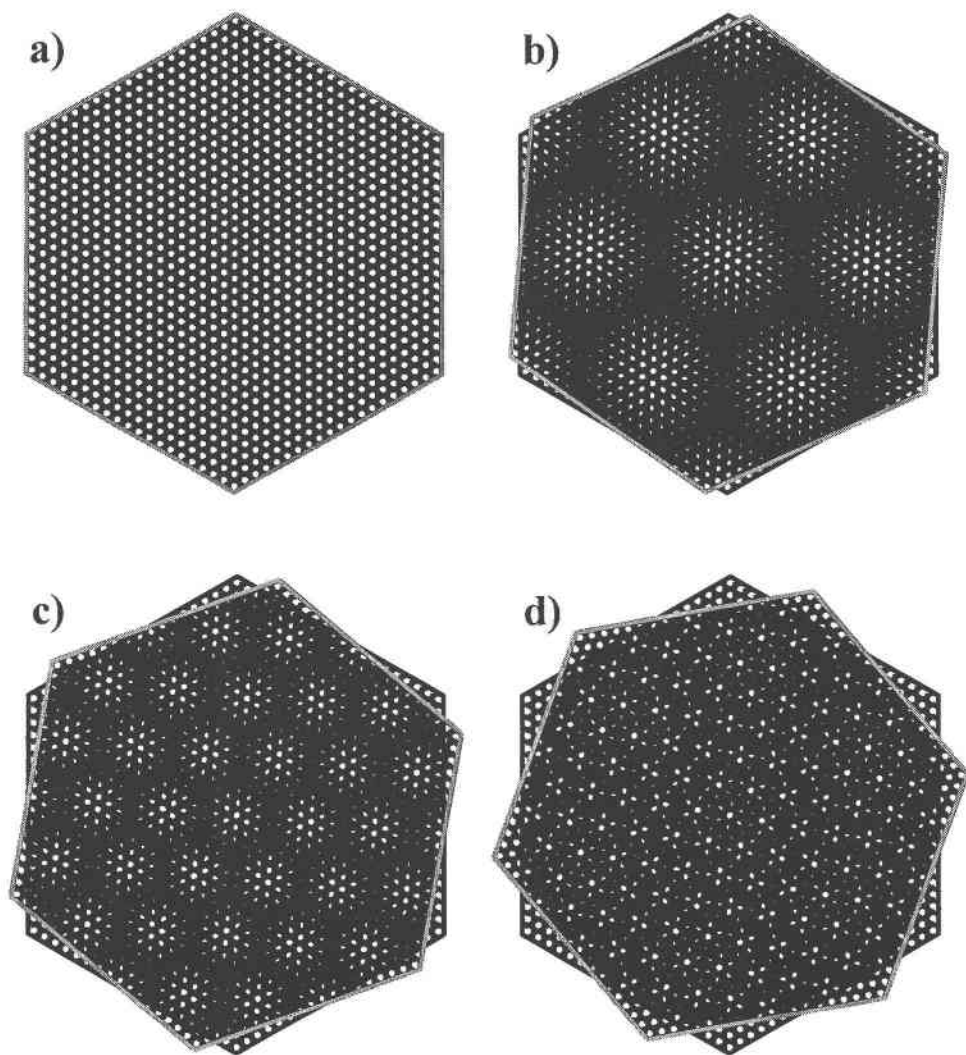


FIG. 3. Rotational Moiré patterns formed by the ditrigonal rings in the two sheets of basal oxygen atoms as the top sheet is rotated clockwise relative to the bottom sheet by 0° (a), 6° (b), 9° (c), and 24° (d). Bright regions correspond roughly to interlayer sites sufficiently large to contain cations.

For small rotations, these regions of occupiable I-sites assume a repeating pattern along the interface, forming a rotational Moiré pattern with a repeat dimension that can be calculated by the simple formula:

$$d_{\text{RM}} = \frac{d_{\text{lattice}}}{2 \sin\left(\frac{\beta}{2}\right)} \quad (1)$$

in which d_{RM} is the spacing of the rotational Moiré pattern, d_{lattice} is the spacing of the two lattices producing

the Moiré pattern (*i.e.*, the lattice formed by the centers of the ditrigonal rings), and β is the angle by which one lattice is rotated relative to the other (Williams & Carter 1996). As the degree of rotation increases, the “islands” of occupiable I-sites become smaller (compare Figs. 3b, c) but more closely spaced. Although the size of the islands becomes smaller upon rotation, the net result is that the fraction of occupiable area within the interlayer region remains fixed over a limited range in rotation. The area of one unit cell of the rotational Moiré pattern can be determined from Eq. 1:

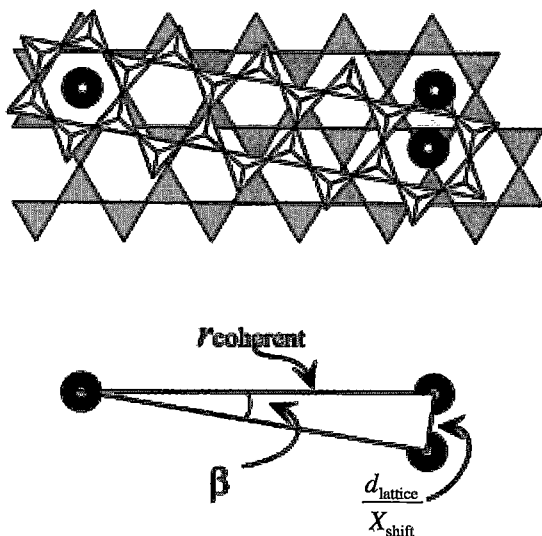


FIG. 4. Schematic diagram showing how rotation of 2:1 layers changes the size of interlayer sites. On left, the two ditrigonal rings are perfectly juxtaposed, and the interlayer site is roughly full size. Moving to right, rings are shifted relative to one another, and the interlayer site decreases in size. The shift of one ring relative to the other (X_{shift}) is a function of the rotation angle (β) and the distance from the perfectly juxtaposed rings (r_{coherent}).

$$A_{\text{RM}} = \frac{d_{\text{RM}}^2}{\sin(60^\circ)} = \frac{d_{\text{lattice}}^2}{\sin(60^\circ) \left(2 \sin\left(\frac{\beta}{2}\right) \right)^2} \quad (2)$$

The size of the occupiable interlayer regions can be determined from:

$$r_{\text{coherent}} = \left(\frac{d_{\text{lattice}}}{X_{\text{shift}}} \right) \left(\frac{1}{2 \sin\left(\frac{\beta}{2}\right)} \right) \quad (3)$$

where r_{coherent} is the radius within which the rotational mismatch is sufficiently small to allow the I-sites to be

occupied, and $\frac{1}{X_{\text{shift}}}$ defines the maximum fraction of

d_{lattice} by which one ditrigonal ring can be shifted away from its opposing ring and still leave a sufficiently large I-site (Fig. 4). In other words, the areas of one occupiable island in the interlayer ($A = \pi r_{\text{coherent}}^2$) and one rotational Moiré unit cell are both functions of

$\left[2 \sin\left(\frac{\beta}{2}\right) \right]^{-2}$, meaning that the ratio of the two is not a function of the rotation angle β , at least up to the angle

at which r_{coherent} approaches the lattice parameter a (~ 0.52 nm). At rotations above this angle, r_{coherent} is smaller than a , and the area of the occupiable region is no longer approximated by $\pi r_{\text{coherent}}^2$ because the occupiable islands disappear (Fig. 3d). The angle at which this occurs is discussed in the Conclusions.

One can solve for specific values of X_{shift} for a given fraction of occupiable interlayer sites. For $\frac{1}{4}$ occupiable I-sites, X_{shift} has a value of $\sqrt{\frac{\sqrt{3}\pi}{0.25 * 2}}$, or 3.30; for $\frac{1}{3}$ occupiable I-sites, X_{shift} has a value of 2.86.

Among the implications of the above model, (1) the distribution of occupied interlayer sites is a function of rotation angle, and (2) cations will not be randomly distributed, but rather will be clustered into islands within the interlayer region. This may be particularly true for larger cations (e.g., K^+ and Rb^+). The distribution of cations (and molecules of H_2O) within the low-charge interlayer region will have a profound effect on the electrostatic energy holding the 2:1 layers together and on the strain energy associated with the boundary. Hence, the rotational relationship between adjacent 2:1 layers is an important parameter to measure in the characterization of low-charge layers in mixed-layer I/S.

ROTATIONAL RELATIONSHIP BASED ON TEM

In TEM, interparticle boundaries can be observed as two-dimensional projections when viewed along the boundary. A typical approach in interpreting the coherency of the boundary relies on high-resolution TEM (HRTEM) images, also called lattice-fringe images or phase-contrast images. Phase-contrast images result when a lens is used to recombine the diffracted electron intensity with the undiffracted electron beam to form an image. Phase differences between the diffracted and undiffracted beams result in constructive or destructive interference and, hence, light and dark regions. Where the material being imaged is crystalline, the diffracted electron intensity occurs in discrete beams that, if recombined with the beam of undiffracted electrons, form an image containing periodic fringes with a primary repeat determined by the repeat of the lattice. Detailed information on image formation in a transmission electron microscope can be found in numerous sources, including Spence (1988) and Buseck (1992).

Phase-contrast images can be used to assess the relative coherency of two adjacent structures by noting the behavior of lattice fringes as they approach and cross the interface. Along a coherent boundary, lattice fringes from one material will extend across the interface and into the other material. Semi-coherent boundaries result in images in which most of the fringes cross the boundary, but occasional edge dislocations (seen as extra fringes on one side) occur (Smith & Barry 1988, p. 494).

Finally, no fringes appear to extend across incoherent boundaries.

The determination of the degree of coherency by TEM is limited by several factors. First, the field of view in a high-resolution TEM image generally includes at most several tens of unit cells along the boundary, and any dislocations that do not occur within the restricted area of view are not observed. Consequently, a semi-coherent boundary may appear to be coherent as a result of an insufficient viewing area. Second, TEM images are projections through numerous unit cells (generally 10–50). Hence, an edge dislocation may occur within the plane of the TEM specimen, and edge dislocations in this orientation cannot be seen, thus making a semi-coherent interface appear coherent. Third, the structures of the two materials on either side of the boundary must both be oriented close to a zone axis in order to produce a lattice-fringe image, so the absence of fringes within a field of view does not necessarily indicate an incoherent boundary. It may indicate improper specimen orientation. Fourth, the orientation tolerances within which fringes will be produced may be several degrees. For example, we demonstrated that significant fringes will arise from 0k0 reflections of dioctahedral 2:1 layer silicates even where the structure is tilted away from perfect orientation by up to 4–6° (perhaps more) (Veblen *et al.* 1990). If one assumes that these calculations are valid for fringes generated by solitary 2:1 layers, two adjacent 2:1 layers may be rotationally disordered by up to 8–12° (± 4 –6°) and still give rise to “cross fringes,” which would be interpreted as evidence of a coherent boundary. As discussed above, rotational disorder of a few degrees results in a semicoherent boundary made up of both coherent and incoherent regions.

Many published high-resolution TEM images of mixed-layer I/S contain no cross fringes, but only fringes associated with 00l reflections. As noted above (reasons 1 and 3), the absence of non-00l fringes provides no constraints on the nature of the coherency along a low-charge interface between 2:1 layers.

Several images published in TEM studies of samples of mixed-layer I/S (*e.g.*, Ahn & Buseck 1990, Veblen *et al.* 1990, Dong *et al.* 1997) do show cross-fringes from non-00l reflections extending across large numbers of layers. Most of these images were obtained at or near the Scherzer focus, which produces HRTEM images that most closely reflect the material's structure (*i.e.*, white regions correspond to low electron density and *vice versa*). However, at the Scherzer focus, low- and high-charge layers are not easily distinguishable (Guthrie & Veblen 1989a, b, 1990), so the presence of low-charge layers cannot be determined readily from such images. Nevertheless, because the cross fringes in these images extend across tens of 2:1 layers (or more) in some cases, it has been assumed that statistically some of these layers must be low charge, on the basis of the proportion of low-charge layers in each sample. Hence, these types of images are generally interpreted as an

indication that at least some low-charge interfaces between 2:1 layers are coherent. Nevertheless, as noted above, the presence of cross fringes allows for the low-charge interfaces to be semicoherent with misalignment of the opposing ditrigonal rings by up to several degrees of rotation (reasons 4 and 1).

Selected-area electron-diffraction (SAED) data obtained while looking down the c^* axis are also consistent with a model in which there is a small degree of rotational disorder within some packets of mixed-layer I/S. Veblen *et al.* (1990) showed two SAED patterns down the c^* axis from a sample of hydrothermal R1 I/S. The pattern that they interpreted as arising from turbostratic stacking (Biscoe & Warren 1942) shows higher intensities in the diffraction ring over several arcs of about 5–10°, indicating that many of the layers contributing to the diffraction in this ring are oriented within less than ~10° of one another. A second SAED pattern, which Veblen *et al.* attributed to non-turbostratic stacking, also shows two additional sets of diffraction spots that are rotated ~3.5° and 6–7° from the main set. In other words, both SAED patterns are consistent with a model in which the 2:1 layers across a low-charge interlayer region may have a limited rotational misalignment relative to one another.

These SAED observations on the low-charge interlayer regions in I/S are consistent with numerous observations made on pure smectite. Some of the earliest TEM studies on clays showed SAED data from pure smectite that support a model in which adjacent 2:1 layers in a turbostratically stacked smectite are within ~10–15° rotation of one another. For example, Mering & Oberlin (1967) reported several SAED patterns of samples prepared from dilute aqueous suspensions of smectite, which produce well-oriented specimens composed of small numbers of 2:1 layers along c^* . One SAED pattern of a 2-layer thick Na-saturated nontronite crystallite (their Plate 9) shows two sets of $hk0$ spots rotated by ~6°, and an SAED pattern from a thicker crystal of the same material (their Plate 10) shows several sets of spots with rotations of ~5° and ~7.5°. This interpretation of the SAED data is supported by a bright-field image (viewed down c^*) from one crystallite of this material (their Plate 3b). This image contains a Moiré pattern with a repeat of about 12 nm, corresponding to a rotational misalignment of 2.5° for the (100) planes ($d_{100} = 0.52$ nm) and 2.1° for the (020) planes ($d_{020} = 0.45$ nm). Mering & Oberlin reported similar SAED data for Na-saturated Wyoming bentonite; their Plate 6 shows several sets of spots, four of which are related by rotations of ~6.5°, ~7°, and ~8°. Finally, their SAED pattern of Na-saturated montmorillonite from Camp Berteaux shows the beginnings of a “ring” pattern, but within the ring are arcs of intense diffraction that span ~14°, implying that many of the 2:1 layers in this sample are within a narrow range of rotational misalignment. Güven (1973) presented similar observations for montmorillonite samples from Wyoming and Camp

Berteaux, and he noted that the crystallites have preferred azimuthal orientations, on the basis of the presence of arcs (instead of spots) in the diffraction patterns.

These TEM observations on mixed-layer I/S and smectite provide important insight into the nature of stacking that may exist across a low-charge interlayer region: a turbostratically stacked set of 2:1 layers may, in fact, have a rotational misalignment within a fairly narrow range. In other words, the turbostratic stacking is not entirely random.

The reason for this narrow range of rotational misalignments may relate to constraints imposed by the need for $1/4$ to $1/3$ occupancy of the interlayer by large cations. As discussed above, for small angles of rotation, the fraction of available I-sites is independent of rotation angle, but (as discussed below in the Conclusions) for large angles of rotation, the fraction of available I-sites strongly depends on rotation angle.

ROTATIONAL RELATIONSHIP BASED ON XRD

Theoretical considerations

The rotational relationship of adjacent 2:1 layers can only be assessed with XRD by evaluating the non-00l reflections. If present, these reflections would indicate that the 2:1 layers adjacent to a low-charge interlayer region are sufficiently oriented relative to one another to produce constructive interference of the diffracted beams. This constructive interference can be destroyed by expansion of a low-charge layer or by rotational misalignment of the 2:1 layers.

Visualize a coherent stack of four illite layers in the 1M orientation. The diffracting planes (*hkl*) are aligned for all layers, and such a stack, rotated throughout all possible orientations, would produce the three-dimensional XRD pattern of a crystallite four layers thick and,

drawing on the observations of others (Drits *et al.* 1984, Nadeau 1985), perhaps 25 to 30 nm in the *X* and *Y* directions.

Next, consider what happens to the diffraction conditions when molecules of H₂O or ethylene glycol (EG) expand the interlayer of this hypothetical crystallite. Figure 5 shows a geometry with the expansion vector normal to (001) (*i.e.*, *c**). The expansion causes a translation of a given (*hkl*) plane in the lower half of the crystallite with respect to the upper half. Consequently, diffraction from the two halves will be partially out of phase, that is, the amplitudes of diffraction from the two will partially cancel. The phase shift due to the planar displacement ($\Delta h0l$) is given by:

$$\text{phase shift} = \left(\frac{2\pi}{\lambda} \right) \left(\frac{\Delta h0l}{d_{h0l}} \right) \quad (4)$$

If the planar displacement is equal to $\frac{nd_{h0l}}{2}$, where *n* is even, there will be no net phase shift, and the intensity will be identical to that from a crystallite that has

not been expanded. If the planar displacement is $\frac{nd_{h0l}}{2}$, where *n* is odd, there will be complete cancellation, resulting in zero intensity. Intermediate values of *n* yield partial cancellation.

The *h0l* planar displacement depends on the magnitude of the expansion normal to *d*₀₀₁ (Fig. 5). In addition, there may be interlayer translations that result from solvation, such as those that occur in hydrated vermiculite that has $\pm b/3$ translations along *Y*. Or, hydration or EG-solvation could lead to expansion vectors that are not parallel to *c**. But regardless of the exact structural details of the collapsed and the expanded states, the effects of any expansion that retains three-dimensional coherency will be to change the relative intensities of the various *hkl* reflections to different degrees.

This analysis describes ordered mixed-layer I/S in which low-charge layers do not follow each other (*R* = 1); these structures consist of different thicknesses of stacks of illite layers separated by non-consecutive expanded interlayers. For highly expandable *R* = 0 structures, long stacks of consecutive low-charge layers occur, and, hence, a model of three-dimensional coherency requires that expansion will change *d*_{*hkl*} because of the increase in the *c* dimension of the unit cell. A quantitative model of the change in diffraction patterns produced by such expanded minerals is fruitless at present because no information is available on their three-dimensional atomic structure. However, the important point here is that if coherence exists in a collapsed I/S structure, its three-dimensional diffraction pattern would be changed by expansion, even if coherence were retained.

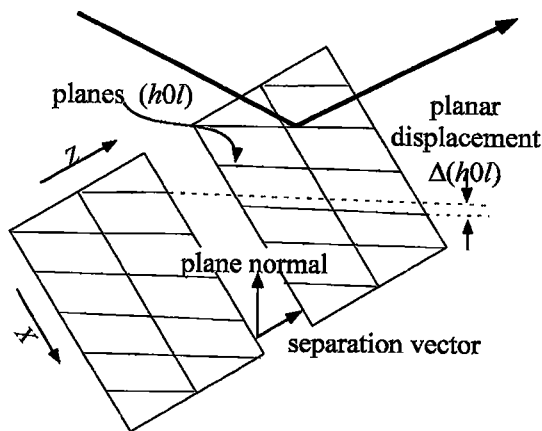


FIG. 5. Displacement of (*h0l*) planes caused by expansion of an interlayer.

XRD EVIDENCE FOR LOW-CHARGE INTERLAYERS AS SITES OF TURBOSTRATIC DISORDER

Figure 6 shows XRD patterns from randomly oriented powders of a mixed-layer I/S that is 20% expandable and ordered ($R=1$). Peaks on the patterns represent diffraction from sixteen different sets of planes. Of these, the diffraction signature between 35

and $39^\circ 2\theta$ is the most diagnostic to evaluate the abundance of turbostratic defects. All peaks in this region belong to the group $20l$; $13l$ (i.e., they are $k = 3n$ reflections). They are unaffected by layer rotations of $n \cdot 120^\circ$ (the type that leads to the $1M_d$ and $2M_1$ polytypes), so their broadening is specific evidence for turbostratic disorder. The other ($k \neq 3n$) peaks are broadened by both $n \cdot 120^\circ$ and turbostratic rotations, so these peaks do not

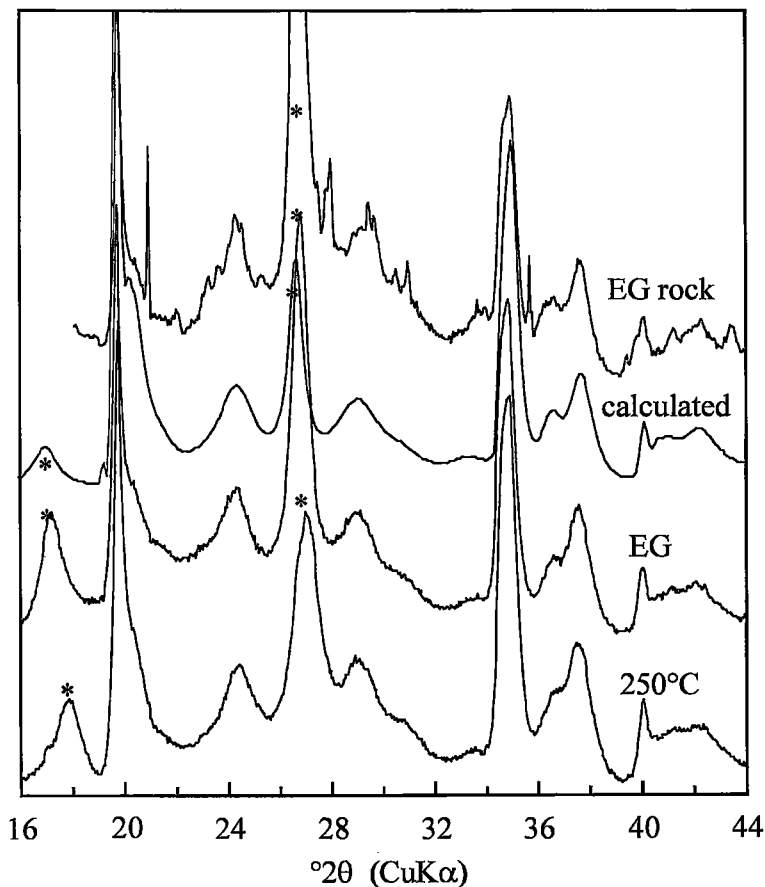


FIG. 6. Three-dimensional X-ray-diffraction data for a Devonian metasaturated bentonite, 20% expandable, $R = 1$. Pattern labeled "250°C" was from a side-pack-mounted, freeze-dried powder heated for 1 hour in air and then analyzed in an enclosed chamber continuously purged with nitrogen to maintain dehydration. Pattern labeled "EG" was from a side-pack-mounted, freeze-dried powder exposed to glycol vapor at 60°C for 24 hrs. Pattern labeled "calculated" was produced by the computer program Wildfire (Reynolds 1993, 1994) and was based on a model using Markovian statistics for 20% smectite interlayers and $R = 1$ (Reynolds 1980); the model treats all stacks of illite as mutually incoherent in all directions except c^* . Pattern labeled "EG rock" was from the bentonite chip from which the powders were prepared; the chip was embedded in epoxy, scraped flat using a razor blade, and then exposed to glycol vapor at 60°C for 24 hrs. Model calculations (Reynolds 1985) of the positions of the basal reflections (indicated by asterisks), particularly those near $18^\circ 2\theta$, indicate that dehydration and EG-solvation have produced the expected d_{001} values for the dehydrated and solvated smectite components.

provide a distinction between the two kinds of stacking disorder.

All of the peaks lie at the positions expected for pure 1M illite regardless of expansion state, and the intensities of the three-dimensional reflections are independent of the degree of expansion across low-charge layers. Both of these observations indicate that the scattering arising from high-charge domains does not constructively interfere, *i.e.*, the high-charge domains are incoherent relative to one another with respect to the diffraction of X-rays. Furthermore, the pattern calculated for incoherent high-charge domains agrees well with the experimental results. In other words, the mixed-layer sample diffracts in three dimensions like an assemblage of independent and very thin crystallites of high-charge layers – the fundamental particles of Nadeau *et al.* (1984a). In the terminology of Nadeau *et al.*, interparticle (interdomain) diffraction occurs along *Z* but not along any other crystallographic direction.

Yet, how do we know that the procedures of size-fractionation and freeze-drying have not produced turbostratic disorder in minerals that originally had completely coherent optical properties? In other words, could the observed turbostratic character merely be an experimental artifact? To address this issue, XRD data were collected from a minimally prepared sample (the pattern labeled “EG rock” on Figure 6), which is one example of data collected from several specimens that were treated similarly, as reported in Reynolds (1992). The “EG rock” pattern has many sharp peaks from feldspar, quartz, and perhaps zeolites, which were removed

in the other samples during size fractionation. Nevertheless, the essential characteristics of the three-dimensional I/S pattern are present, and it is clear that the pattern from this minimally prepared sample is similar to the patterns from samples that have undergone size fractionation. This comparison argues against the contention that dispersion and size fractionation have generated turbostratic defects in a mixed-layer I/S sample that originally was free of them. The same conclusion is reached from a study of rectorite, as described below.

MODEL STRUCTURE OF RECTORITE

The rectorite studied is from Allevard, France, and is *R* = 1 paragonite (0.5)/dioctahedral smectite. The perfect regularity of the interstratification and the equal proportions of expandable and unexpandable layer types cause this material to produce sharp basal reflections whose positions, based on a sum of d_{001} values for the two layer types, follow the Bragg Law as closely as experimental resolution allows. The leather-like consistency of the sample precluded normal techniques of sample mounting. Thin strips of the aggregate mineral sheets were cut with scissors. These were rolled into thin tubes, mounted in epoxy, and ground flat for X-ray analysis. The sample was analyzed as prepared, that is, the air-dried sample was never dispersed. Thus it is like the “rock” sample described above.

Figure 7 shows a diffraction pattern from a randomly oriented preparation of the rectorite along with a calculated pattern (Reynolds 1993, 1994). The calculated pattern is based on the model shown schematically in Figure 8. The basal reflections in Figure 7 were calculated for a coherent stacking sequence of regularly

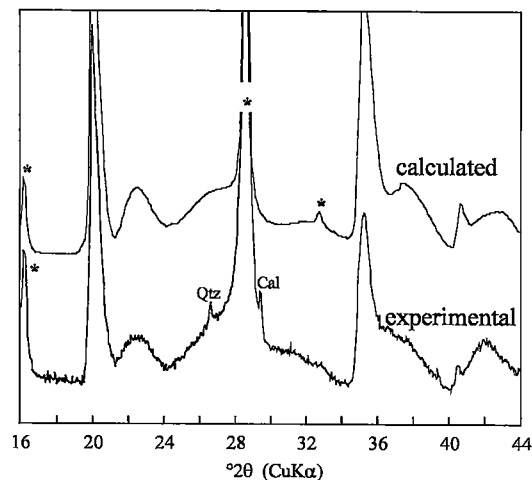


FIG. 7. XRD pattern from a rectorite “rock” (experimental pattern) and a model pattern based on turbostratic interlayers of smectite. Asterisks indicate basal reflections. Qtz and Cal refer to quartz and calcite.

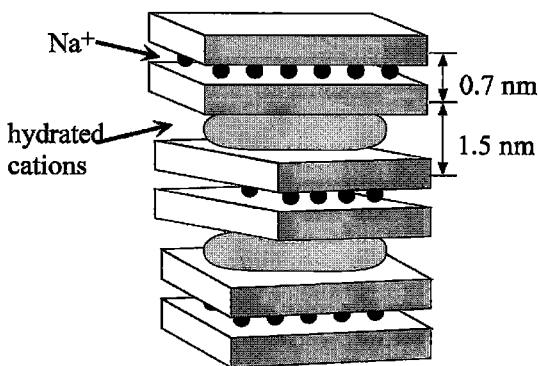


FIG. 8. Sketch of the crystal-structure model used for the calculated diffraction-pattern shown in Figure 7. Coherence exists for the basal diffraction series, but rotations by random amounts of the two-layer paragonitic portions of the crystal cause them to diffract in three dimensions independently of each other.

alternating interlayers of Na and hydrated cations (Fig. 8), and the hkl reflections were calculated for crystals that consist of two 2:1 layers separated by Na ions. That is, the double layer units of Figure 8 were assumed to be separated from each other by random rotations that destroyed the coherence among them, causing each to diffract like a single, independent, thin crystal. The close agreement between observed and calculated traces gives confidence in the validity of this model.

Confirmatory evidence for the high incidence of turbostratic dislocations lies in the unmodulated character of the 20 l ; 13 l diffraction signature between about 34 and 40°2 θ .

Figure 9 shows this diffraction region for EG-solvated and air-dried preparations. Note that there are no differences between the two diffraction patterns, within the precision of the X-ray analyses, indicating that the three-dimensional diffraction pattern is unaffected by interlayer expansion.

RESOLUTION OF DIFFERENCES BETWEEN TEM- AND XRD-BASED INTERPRETATIONS OF COHERENCE

Figure 10 shows a sketch of the 020 diffraction geometry for two stacks of three-layer-thick high-charge domains rotated with respect to each other. For the Debye-Scherrer geometry, and assuming that the crystallite is suitably oriented in the powder sample, the rotation of such a crystallite will allow both segments to diffract, but not at the same time. For example, if the rotation is in the sense of the axis shown by Figure 10, then the upper half will diffract first, followed by the lower half. There can be no optical coherence between

these diffraction events because they do not happen simultaneously.

For the Bragg-Brentano reflection geometry used in most modern diffractometers, the crystallite shown in Figure 10 could be oriented in the powder so that neither segment diffracts as the diffraction angle sweeps through the Bragg angle. Or, the (020) planes from one segment or the other, but not both, could be parallel to the sample surface and thus produce a diffraction event. There can be no optical coherence between these two crystallite segments because only one of them can be suitably oriented for diffraction at a given time. However, how large must the intracrystalline turbostratic rotation be to preclude the simultaneous diffraction of both segments?

Diffraction requires that two conditions be met. The first is that the diffraction angle, the wavelength, and the interplanar spacing satisfy the Bragg Law. The second is that the incident X-ray beam makes the same angle (θ) with respect to diffracting planes of atoms as the reflected ray. If the angle of incidence is equal to the angle of reflection, there is no net phase shift over the surface of the plane, and a reflection results. Diffraction is produced by the addition of the amplitudes of the reflections from parallel and equispaced planes of atoms. If the incident and reflection angles are not equal, successive cancellation takes place across each plane, and the cancellation will vary from partial to total depending on the plane length with respect to the wavelength, and on the degree to which the incident angle differs from the reflection angle.

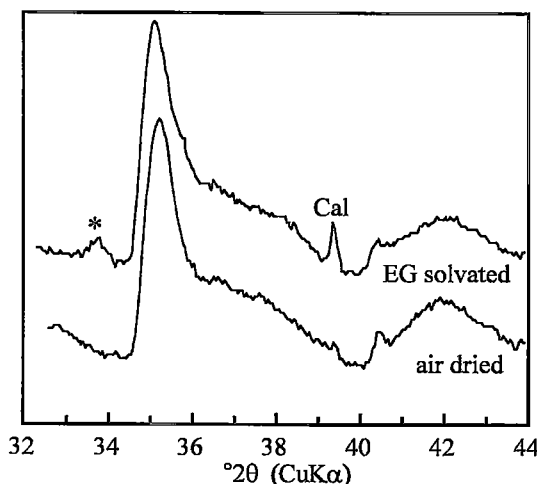


FIG. 9. The 13; 20 diffraction signature for rectorite. Asterisk labels an 00 l peak, and Cal refers to calcite.

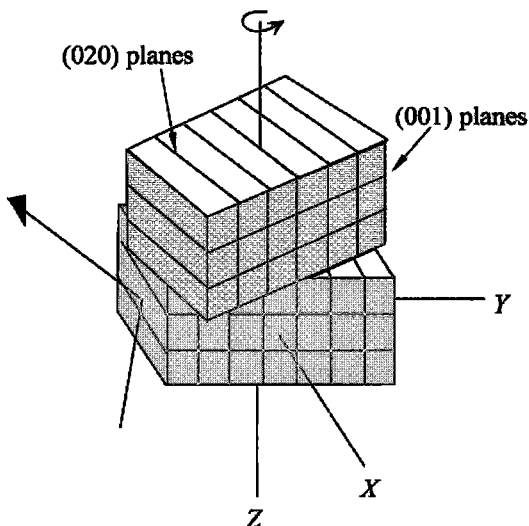


FIG. 10. Diffraction from the (020) planes of two misaligned three-layer crystallites of illite.

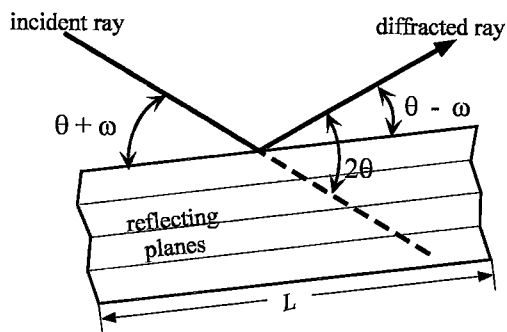


FIG. 11. Definitions of the parameters of Equation 5.

Reynolds (1989) derived an equation for the reflected intensity from a finite plane of atoms of length L that has been tilted by an angle ω away from the orientation that satisfies Bragg's Law:

$$I(\omega) = \frac{\sin^2(2\pi L \sin(\theta) \sin(\omega) / \lambda)}{(2\pi \sin(\theta) \sin(\omega) / \lambda)} \quad (5)$$

where the variables are as defined in Figure 11. The tilt of the planes by ω results in unequal angles of incidence and diffraction. For infinite planes, any tilt away from perfect orientation results in complete destructive interference of X-rays diffracted in one part of the crystal by X-rays diffracted in some other part of the crystal. However, for small crystals tilted slightly away from perfect orientation, the X-rays diffracted in one part of the crystal may not be completely canceled out, because there

may not be another part of the crystal with which it is exactly out-of-phase. Equation 5 describes the extent to which constructive interference occurs for small crystals at small tilts (ω) away from perfect orientation.

Figure 12a shows the behavior of this function at $19^\circ 2\theta$ for $\text{CuK}\alpha$ radiation [*i.e.*, $d = 0.45$ nm, which corresponds to the (020) fringes observed in some HRTEM images] and for two different sizes of diffracting planes. The larger planes (30 nm) are of a length comparable to those commonly reported for the X and Y dimensions for many crystallites of mixed-layer I/S and smectite, and the shorter planes are approximately the size of a typical TEM specimen along the viewing direction. For the 30-nm planes, misalignments of about $\pm 0.8^\circ$ (1.6° total) reduce the constructive interference to only a few percent of the value for complete constructive interference (*i.e.*, nearly complete destructive interference). For the 10-nm plane, intensity is diminished only by about 25% at the same misalignment. In other words, randomly distributed rotations of only ± 1 – 2° between two sets of 2:1 layers would be indistinguishable by powder XRD methods from totally turbostratic stacking in which rotations could have any values, such as 10° , 25° , 70° , *etc.* But the shorter plane-lengths encountered in HRTEM would produce partial constructive interference for small rotations and, hence, produce cross-fringes in HRTEM images.

The amount by which the 2:1 layers may be rotated and still produce partial constructive interference of diffracted beams can be evaluated as a function of plane length by considering the 50% contour for plots such as those in Figure 12a. Figure 12b shows the 50% contours as a function of crystal size (plane length) and rotation angle for three different interplanar spacings, corresponding approximately to d_{001} , d_{020} , and $d_{13;20}$.

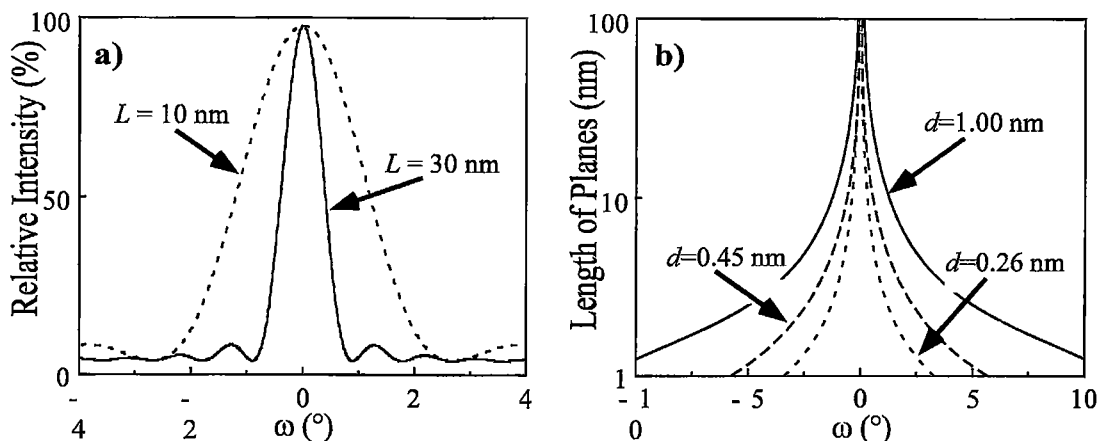


FIG. 12. Constructive interference from finite planes as calculated by Eq. 5. a) Decrease in relative intensity as a function of rotation (ω) from perfect diffracting orientation. b) Contours for 50% constructive interference as a function of the crystallite size (plane length) and rotation (ω).

The tolerances for the large d -values are relatively loose: planes corresponding to d_{001} can be tilted large amounts away from perfect orientation and yet still diffract, whereas planes corresponding to $d_{13,20}$ must be much closer to perfect orientation to diffract. In addition, the tolerances for short planes are looser than for long planes. Hence, parts of the sample at the thin edge of a TEM specimen would be more likely to diffract at a given deviation from perfect orientation than would the thicker parts of the specimen. Indeed, cross fringes extending over large parts of the image are often at the thin edge of the specimen, where the sample thickness (and, hence, plane length) may be only a few nanometers.

CONCLUSIONS

The fundamental debate over the existence of smectite in mixed-layer I/S notwithstanding, TEM and XRD have provided the makings of a consistent model for the nature of the low-charge layers in mixed-layer I/S. The structure of this region is controlled to a large extent by the relationship of the 2:1 layers (specifically, their basal oxygen atoms) on either side, because this will determine the distributions of interlayer sites and, hence, interlayer cations and H_2O . If one assumes a general topology for the 2:1 layers based on other 2:1 layer silicates, then only three other parameters relating to the spatial relationship of the 2:1 layers are needed: the angle between the normals to the 2:1 layers (*i.e.*, are they parallel?), the separation of the 2:1 layers, and the rotational relationship between the 2:1 layers. As noted above, translation without rotation is unlikely to be energetically favorable, particularly for large cations. Furthermore, because rotation produces a periodic Moiré pattern in the interlayer region, translation becomes moot with rotation, provided the crystal size is large relative to the unit cell of the Moiré pattern. In other words, translation of an already rotated 2:1 layer merely results in a shift of the origin of the Moiré unit cell.

XRD and TEM have already provided a substantial amount of information on each of these parameters. Both techniques have shown that the 2:1 layers adjacent to low-charge interlayer regions are parallel or nearly so. Both techniques have documented the separation of the 2:1 layers as a function of state of hydration, type of interlayer cation, and presence of other expanding agents. Finally, both techniques have provided some information pertaining to the rotational relationships between the 2:1 layers: for XRD, no discrete non-00 l reflections have been reported to arise from 2:1 layers adjacent to low-charge interlayer regions in I/S or in smectite alone as discussed above, implying that the rotational mismatch must be greater than perhaps 1–2°. For TEM, lattice-fringe images and SAED patterns suggest that rotational mismatch across at least some layers is limited to perhaps less than ~10°. Taken together, XRD and TEM data support a model in which the low-charge interlayer regions between adjacent 2:1

layers are semicoherent interfaces due to rotational misalignment, but where the degree of rotation is limited.

Why would low-charge layers have a restricted degree of rotational mismatch? One explanation may lie in the constraint that the interlayer space must provide a sufficient number of I-sites for the cations that offset the negative charge on the 2:1 layers. As discussed above, where the 2:1 layers are rotationally misaligned, the regions in which I-sites are occupiable can be defined by a simple relationship (Eq. 3). This relationship implies that rotations greater than ~15° will reduce the diameter of the occupiable regions to less than the cell dimension a (~0.52 nm) for X_{shift} corresponding to a $1/4$ to $1/3$ occupancy of the interlayer. The net result is that at rotations greater than ~15°, the total percentage of I-sites available for large alkalis is not independent of rotation angle (as discussed above) and drops below the amount necessary to offset the negative charge on the 2:1 layer (Fig. 3d).

In addition, one would expect a minimum angle of rotation below which only one island of occupiable I-sites exists within the interlayer region and, hence, turbostratic rotation could not exist. Consider two adjacent 2:1 layers that are rotated about a normal at their centers that passes through two perfectly juxtaposed ditrigonal rings. The ditrigonal rings become offset relative to one another as a function of their distance from this rotation axis (Fig. 4) and as a function of the angle of rotation. For small angles of rotation and small crystallites, the offsets of the ditrigonal rings at the edges of the crystallite will never be enough to cause one ditrigonal ring to be shifted to overlie another ditrigonal ring in order to allow the formation of another island of occupiable I-sites. The angle to permit this shift can be estimated from Eq. 1 by setting d_{RM} to the crystallite size and d_{lattice} to a (0.52 nm). For a 30-nm crystallite, this minimum angle of rotation would be ~1°. For angles less than ~1°, crystallites of this size would have only one island of occupiable I-sites, so there would be no occupied I-sites at the edges of the crystallites to pin the energetically unfavorable rotation of the 2:1 layers. Hence, the rotation would spontaneously return to 0°.

In other words, there may be a structural reason to suspect that rotational disorder for 2:1 layers across a low-charge interlayer region would be limited to the range ~1° to ~10–15°. This limited range is fortuitously (?) greater than the angle for constructive interference of X-rays diffracted by XRD samples, but smaller than the angle for constructive interference of electrons diffracted by TEM specimens. Hence, one might observe cross-fringes in HRTEM images of mixed-layer I/S despite the fact that the boundaries between 2:1 layers adjacent to low-charge interlayer regions are semicoherent. One would predict, however, that the angle made by c^* and the stacking vector across these boundaries would vary slightly in response to the variation in rotation angle, as observed by Ahn & Buseck (1990).

The rotational relationship is likely to be a critical factor in determining the energy of the interlayer, inasmuch as the rotational relationship determines the distribution of cations, molecules, and defects along the boundary. Rotational mismatch may vary within a sample and between samples, and it may change in the sample following sample preparation. For example, potassium fixation following wetting and drying cycles (Eberl *et al.* 1986) may reflect a change in rotational mismatch and, hence, a change in the energetics of the interlayer. Additional work is needed to evaluate the limits of the rotational range for low-charge layers and the other implications of this model (*e.g.*, the clustering of interlayer cations into islands). Clearly, the rotational disorder must be characterized before we can begin to understand the nature of mixed-layer I/S more fully.

ACKNOWLEDGEMENTS

We thank Peter Buseck, Bill Carey, Victor Drits, and Bob Martin for helpful reviews of the manuscript, and Dave Bish and David Veblen for helpful discussions on the topic. This work was supported in part by the Department of Energy through contract number W-7405-ENG-36 to Los Alamos National Laboratory.

REFERENCES

- AHN, JUNG-HO & BUSECK, P.R. (1990): Layer-stacking sequences and structural disorder in mixed-layer illite/smectite: image simulations and HRTEM imaging. *Am. Mineral.* **75**, 267–275.
- _____, & PEACOR, D.R. (1989): Illite/smectite from Gulf Coast shales: a reappraisal of transmission electron microscope images. *Clays Clay Minerals* **37**, 542–546.
- BAILEY, S.W. (1984): Crystal chemistry of the true micas. In *Micas* (S.W. Bailey, ed.). *Rev. Mineral.* **13**, 13–60.
- BISCOE, J. & WARREN, B.E. (1942): An X-ray study of carbon black. *J. Appl. Phys.* **13**, 364–371.
- BUSECK, P.R., ed. (1992): Minerals and Reactions at the Atomic Scale: Transmission Electron Microscopy. *Rev. Mineral.* **27**.
- DONG, HAILIANG, PEACOR, D.R. & FREED, R.L. (1997): Phase relations among smectite, R1 illite-smectite, and illite. *Am. Mineral.* **82**, 379–391.
- DRITS, V.A., PLANÇON, B.A., SAKHAROV, B.A., BESSON, G., TSIPURSKY, S.I. & TCHOUBAR, C. (1984): Diffraction effects calculated for structural models of K-saturated montmorillonite containing different types of defects. *Clay Minerals* **19**, 541–561.
- EBERL, D.D., ŚRODOŃ, J. & NORTHROP, H.R. (1986): Potassium fixation in smectites by wetting and drying. In *Geochemical Processes at Mineral Surfaces* (J.A. Davis & K.F. Hayes, eds.). American Chemical Society, Washington, D.C. (296–326).
- GUTHRIE, G.D., JR. & VEBLEN, D.R. (1989a): High-resolution transmission electron microscopy applied to clay minerals. In *Spectroscopic Characterization of Minerals and their Surfaces* (L.M. Coyne, S.W.S. McKeever & D.F. Blake, eds.). American Chemical Society, Washington, D.C. (75–93).
- _____, & _____ (1989b): High-resolution transmission electron microscopy of mixed-layer illite/smectite: computer simulations. *Clays Clay Minerals* **37**, 1–11.
- _____, & _____ (1990): Interpreting one-dimensional high-resolution transmission electron micrographs of sheet silicates by computer simulation. *Am. Mineral.* **75**, 276–288.
- GÜVEN, N. (1973): Montmorillonite: electron-optical observations. *Science* **181**, 1049–1051.
- MÉRING, J. & OBERLIN, A. (1967): Electron-optical study of smectites. *Clays Clay Minerals, Proc. 15th Conf., Symp. on Electron Optical Study of Smectites* (Pittsburgh), 3–25.
- MOORE, D.M. & REYNOLDS, R.C., JR. (1989): *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, Oxford, U.K.
- NADEAU, P.H. (1985): The physical dimensions of fundamental clay particles. *Clay Minerals* **20**, 499–514.
- _____, TAIT, J.M., MCHARDY, W.J. & WILSON, M.J. (1984a): Interstratified XRD characteristics of physical mixtures of elementary clay particles. *Clay Minerals* **19**, 67–76.
- _____, WILSON, M.J., MCHARDY, W.J. & TAIT, J.M. (1984b): Interparticle diffraction, a new concept for interstratified clays. *Clay Minerals* **19**, 757–769.
- _____, _____, _____ & _____ (1984c): Interstratified clays as fundamental particles. *Science* **225**, 923–925.
- PUTNIS, A. (1992): *Introduction to Mineral Sciences*. Cambridge University Press, Cambridge, U.K.
- REYNOLDS, R.C., JR. (1967): Interstratified clay systems: calculation of the total one-dimensional diffraction function. *Am. Mineral.* **52**, 661–672.
- _____, (1980): Interstratified clay minerals. In *Crystal Structures of Clay Minerals and their X-Ray Identification* (G.W. Brindley & G. Brown, eds.). The Mineralogical Society, London, U.K. (249–303).
- _____, (1985): *NEWMOD, A computer program for the calculation of the basal diffraction intensities of mixed-layered clay minerals*. R.C. Reynolds, 8 Brook Rd., Hanover, New Hampshire 03755, U.S.A.
- _____, (1989): Principles of powder diffraction. In *Modern Powder Diffraction* (D.L. Bish & J.E. Post, eds.). *Rev. Mineral.* **20**, 1–17.

- _____ (1992): X-ray diffraction studies of illite/smectite from rocks, <1 mm randomly oriented powder aggregates, and <1 μ m oriented powder aggregates: the absence of laboratory-induced artifacts. *Clays Clay Minerals* **40**, 387-396.
- _____ (1993): Three-dimensional powder X-ray diffraction from disordered illite: simulation and interpretation of the diffraction patterns. In *Computer Applications to X-ray Diffraction Methods* (R.C. Reynolds & J. Walker, eds.). Clay Minerals Soc., Workshop Lectures **5**, 44-78.
- _____ (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 03755, U.S.A.
- SMITH, D.J. & BARRY, J.C. (1988): Materials science: metals, ceramics and semiconductors. In *High-Resolution Transmission Electron Microscopy and Associated Techniques* (P.R. Buseck, J.M. Cowley & L. Eyring, eds.). Oxford University Press, Oxford, U.K. (477-518).
- SPENCE, J.C.H. (1988): *Experimental High-Resolution Electron Microscopy*. Oxford University Press, New York, N.Y.
- VALI, H., HESSE, R. & MARTIN, R.F. (1994): A TEM-based definition of 2:1 layer silicates and their interstratified constituents. *Am. Mineral.* **79**, 644-653.
- VEBLEN, D.R., GUTHRIE, G.D., JR., LIVI, K.J.T. & REYNOLDS, R.C., JR. (1990): High-resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: experimental results. *Clays Clay Minerals* **38**, 1-13.
- WILLIAMS, D.B. & CARTER, C.B. (1996): *Transmission Electron Microscopy*. Plenum Press, New York, N.Y.

Received February 15, 1998, revised manuscript accepted October 4, 1998.