Interstratified Clays. II. Some Experimental Results

RODNEY TETTENHORST

*Department of Geology and Mineralogy, The Ohio State University,
Columbus, Ohio 43210*

AND RALPH E. GRIM

*Department of Geology, University of Illinois,
Urbana, Illinois 61801*

Abstract

Theoretical diffraction patterns and experimental results with natural clays are compared and indicate the relative importance of one-glycol-layer spacings in the analysis of interlayered clays. One-layer spacings modify, shift, and attenuate main maxima. Generally, one-layer spacings are not important in ethylene glycol-clay complexes but, when present, can influence the interpretations of either the kind of interlayering or the composition of the sample. One-layer spacings are important in virtually all other polyalcohol- polyether- or water-clay complexes and thereby influence the diffraction effects. Calculated diffraction effects for a distribution of *d* values were made and resulted in the production of broad maxima whose presence on real patterns can affect interpretations of the kind of interstratification.

Introduction

A method alternative to that of MacEwan for calculating the diffraction effects from interstratified clays yielded results (Part I) that were in reasonable accord, especially when the composition distribution inherent in the MacEwan method was simulated. Either method has some difficulties and some strong points. MacEwan's method superimposes a particular composition distribution upon the calculations which influences the results and may not accurately account for some real cases. However, MacEwan's method produces "realistic-looking" transforms and can easily handle composition and crystallite-size variations. The method described in Part I is capable of simulating any composition distribution and can, practically speaking, deal with more complex situations, *e.g.*, three-component systems. However, the method described in Part I is best suited for computations involving restricted compositions having a single crystallite thickness; however, the resulting transforms contain diffraction ripples. On viewing some of the computed patterns produced by the present authors (*e.g.*, Fig. 4), one may wonder which "peaks" are "real" and which are "ripples," *i.e.*, which maxima would really be retained on diffraction patterns of natural clays.

This is a legitimate concern. It is suggested that in those instances where "ripples" and "peaks" (*i.e.*, "peaks" are those "ripples" labeled with *d* values on the calculated traces) are virtually indistinguishable, the comparable real patterns would show broad and diffuse scattering, an observed fact on many diffraction patterns of naturally interstratified clays.

We now compare theoretical patterns produced by the method described in Part I with some experimental results. In particular, the effect of the presence of one-layer spacings and *d* value distributions is considered. The experimental patterns provide a basis for indicating various factors whose effect can be then tested on the calculated patterns so that a further comparison of the two can be made.

Results

One-Layer Complexes

A part of this study was to determine the quantity of the one-layer glycol complex in interstratified *I/M* clays and its influence on the diffraction patterns. The result of these investigations indicated the one-layer glycol spacing was not in general abundant compared with the two-glycol layer or collapsed

spacings but as little as 5-10 percent can profoundly alter the diffraction patterns. The evidence for these conclusions is presented in this section.

Evidence for the existence of the one-layer complex in clay-organic complexes and in ethylene glycol complexes in particular has been adequately documented. Tettenhorst (1957) studied a group of potassium-saturated montmorillonites, among which were the type material from Montmorillon, France, and A.P.I. No. 20 from Polkville, Mississippi; these were subsequently heated at 300°C and then solvated with ethylene glycol and glycerol. Thus modified, these clays showed a reduced *001* intensity with little change in the 17 Å position compared to the untreated glycol-solvated clays. Also, the *002* "peak" for the modified samples was indistinct and appeared only as a break or shoulder in the curve on the high angle side of *001*; the position of this break being at about $10.0-10.1°2\theta$ compared to the normal, well-resolved *002* at $10.3-10.4°2\theta$ for the untreated clays. The reason for these changes in the patterns was the existence of some one-layer glycol spacings in the modified clays. The influence of the one-layer complex with glycerol was even more apparent, because in the 8-17 Å region only a single peak centered at about 14 Å results. The patterns with glycerol were similar to Figure 1b in Kinter and Diamond (1958).

Subsequently, Tettenhorst (1960) and Brunton, Tettenhorst and Beck (1963) examined the complexes formed by montmorillonites with many polyalcohols and polyethers. These investigations showed that a one-layer complex, the patterns of which were quite similar for all organic compounds studied, could be formed with any of the organic compounds and that it became dominant for compounds with large chain lengths; *e.g.*, montmorillonite complexed with 1,5 pentanediol rarely expanded more than 13.6Å. The spacings of the one-layer complexes were variable, depending on factors such as position of OH groups on the organic chain, identity of the interlayer cation, and layer charge. Spacings for complexes whose organic molecules had OH groups at the ends of the chain were always about 13.6 Å.

These studies placed ethylene glycol at or near the top of the list of all the polyalcohol-polyethers in its ability to expand layer silicates; *i.e.*, glycol did not favor the formation of one-layer spacings. The one-layer complex could be induced to form by heating any of the two-layer complexes, thereby de-solvating the organic molecules. Organic compounds such as ethylene glycol monoethylether (EGEE) or diethylene glycol (DEG), which normally form two-layer complexes, were observed to form one-layer complexes more readily upon heating than the shorter chain ethylene glycol. Complexes with EGEE were used by Reynolds and Hower (1970: hereafter R&H) to apparently confirm the existence of *IMII* superlattice units in Kalkberg-type clays, a conclusion not in accord with the results of this study. Let us digress to examine this conflict. In passing it is noted that the diffraction patterns of DEG complexes and EGEE complexes are quite similar.

If the premise of *IMII* superlattice units of R&H is accepted, then the difference in the Kalkberg-glycol and Kalkberg-EGEE diffraction traces (Figs. 2 and 3c in R&H) is due to the proposed difference in the arrangement of the glycol and EGEE molecules in the complexes. Reynolds (1965) suggested a structure for the glycol complex in reasonable accord with previous structure determinations (Brindley, 1956; Bradley, Weiss, and Rowland, 1963). Reynolds (1969) also suggested a structure for EGEE complexes which only grossly resembled the glycol structure. The latter analysis attempted to fit about a dozen parameters with the same number of X-ray reflections, a situation that can lead to many possible answers. A low *R* factor was cited for the proposed structure, but it has little meaning with so few orders of diffraction. It is suggested that the proposed structure for the EGEE complex is not correct. The close correspondence of the patterns of all polyalcohol-polyether complexes suggested a close correspondence in their structures. The spacing differences for the two-layer complexes, *e.g.*, 17 Å for glycol complexes and 16 Å for EGEE complexes with montmorillonite, are likely the effect of packing differences between the organic molecules. No such differences in *d* are noted for the one-layer complexes (obtained by heating the two-layer complexes), all being close to about 13.6 Å with virtually identical patterns; *i.e.*, the clay-organic interactions are quite similar for all the complexes.

As cited in Part I, Kalkberg-type patterns could possibly result from a 17 Å layer buried inside an otherwise normal illite crystallite and that EGEE complexes have a greater tendency to form the one-layer complex. This suggested that the EGEE-Kalkberg pattern of R&H was influenced by the presence of one-layer spacings. This hypothesis was

substantiated in two ways. First, two transforms were calculated for $NI = 10$, both of which had $9I$ layers. One transform was that shown in Figure 6d of Part I with an M in position 4; the other had a 13.5 Å spacing in position 4. The mean of these two transforms (Fig. 1) resembles the EGEE-Kalkberg pattern of R&H. It is *not* suggested that the EGEE-Kalkberg patterns necessarily have exactly equal proportions of crystallites which contain a 17 Å spacing on the one hand and a 13.5 Å spacing on the other, but it is suggested that the one-layer EGEE spacing makes an important contribution to the pattern. Further, it is *not* suggested that the one-layer spacing necessarily equals 13.5 Å. This spacing remains to be determined. In particular, the computed transform (Fig. 1) shows a doublet at about 17-18°2θ which the EGEE-Kalkberg pattern of R&H does not show. Although a distribution of crystallite compositions and thicknesses might cause the two to merge, R&H observed that their EGEE complexes showed rather broad peaks and that their computed spacings based on an $IMII$ superlattice did not agree as well with the experimental patterns as did their glycol counterparts. The influence of the one-layer complex suggested here is probably responsible for these spacing differences. A second mean transform such as that shown in Figure 1 was computed with a one-layer complex having a 14.5 Å spacing. This pattern matched closely the pattern shown in Figure 1 in the 8-10°2θ region and produced a single broad peak centered at about 17.6°2θ (= 5.04 Å).

In a second experiment, a K-bentonite from Lamont, Pennsylvania (University of Illinois No. 155)

gave an X-ray pattern with glycol virtually identical to that of the glycol-Kalkberg pattern of R&H. The region from 2-10°2θ of the glycol-Lamont pattern is shown in Figure 2a. Heating for 3-4 minute intervals at 90°C produced patterns shown in Figure 2, b-d, which are nearly exact duplicates of the normal unheated EGEE-Lamont or EGEE-Kalkberg patterns. Continued heating produced a single sharp maximum centered at about 8.1-8.2°2θ which duplicated nearly exactly the normal unheated 1,5 pentanediol-Lamont pattern for which the one-layer spacing is dominant. These results were confirmed by replicating them with additional interstratified clays having p_I values similar to Lamont complexed with a variety of polyalcohols-polyethers. Increasing organic chain length produced more one-layer spacings for these I/M clays as well as for pure montmorillonites. We conclude that the EGEE-Kalkberg pattern of R&H is strongly influenced by one-layer spacings and is not due to the EGEE-clay structure proposed by Reynolds (1969). However, these experiments confirm the assignment by R&H of the peak at ~9°2θ on these I/M clays to the presence of the two-layer complex.

Perry and Hower (1970) noted that glycol complexes provide a more readily interpretable analysis of interstratification than do the air-dry (water) complexes (see Hower and Mowatt, 1966, for a representative air-dry Kalkberg-type pattern). The present study shows their conclusion is a direct result of the strong contribution of the one-layer spacing in the water complexes so as to produce a three-component system whereas the glycol complexes of many I/M clays essentially produce two-component systems.

In summary, the foregoing analysis suggests that the concept of $IMII$ superlattice units may be in error and indicates that significance of the one-layer complex in EGEE or air-dry (water) clay complexes. However, the importance and effect of the one-layer complex with ethylene glycol remains to be assessed and we now turn to this matter.

Glycol Complexes

Determination of the kind of interlayering for $p_M > 0.80$ or $p_M < 0.20$ should be difficult, as indicated in Part I. In fact, computed patterns for $p_M > 0.80$ for random and ordered interlayering are virtually identical. However, the situation at $p_M = 0.20$ is more difficult to distinguish, as indicated in Figures 2 and 8 of Part I which show that
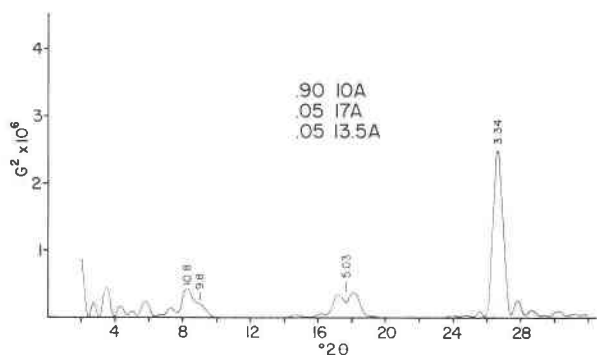

FIG. 1. Calculated diffraction pattern for $p_I = 0.9$ which is the mean of two patterns one of which has M in position number 4, the other has the one-glycol spacing in position number 4.
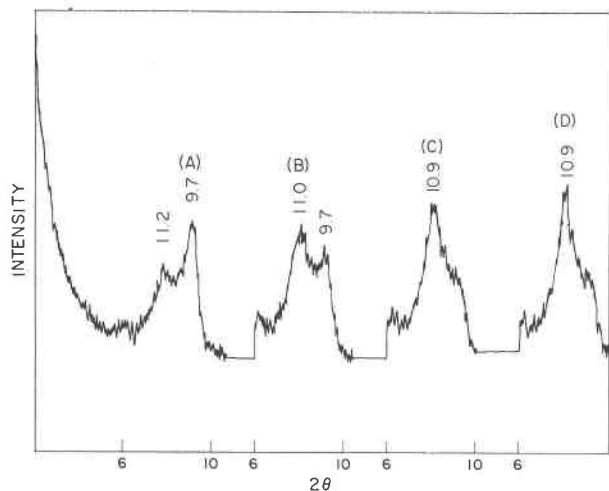
FIG. 2. Experimental diffraction pattern of glycol-treated Lamont, Pennsylvania, K-bentonite (University of Illinois No. 155); (a) original, (b) after heating 3 minutes at 90°C, (c) after an additional 3 minutes at 90°C, (d) after 4 additional minutes at 90°C. Full scale deflection is 400 cps. Scan speed: $1°2\theta$/min.

a broad maximum at about $6.5\text{-}7°2\theta$ is rather more pronounced for ordered than for random mixing. Reynolds (1967) first indicated that patterns showing a peak at about $6.0\text{-}8.0°2\theta$ and another at $9\text{-}10°2\theta$ could not be interpreted as random mixing but only as ordered. The results of the present work are in general agreement with this conclusion. A good natural example of such an I/M clay is given by R&H in their Figure 9G. However, not all patterns of natural I/M clays agree in detail with the data predicted from the computations of a two-component I/M mixture. The pattern of one such clay is shown in Figure 3. The resolution between $7\text{-}9°2\theta$ is poor although the general nature of the pattern suggests a $p_I \sim 0.8\text{-}0.9$. Other patterns have been observed which show a steeply declining background from 2 to $5.5°2\theta$, a constant intensity from 5.5 to $9°2\theta$, and finally a sharp decrease in intensity at $9°2\theta$. This lack of resolution in the 7 to $9°2\theta$ range is probably the effect of a small percentage of one-glycol layer spacings.

Calculated patterns for a three-component I/M system $(17/13.5/10\,\text{Å})$ have been made for a variety of cases both with and without composition distributions. One such pattern (Fig. 4) represents the mean of 100 layer configurations, each of which had $6I\text{-}3M$ and a single $13.5\,\text{Å}$ spacing with $p_M = 0.3$, i.e., random mixing. This pattern can be compared with that shown at the bottom of Figure 4a

of Part I to illustrate the effect of the one-layer spacing. The most outstanding feature is the attenuation of the peak at $9.2\,\text{Å}$ and its shift to about $9.7\,\text{Å}$. Further, the well-defined peak at $5.36\,\text{Å}$ is considerably broadened, weakened, and shifted. Only if one-layer spacings exceed 20 percent does a maximum actually develop at about $13.5\,\text{Å}$, but, for these, little trace remains of a maximum at $9+°2\theta$, i.e., the $00lI/002M$ peak. In short, an effect of as little as 10 percent or less one-layer spacings is to decrease the resolution in the $7\text{-}9°2\theta$ region and to shift the peak at $9\text{-}10°2\theta$ to lower angles, an effect observed on patterns of real I/M clays.

Perry and Hower (1970, 1972) have made quantitative estimates of I/M clays based on the data of R&H to support their theory on the dehydration of shales with depth. Their X-ray patterns show a general decrease in the percentage of M with depth and random interlayering until a depth where $p_M = 0.40$ at which point ordered interstratification presumably occurs and p_M drops abruptly to 0.20 and does not decrease further to the limit of their data. It appears that Perry and Hower (1970) have been very liberal in their interpretation of ordered mixing at $p_M = 0.20$. Only one or two of their eight patterns cited as $p_M = 0.20$ and ordered really agree reasonably well with the predicted effects of a peak at $6\text{-}8°2\theta$ and another at $9+°2\theta$, e.g., their Well E sample at a depth of 11,563 ft. Note further the break in the background at low 2θ for this clay, a feature suggestive of order. The remaining patterns which Perry and Hower interpret as $p_M = 0.2$ and ordered show a broad maximum whose position is rather variable ranging from about $12.5\text{-}15.5\,\text{Å}$ (some discrete chlorite is present too) and a $10\,\text{Å}$ peak which often has a shoulder at about $9.8\,\text{Å}$. Further, the intensity distribution between $16\text{-}18°2\theta$ is broad and weak, reminiscent of the effect produced by the one-glycol layer complex (Fig. 4).

Perry and Hower recognized that the presence of a $10\,\text{Å}$ peak on their patterns was not consistent with $p_M = 0.2$ and ordering. They suggested that the $10\,\text{Å}$ peak represents the presence of additional "detrital illite" and have estimated its amount at 6 percent for Well E at the 8379 ft level. Computation of the diffraction effects to be expected for mechanical mixtures of an (a) I/M ordered clay for $p_M = 0.2$ with (b) "detrital illite," $p_M = 0$, of the same crystallite size was made in the present
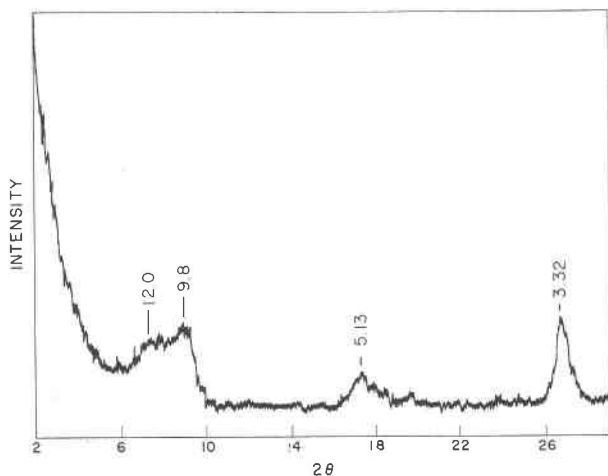
FIG. 3. Experimental diffraction pattern of glycol-treated Alabama K-bentonite from Red Mountain, Alabama (collected by Joe Fetzer).

study. Allowing for a 100 percent error in the detrital illite estimate of Perry and Hower (detrital illite = 12 percent), no modification of the 9.8 Å peak was observed. When the detrital illite content was increased to 50 percent the computed patterns showed the effect observed by Perry and Hower, a 10 Å peak modified at higher angles by a shoulder at about 9.4–9.8 Å. Therefore, most of the patterns of Perry and Hower cannot be taken as proof of ordered interlayering. Their patterns are consistent with the presence of one-glycol layer spacings or a considerably larger amount of detrital illite than they supposed or both. Also, the observation that a small amount of one-layer spacings alters the maximum in the 16-18°2θ range may limit its usefulness for determination of composition (R&H, p. 33).

The clay mineralogy evidence which Perry and Hower cite in support of their theory of the dehydration of shales is not sufficiently definitive to support I/M ordering. Of importance to their theory is the hypothesis (Hower, 1967) that ordered clays are less expandable than randomly mixed clays of the same composition, i.e., the same p_M. This hypothesis follows only if one accepts an unproved presumption (Hower, 1967) concerning the lack of expandability of an interlayer region bounded by a highly charged mica-like 2:1 unit on one side and a low-charged montmorillonite 2:1 unit on the other. Alternatively, a polar charge distribution within the 2:1 silicate unit has been proposed (but not proven) to explain ordered interlayering (Sudo, Hayashi, and Shimoda, 1962) and random inter-

layering (Tettenhorst and Johns, 1965), and shown by Gatineau (1964) to explain features of the X-ray data of muscovite. The evidence available suggests that the kind of interlayering, ordered or random, does not affect the amount of expandability of an I/M clay.

In summary, it has been shown that one-layer spacings are common in most polyalcohol-polyether clay complexes and clay-water complexes. Ethylene glycol complexes are rather unique since one-layer spacings are not quantitatively important. However, even a few percent of one-layer spacings can have a significant influence on the diffraction patterns. The presence of so small an amount can hardly be denied, especially since features such as poor resolution in the 8–10°2θ range are observed on patterns of natural clays and this observation agrees with computed effects. A peak in the 12–14 Å region is not explicable by so small a percentage of one-layer glycol spacings. Its presence must be due to ordered interlayering, d value distributions as shown in the next section, or some other factor.

Variations in d

The concept of layer silicates having frayed edges originated with Bray (1937) and later with MacEwan (1949) and has been cited from time to time to explain various observable phenomena (Jackson, 1963; Gaudette et al, 1966; Reichenbach and Rich, 1969). The physical picture that emerges from this concept is that of a core of a coherently diffracting substance having some (minimum) spacing (e.g., 10 Å) which grades outward into a zone of matter having a continuous series of spacings up to some maximum (e.g., 14 Å) at the limit of the particle. A distribution of expanded (i.e., > 10 Å) spacings is a result. Calculation of the diffraction effects to
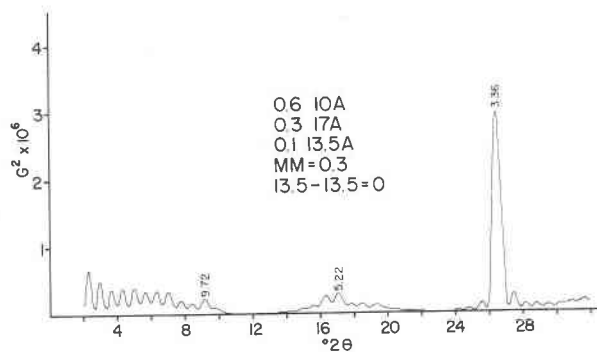

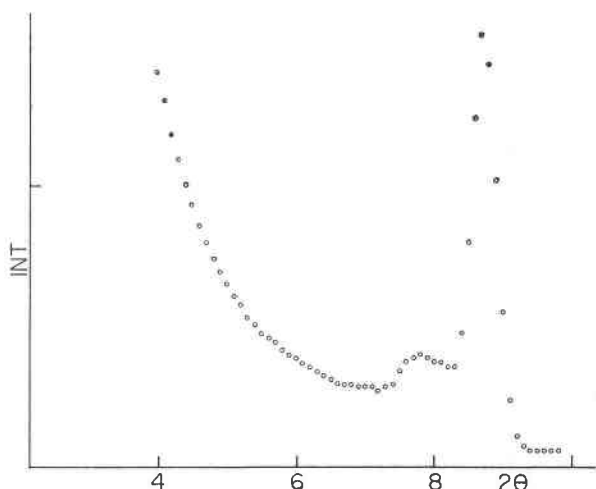FIG. 4. Calculated diffraction pattern for $NI = 10$, $p_I = 0.6$, $p_M = 0.3$, $p_{13.5} = 0.1$, $MM = 0.3$.

FIG. 5. Calculated diffraction pattern for a d-spacing distribution; $p_I = 0.97$, expandables $= 0.03$ with d values ranging from 10.05–11.50 A°.

be expected from such a model has been made as part of another unpublished study (Tettenhorst, 1969). Whether or not the concept of a frayed edge is accepted, variation in d is a reasonable possibility in natural I/M clays, and it seemed desirable to determine some of the expected diffraction effects. For this reason the pattern for one such case (Fig. 5) was computed for a "mechanical mixture" of crystallites whose average $N = 16$ for $p_I = 0.97$ and 0.03 expandable material. The expandable material was assumed to be equally divided between spacings ranging from 10.05–11.50 A in 0.05 A increments. The layer transform for illite was used for all spacings and the powder Lp factor was also included. Figure 5 shows a large peak centered at $10+$ A and a smaller one centered at about 11.2 A, the relative height of the two peaks being a function of their amounts. The 2θ position of the smaller peak is a function of the width of the degree of variation in d. This result suggests that maxima in the 11–14 A range can result from variations in d and do not necessarily reflect ordering. However, the presence of one such peak *and* another having a spacing between approximately 8.5–9.8 A probably indicates ordered interlayering as noted earlier.

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