THE DISTRIBUTION AND IDENTIFICATION OF MIXED-
LAYER CLAYS IN SEDIMENTARY ROCKS*

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ABSTRACT

Recent work has shown that randomly interstratified 2:1 clays are abundant in sedimentary rocks. X-ray diffraction patterns are presented which show a wide variety of randomly interstratified clays composed of illite-montmorillonite, chlorite-vermiculite, illite-chlorite-montmorillonite, and regularly interstratified chlorite-vermiculite. Methods of identifying and estimating the ratio of mixed layers are demonstrated.

INTRODUCTION

Various authors have reported the occurrence of mixed-layer clays in relatively pure clay deposits and in soils. There is little, if any, literature concerning the abundance and varieties of mixed-layer clays occurring in shales, sandstones, and limestones. The author’s investigation of the clay minerals in sedimentary rocks has shown that a large number of mixed-layer varieties are present, and that mixed-layer clays occur in abundance throughout the geologic section.

From an examination of over 6000 sedimentary rock samples from all over the United States, ranging in age from Cambrian to Recent, it is estimated that over 70 per cent of the samples contain some variety of mixed-layer clay.

Ability to recognize and identify mixed-layer clays will considerably increase the criteria used for the zonation and characterization of sedimentary rocks. It also appears likely that if minor environmental differences can be determined by clay mineral studies the mixed-layer clays hold the answer. It is more likely that mixed-layer illite-montmorillonite and chlorite-montmorillonite, rather than pure illite and chlorite clays, are formed by marine diagenesis.

The 2:1 clay minerals (illite, montmorillonite, chlorite, vermiculite) can be considered to be formed of similar flake-shaped layers. The type of cation which occurs between these layers determines the type of clay, i.e. K⁺=illite, (Mg·Al)(OH)₂⁺=chlorite, Ca⁺⁺, Na⁺, Mg⁺⁺, and H₂O =montmorillonite and vermiculite (vermiculite is considered to be a coarse-grained montmorillonite). A non-mixed-layer clay will contain the same type of cation between each layer; however, if 5 or 10 layers contain K⁺ in the interlayer position (illite) and another 10 or 15 contain Ca⁺⁺ and H₂O (montmorillonite), etc., a mixed-layer clay is the result. Mixed-layer clays apparently can form in all possible combinations of

* Publication No. 57, Shell Development Company, Exploration and Production Division, Houston, Texas.
Different layers (illite-montmorillonite, illite-chlorite, chlorite-montmorillonite, illite-chlorite-montmorillonite).

Mixed-layer clays in most cases are derived from the degradation or aggradation of pre-existing clay minerals; i.e. during weathering, K⁺ can be removed from some biotite layers, Mg²⁺ and H₂O deposited, and a mixed-layer biotite-vermiculite formed; or in sea water the Ca⁺⁺ and H₂O between some montmorillonite layers can be replaced by K⁺, and a mixed-layer illite-montmorillonite formed. Mg(OH)₂ also readily replaces Ca⁺⁺ and H₂O and forms mixed-layer chlorite-montmorillonite.

It is difficult, at the present time, to determine if a mixed-layer clay in a sediment was formed by diagenesis in the basin of deposition or by weathering in the source area. However, it is believed that originally a large part of the mixed-layer illite-montmorillonite and chlorite-montmorillonite clays were formed by marine diagenesis, and mixed-layer chlorite-vermiculite clays, primarily because of their relatively large grain size, are usually considered to have been formed by weathering.

Identification

Monomineralic clays produce an (00l) series of x-ray reflections which are integral sequences of the (001) reflection. The (001) reflection is a measure of the clay thickness, e.g. 10 Å for illite. Thus, the (00l) series for illite would be: (001) = 10 Å, (002) = 5 Å, (003) = 3.3 Å, (004) = 2.5 Å, (005) = 2 Å, etc.

When the two different types of layers which form a mixed-layer clay occur in random intergrowth the clay is referred to as a random mixed-layer clay. In this case the (00l) series is not an integral sequence.

The (00l) values are average values resulting from the simultaneous scattering by both types of layers. This can be seen more clearly in Fig. 1.

The vertical lines in the diagram below each x-ray diffraction pattern show the position of the (00l) reflections for each type of layer. The longer lines show the position of the 10-Å (00l) series (10, 5, 3.3, 2) and the shorter lines the position of the (00l) reflections of the expandable layers (12.4, 6.2, 4.13, 3.10, 2.07). The dark horizontal line indicates which adjacent reflections combine to produce the observed average reflection. These average reflections are referred to as (001)/(001), (002)/(003), etc. indicating which two values combine to form the average value. The precise position will depend upon the relative amounts of the two layers, the form factor, and particularly in the case of the first maximum, the polarization factor. Actually, averages are effective between every pair of adjacent specific positions, but the intensity and sharpness of maxima are directly proportional to proximity. In those instances in which a node for one dominant species is flanked on both sides by equally
removed nodes for the minor component, the observed maximum merely exhibits minor broadening toward both sides. (See Fig. 1: 1 at 5.02 Å, or 1, 3 at 2.0 Å).

The theoretical basis for the identification of mixed-layer clay minerals has been developed in papers by Hendricks and Teller (1942), Bradley (1945, 1950, 1953), MacEwan (1949), and Brown and MacEwan (1950).

Figure 1 contains x-ray diffraction curves of a clay composed of randomly interstratified nonexpanded 10-Å layers (illite) and 12.4-Å and

![Figure 1](image-url)
14.5-Å expanded layers (montmorillonite). When the exchangeable cations on the expanded layers are Na or K, the expanded layers contain only one layer of water and are approximately 12.4 Å thick. The (001)/(001) spacing occurs at 10.3 Å, the (002)/(002) at 5.02, and the (003)/(004) at 3.30. The 10.3-Å (001)/(001) spacing is an average obtained from the 10-Å and 12.4-Å reflection. The (002)/(002) value in curve 1, Fig. 1, lies between the (002) 6.2-Å reflection and the (003) 4.13-Å reflection and has a maximum near the (002) 5-Å maximum.

In the H+ treated sample the expandable layers contain two layers of water and are approximately 14.5 Å thick. The first-, third-, and fifth-order peaks are broader and decreased in intensity as compared to the Na+ sample, whereas the second-order peak is sharpened and increased in intensity. The broadening is caused by (00l) values which form the first-, third-, and fifth-order values moving farther apart; the sharpening by the (00l) values which form the second-order peak coming closer together.

In glycolated specimens, both the (001)/(001) and the (001)/(002) proximities are sufficient that they furnish observable maxima. The first is diffused at about 11 Å and the second much sharper at about 9.7. The (003) and (005) reflections nearly coincide, and the increased intensity of the 3.3-Å reflection is quite marked.

When the mixed-layer clay is heated to 550° C. the expanded layers collapse to a thickness of from 9.4 Å to 9.8 Å, depending upon the type of exchange cation. The resulting reflections are average values formed by adjacent (00l) values of the 10-Å layer and 9.4-Å to 9.8-Å layers.

In an untreated mixed-layer illite-montmorillonite clay it is often possible to tell whether the expanded layers have one or two layers of water by observing the relative sharpness and intensities of the peaks and by observing on which side of the 5-Å and 3.3-Å position the peaks lie. The reason for this can be seen in the diagrams in Fig. 1 which show the relative positions of the (00l) reflections.

Brown and MacEwan (1950) have computed theoretical curves for random mixtures of 10/12.4-Å, 10/14-Å, 10/15.4-Å, 10/17.7-Å, and 7.14/10-Å layers. With their formula, theoretical scattering curves were computed for the (001)/(001) reflection of randomly interstratified 10-Å and 17-Å layers at intervals of 10 per cent.
The form factor, $F$, and the polarization factor, $\Xi$, were not computed but were read from Bradley’s (1945) experimentally estimated form factor curve which was compiled from various montmorillonite complexes.

Figure 2 is a curve showing the migration of this (001)/(001) peak as the percentage of expanded 17-Å layers is varied. The (001)/(001) was not calculated below about 30 per cent expanded layers. At 30 per cent the peak is very weak but increases as the percentage of expanded layers increases.

**Examples of Randomly Interstratified I llite-Montmorillonite Clays Occurring in Shales**

Examination of a large number of shale samples indicates that the randomly interstratified expanded and nonexpanded layers occur in all possible ratios. Figures 3 and 4 contain a sequence of x-ray diffraction curves of mixed-layer clays in which the expanded layers range, at intervals of approximately 10 per cent, from less than 10 per cent to 80 per cent. Curves are given for mixtures of nonexpanded 10-Å layers and expanded 12.4-Å layers, and for 10-Å layers and 17-Å glycolated layers. In addition to a mixed-layer clay, kaolinite, chlorite, illite, and quartz are present in many of these samples.

In some cases the ratio of layers determined from the 10/12.4-Å curve
and the 10/17-Å do not show exact agreement. In most cases this discrepancy may be caused by the presence of a few intergrown chlorite layers, as the measured 10/12.4-Å value is usually too high and the 10/17-Å value too low. Heat treatment indicates that the chlorite layers are relatively scarce. Table 1 lists the (001)/(001) values obtained from

![Graph of 001/001 values](image)

**Fig. 3.** Sequence of randomly interstratified clays (expanded and nonexpanded layers).

The curves in Figs. 3 and 4 and the calculated values taken from the curve, in Fig. 2 (10-Å/17-Å) and from Brown and MacEwan (10-Å/12.4-Å).

Curve 1 on Fig. 3 is an example of a mixed-layer clay which contains less than 10 per cent of expanded layers. When the clay is glycolated
there is no shifting of the peaks but there is a relative increase in the intensity of the (003)/(005), 3.33-Å peak as the (005) reflection of the expanded layers is moved closer to the (003) reflection of the 10-Å layers.

When the expanded layers are increased to 20 per cent the reflection resulting from the mixture of 10-Å and 12.4-Å layers has moved to 10.3 Å. When this material is glycolated, two high-angle peaks are formed, 11.0 Å and 9.7 Å, one resulting from a 10-Å/17-Å combination and the other from a 10-Å/8.5-Å combination. The combination 10-Å/17-Å peak gradually approaches a 17-Å value and the 10-Å/8.5-Å peak approaches an 8.5-Å value as the percentage of expanded layers increases, though there is not a straight-line relation as can be seen from the measured values and from the calculated curve. Brown and MacEwan (1950) have shown that when the two interfering reflections are relatively close, 10 Å and 12.4 Å, the calculated curve is nearly a straight line, and as the reflections move farther apart, the curve becomes more S shaped.

At a concentration of 30 to 40 per cent expanded layers the combination 5.0-Å/6.2-Å peak of the glycolated material increases suddenly from around 5.0 Å to 5.30 Å and continues increasing to a value of 5.6 Å, when 80 to 90 per cent of the layers are expanded. The 3.33-Å/3.40-Å peak approaches a 3.40-Å position as the per cents of expanded layers increase. This peak is obscured by the 3.35-Å quartz peak, but the asymmetrical shape of the 3.35-Å peak indicates that the mixed-layer clay has a peak near to 3.40 Å.

The composite 10-Å/12.4-Å peak approaches a 12.4-Å value as the proportion of expanded layers increases. The 5.0-Å/6.2-Å peak remains
near 5.0 Å throughout this range of values. This peak is quite weak and, if present, is probably obscured by the 5.0-Å peak of the illite, which is present in most of the samples. The 3.33-Å/3.10-Å peak decreases from a

![Graph showing the sequence of randomly interstratified clays (expanded and nonexpanded layers).](image)

value of 3.31 Å to 3.24 Å as the percentage of expanded layers increases from 20 per cent to 30 per cent. Thereafter the decrease is less rapid.

Curve 4, Fig. 3, has a broad (001)/(001) peak for both the 10/12.4-Å
curve and the 10/17-Å curve. This sample appears to contain mixed-layer crystallites in which the percentage of expanded layers ranges from 30 to 50. Mering (1949) has shown that the smaller the number of unit layers in each crystallite, the broader the diffraction maxima. However, in this case it appears that the broad maximum is due to the presence of

Fig. 5. Occurrence of mixed-layer clays with other clays (mixed layers—10–20% expanded/80–90% nonexpanded).
crystallites with varying percentages of expanded layers rather than to the smallness of the crystallites.

Figure 4* contains curves for 50, 60, 70, and 80 per cent expanded layers. It should be noted that for clays containing 60 to 100 per cent ex-

* In the following figures an asterisk (*) at the bottom of an X-ray diffraction curve indicates that the peak to the right of the asterisk is run at a setting having only one-half the sensitivity as the setting used in recording the curve to the left.
panded layers, there is only a 1-Å shift of the (001)/(001), 10/17-Å maxima, whereas there is a 6-Å shift in the interval from 10 to 60 per cent expanded layers.

Fig. 7. Occurrence of mixed-layer clays with other clays (mixed layers—30% expanded/70% nonexpanded).

Figures 5, 6, 7, and 8 contain x-ray diffraction curves of the less-than-two-micron fraction of a variety of shales and sandstones. These curves illustrate a variety of ways in which the mixed-layer clays just discussed can combine with other clays to complicate the interpretation of the x-ray curves.
Figure 5 illustrates the case where a 10-Å illite and a 10.1-Å to 10.5-Å mixed-layer clay (10 per cent to 20 per cent expanded layers) occur together. In the first glycolated curve the presence of the mixed-layer clay is shown only by a slight sharpening of the first- and third-order peaks and an increase in intensity of the third order. In the second curve glycolation has caused the development of a more symmetrical first-order peak and formed a minor peak at 9.8 Å. In the third curve in which the first peak of the untreated sample has a broad 10.0-Å to 10.5 Å top, the
mixed-layer phase is quite obvious in the glycolated sample. The 10-Å peak of the fourth curve suggests the presence of normal illite clay; however, the glycolated sample shows the presence of considerable mixed-layer material.

The x-ray patterns in Fig. 6 illustrate a variety of ways in which 10-Å illite and 10.5-Å to 11.0-Å mixed-layer clays (20 to 30 per cent expanded layers) can occur. In all cases the presence of the mixed-layer clays becomes evident when a glycolated sample is x-rayed.

Figure 7 shows typical combinations of 10-Å illite and 11.5-Å to 12.0-Å mixed-layer material (30 per cent expanded layers). The mixed-layer clays in the unglycolated patterns are largely in the 10/14-Å form rather than the 10/12-Å. Curve 4 shows, in addition to a mixed-layer illite-montmorillonite (13 Å), a mixed-layer chlorite-vermiculite reflection (15.5 Å).

Figure 8 shows patterns resulting from mixtures of 10-Å illite peaks and broad 10-Å to 14-Å mixed-layer peaks (40 to 100 per cent expanded layers). In the glycolated patterns the high-angle mixed-layer peak is frequently obscured by the 14-Å chlorite peak.

X-ray patterns of over 6000 sediments have revealed that approximately 50 per cent of them have mixed-layer clays of the types shown in the previous figures.

**EXAMPLES OF RANDOMLY INTERSTRATIFIED CHLORITE-VERMICULITE**

Figure 9 contains x-ray patterns of randomly interstratified chlorite and vermiculite layers. Chlorite has strong second-order (7.1-Å) and fourth-order (3.55-Å) reflections and weak first-order (14.2-Å) and third-order (4.73-Å) reflections. In vermiculite the interlayer matter (Mg²⁺ and H₂O) is less dense than in chlorite [Mg(OH)₂] and as a result the first-order reflection (14.2 Å) is strong and the second and third orders are weak. Thus, in a mixed-layer chlorite-vermiculite clay the relative intensities of the 14.2-Å and 7.1-Å peaks can be used to estimate qualitatively the relative percentage of chlorite and vermiculite. However, as the relative height of the 7.1-Å and 14.2-Å chlorite peaks vary with chemical composition, quantitative evaluation would be complex.

The first three curves in Fig. 9 are x-ray patterns of treated bulk samples of randomly interstratified vermiculite-chlorite layers. The presence of such a mixture is suggested in the first curve by the relative intensities of the 14.0-Å and 7.2-Å peaks. When the sample is heated to 400° C., approximately 50 per cent of the layers collapse to 10 Å and the resulting x-ray curve has peaks at 12.6 Å (10-Å/14.2-Å), 8.0 Å (7.1-Å/10-Å), 4.90 Å (4.73-Å/5.0-Å), and 3.49 Å (3.33-Å/3.55-Å) which are average values obtained by interaction of the 14.2-Å (00l) series and the
10-Å (00l) series. When the sample is heated to 550°C and the OH− is removed from the chlorite interlayer positions the second-, third-, and fourth-order chlorite reflections are destroyed and the curve contains only an 11.6-Å reflection formed by the 10-Å and 13.8-Å (with the loss...
of OH\textsuperscript{−} the chlorite shrinks from 14.2 Å to approximately 13.8 Å, (001) values and a 2.89-Å reflection (003)/(005).

Curve 4 shows a mixed-layer chlorite-vermiculite in which the chlorite is more abundant than in curve 1. The mixed-layer clay illustrated by curve 5 consists almost entirely of vermiculite layers. In the pattern of the glycolated sample it can be seen that the (001)/(001) peak has shifted to 15 Å and the (002)/(002) peak to 7.6 Å.

When the sample is heated to 550° C. and the expanded layer collapses to 10 Å the (001)/(001) peaks shift to a lower spacing of 11.2 Å.

**Three-Component Mixed-Layer Clay Minerals**

Mixed-layer clays containing three components—illite, chlorite, and montmorillonite—are fairly common in shales. Figure 10 contains x-ray

![Figure 10: Mixed-layer clay (illite/chlorite/montmorillonite).](image-url)
diffraction curves of a typical clay of this type. Although interpretation of the data is rendered difficult by the presence of some discrete chlorite and illite, the following observations appear justified: The presence of chlorite layers is shown by the curves of the heated samples. The curve of the 400° C. treated clay has only collapsed to 11 Å and the 550° C. curve actually shows an increase in intensity as OH⁻ is removed from the brucite layer of the chlorite.

When the mixed-layer clay is leached with MgCl₂, the expanded layers absorb two layers of water and are approximately 14 Å thick. The form factor for chlorite is sufficiently similar to that for montmorillonite (Bradley, 1953), that the illite (10 Å)-chlorite (14 Å)-montmorillonite (14 Å) mixed-layer clay can be treated as a two-component, 10-Å and 14-Å system. The curve of the Mg⁺⁺ treated material indicates a mixture of approximately 40 per cent 14-Å chlorite-montmorillonite layers and 60 per cent 10-Å illite layers. Leaching the material with KOH collapses the expanded layers to 12 Å and lowers the (001)/(001) peak to 10.8 Å. The curve of the K⁺ treated clay indicates that the mixed-layer clay has between 25 per cent and 30 per cent of layers greater than 10 Å. This lower value may be caused by the K⁺ collapsing some of the expanded layers to 10 Å.

When the sample is heated to 400° C. the expanded montmorillonite layers collapse to 10 Å [illite(10 Å)-chlorite(14 Å)-montmorillonite (10 Å)] and a different two-component system, 10-Å and 14-Å layers, is formed. The 10-Å/14-Å peak at approximately 11 Å indicates a mixture of 75 per cent 10-Å illite-montmorillonite and 25 per cent 14-Å chlorite material. The mixed-layer clay is therefore composed of approximately 60 per cent illite layers, 25 per cent chlorite layers, and 15 per cent montmorillonite layers.

**Regular Mixed-Layer Clays**

Regular mixed-layer clays are those in which two or more different types of layers occur in a regular sequence, i.e., AB, AB, AB, or AAB, AAB, etc. (Bradley, 1950 and 1953).

The (001) value of a regular mixed-layer clay is equal to the total thickness of the two or more types of layers which are present, i.e., the (001) value of a regular mixed-layer illite (10 Å) and montmorillonite (14 Å) would be 24 Å. Regular mixed-layer clays are differentiated from random mixed-layer clays in that the (00l) series occurs in an integral sequence. It has been pointed out by Bradley (personal communication) that large (001) values (24 to 30 Å) are, in themselves, not proof of regularity. In random mixed-layer clays where the form factors are sufficiently different, in addition to an (001)/(001) average reflection, a low-angle
reflection will occur in the 24-Å to 30-Å region because the contributions from the layers with the higher scattering power are not completely canceled by those of the lower power. For example, in a random mixed-layer clay containing 50 per cent 10-Å illite layers and 50 per cent 14-Å montmorillonite layers a given 120-Å interval will contain approximately five 10-Å illite layers and five 14-Å montmorillonite layers. The stronger scatterer will be encountered 5 times per 120 Å, yielding an ill-defined

Fig. 11. Regular mixed-layer clays.
period of about 24 Å, for which a diffuse scattering maximum is to be observed. In the regular mixed-layer clay the value 120/5 is consistent and the resulting x-ray reflection is relatively sharp; however, in random mixed-layer clays this value is only a statistical average of a population which may have values ranging from 120/1 to 120/12 and thus the reflection is relatively broad and variable.

Regular mixed-layer clays are not common in sedimentary rocks but several have been found. Figure 11 contains x-ray diffraction patterns of two identical regular mixed-layer clays. One is from a Pennsylvanian shale and the other from a Mississippian limestone residue. The two clays in Fig. 11 are apparently composed of alternating 14.4-Å chlorite layers and 14.8-Å vermiculite layers. The (001) value is approximately 29.2 Å. Listed below are the calculated (001) series and the measured (00l) series for untreated, glycolated, and heated patterns.

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When the sample is treated with ethylene glycol the vermiculite layers are increased to 17 Å and an (001) value of approximately 31 Å is obtained. Again the (00l) sequence is integral. The 7.2-Å and 3.60-Å lines indicate the presence of some unmixed chlorite. After being heated to 550°C the vermiculite layers collapse to 10 Å and the chlorite to 14.0 Å. The resulting (00l) values are an integral sequence of 24 Å.

**Example of How Mixed-Layer Clay Minerals Can Be Used for Zonation**

Mixed-layer clays, though presumably quite sensitive to environmental changes, can be found to maintain a consistent ratio through several hundred feet of sedimentary rock. Figure 12 contains x-ray patterns
which illustrate how it is possible to zone a thick section of sedimentary rock by using the mixed-layer clays.

The sample from the upper zone, in addition to illite, contains a mixed-layer vermiculite-chlorite, with the vermiculite layers predominating.

The sample from the middle zone contains a mixed-layer vermiculite-chlorite which is predominantly chlorite. The lower zone contains illite, a mixed-layer illite-montmorillonite, and a mixed-layer vermiculite-chlorite.
ACKNOWLEDGMENT

The writer wishes to express his gratitude to Dr. W. F. Bradley for the many discussions on mixed-layer clays.

REFERENCES


*Manuscript received April 19, 1955.*