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GEOCHEMISTRY OF THE PIERRE SHALE AND EQUIVALENT ROCKS
OF LATE CRETACEOUS AGE

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ABSTRACT

Mixed-layer illite-smectite is the most abundant constituent in much of the Pierre Shale and equivalent rocks. X-ray diffraction data on both peak positions and intensities have been used to distinguish illite-, beidellite-, and montmorillonite-type layers and to evaluate their proportions. The proportion of beidellite is fairly constant at about one-third of the layers. In most samples, illite makes up from 20 to 60 percent of the layers. Montmorillonite makes up from 5 to 60 percent of the layers and is generally complementary to illite. Smectite in bentonite commonly is composed of 60-90 percent montmorillonite-type layers, the remainder being beidellite-type. Interlayering is random.

Average structural formulas for the mixed-layer illite-smectite inferred from 191 whole samples of shale and 22 samples of bentonite and from 15 purified and fractionated samples of shale are as follows (X denotes exchangeable cations, $\sim$ denotes approximate):

	K+	X+	(Al+³	Fe+³	Fe+²	Mg+²)	Al+³	Si+⁴	O-²	(OH)
Illite-smectite in shale	0.7	0.6	2.8	0.5	0.1	0.6	0.6	7.4	$\sim$20	$\sim$4
Individual layers in shale:										
Illite	1.2	.2	2.9	.5	.1	.6	1.0	7.0	$\sim$20	$\sim$4
Beidellite	.2	1.0	2.9	.5	.1	.6	.6	7.4	$\sim$20	$\sim$4
Montmorillonite	.1	.7	2.8	.5	.1	.6	.1	7.9	$\sim$20	$\sim$4
Smectite in bentonite	.1	.6	3.0	.3	.1	.6	.2	7.8	20	4

The mixed-layer clay differs little in marine and nonmarine rocks. Thermogravimetric measurements of clay purified from shale generally indicate that OH⁻ deviates slightly but significantly from the ideal, and the nonideal structural OH- apparently causes dehydroxylation at temperatures consistently lower than those typical of montmorillonite in bentonite that has an ideal 4(OH). The relatively high dehydroxylation temperatures of bentonite persist even where its normal montmorillonitic composition has been altered to highly illitic mixed-layer clay.

In the Montana disturbed belt in northwestern Montana something akin to depth diagenesis, as it is commonly called in the Gulf Coast, has altered much of the clay to regularly interlayered IS-ordered mixed layer clay containing 60-85 percent illite-type layers. Such clay occurs in shale or claystone, in bentonite, and even locally in argillized intrusive igneous rock. Almost all of the randomly mixed-layer clay outside the disturbed belt apparently is essentially as it was deposited and has not been altered by depth diagenesis. In the few places outside the disturbed belt where clay has been altered diagenetically, such as in cuttings from deep wells in the Powder River basin, it is the montmorillonite in bentonite beds rather than the mixed-layer clay in the shale that is altered first.

INTRODUCTION

The Pierre Shale Project has been a long-term study by H. A. Tourtelot, the late J. R. Gill, and L. G. Schultz of the geochemistry, mineralogy, and physical properties of a large mass of sedimentary rock, mainly shale, such as has contributed significantly through geologic time to the makeup of the Earth's crust. Several preliminary and related reports have been published as U.S. Geological Survey Professional Papers 390, 391-A-C, and 392-A and B. The final report of the Pierre Shale Project, informally referred to herein as the main Pierre Shale report, will be Professional Paper 1064-B. The purpose of the present report is to give details of the interpretation of X-ray diffraction patterns and of the chemical composition of the mixed-layer clays in the Pierre Shale. The range of composition of these mixed-layer clays is considered in terms of their origin, particularly with regard to depth diagenesis.

The bulk of the material in this report came directly from the Pierre Shale Project and is representative of the rock unit and its equivalents in the area of study across the northern Great Plains. Two smaller complementary investigations are also described that are directed specifically to the problem of depth diagenesis. One is of well cuttings in the Powder River basin, and the other is of mixed-layer clay in the Montana disturbed belt.

GENERAL GEOLOGY AND MINERALOGY

In the northern Great Plains the Pierre Shale and equivalent rocks form a wedge (fig. 1) composed in the west of 2,000-5,000 feet of predominantly nonmarine claystone, sandstone, and conglomerate, and in the east along the Missouri River of less than 500 to 1,000 feet of dark-gray marine shale containing some marl. In the west, volcanic
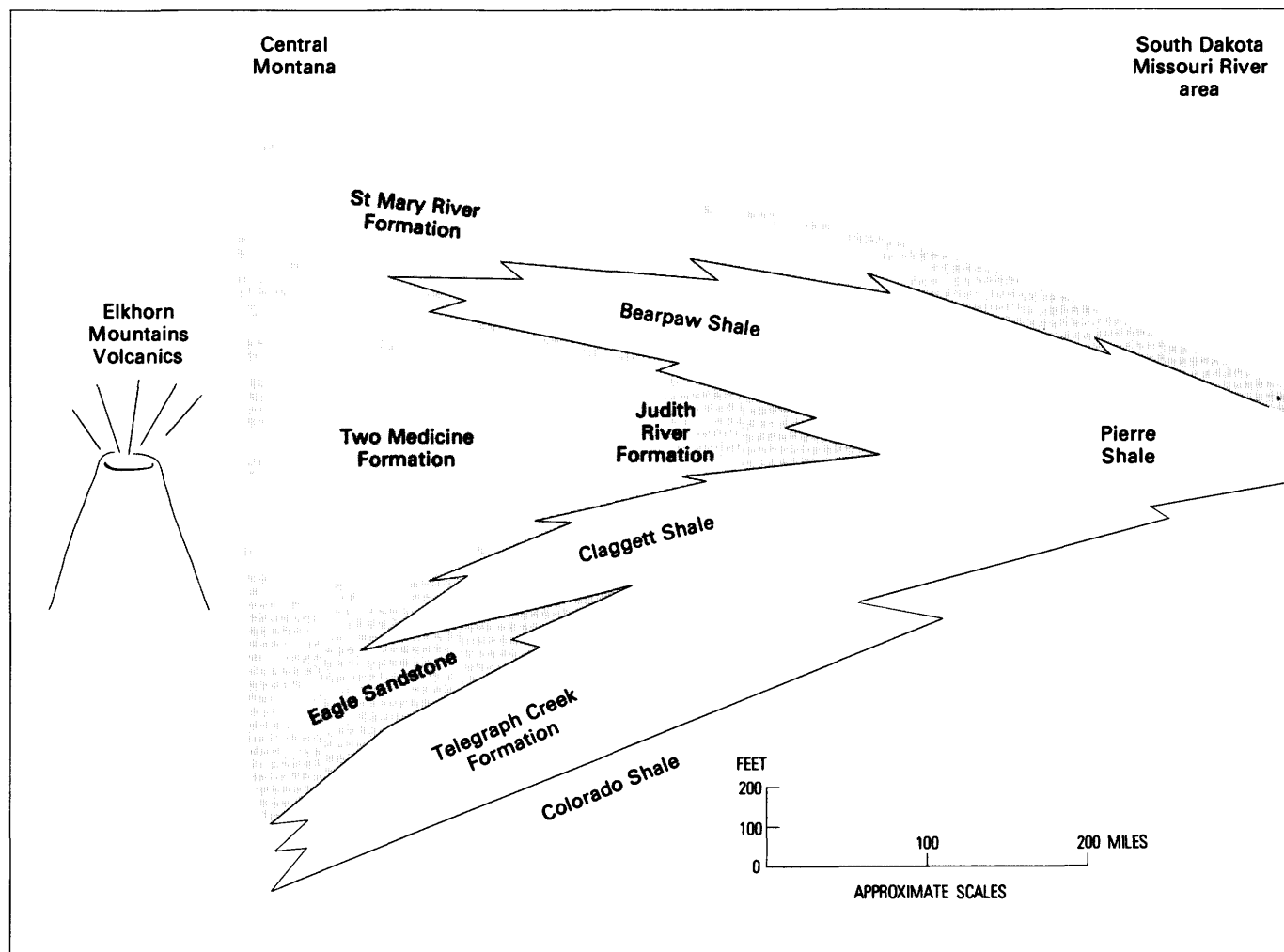
FIGURE 1. — Diagrammatic cross section of the Pierre Shale and some of the equivalent marine and nonmarine rocks. Nonmarine rocks are shaded.

debris derived locally from the Elkhorn Mountains volcanic field is abundant, and thin bentonite beds occur throughout. Sediments of the Pierre Shale and equivalent rocks came mostly from the western side of the basin. In the area studied the name Pierre Shale applies strictly only to rocks along the Missouri River and around the Black Hills, other formation names being used to the west (fig. 1). However, in this report Pierre Shale and equivalent rocks refers to the whole body of rock investigated, including the equivalent marine and nonmarine rocks. For the main study of the Pierre Shale, this rock body was sampled at stratigraphic sections indicated by the numbered localities in figure 2. Details of the composition of these rocks will be given in the main Pierre Shale report. Only a brief summary is given here as a framework for the occurrence of the mixed-layer smectitic clays.

The common mineralogical composition of the Pierre Shale and its equivalents is fairly uniform (table 1). Variation in proportions of minerals is considerably greater in the western predominantly nonmarine claystone than in the eastern marine shale, but the average composition differs little. The most consistent differences are the slightly higher quartz and considerably higher plagioclase content of the western samples. In both, kaolinite and chlorite generally are minor and make up less than 10 percent of the clay minerals, illite commonly makes up 15-20 percent of the clay minerals, and mixed-layer clays make up half or more of the clay-mineral content and 30-60 percent of the total rock. These mixed-layer clays are the principal concern in this report.

Composition of bentonite in the Pierre Shale and its equivalents varies widely, as shown in the main Pierre Shale report, but the composition shown in table 1 is representative of most of it. Completely expanding smectite is predominant and may be the only constituent found in bentonite. A few percent of kaolinite is found in about one-tenth of the bentonite samples, whereas chlorite or illite are rare or absent. Quartz rarely makes up more than a few percent of most bentonite, and plagioclase and biotite may be abundant, particularly at the base of the bed.
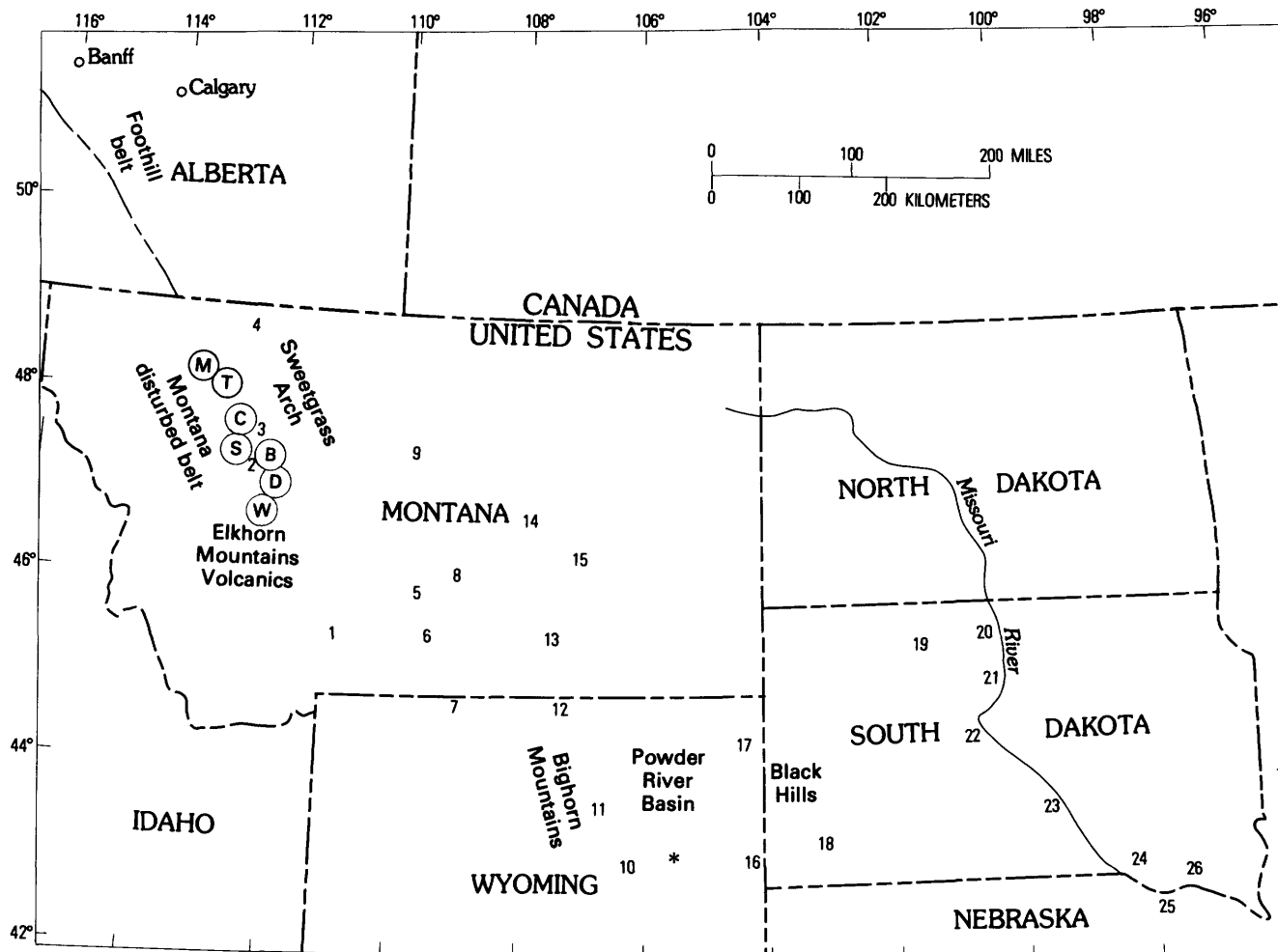
FIGURE 2.— Index map of the northern Great Plains region, showing sample localities and pertinent physiographic features. Numbers indicate the general area of localities from the main study of the Pierre Shale and equivalent rocks, which are described by Schultz, Tourtelot, and Gill (1978). Letters indicate localities in the Montana disturbed belt (table 8); well-cutting locality (table 7) is starred (*).

DEFINITION OF MINERAL AND MIXED-LAYER TERMS

Most minerals are essentially homogeneous crystals composed of orderly repetitions of unit cells of similar composition and geometry. Mixed-layer clay minerals differ in that individual layers of the crystal have different compositions and properties.

Commonly, layers in mixed-layer clays of Pierre age are illite-type and smectite-type. Two kinds of smectite-type layers also are differentiated, those that are montmorillonite-type and those that are beidellite-type. Structures of all of these clay-mineral types (fig. 3) have a middle sheet of alumina octahedra and two outer sheets of silica tetrahedra. In aluminous varieties like those in the Pierre Shale, only two of every three octahedral cation positions are filled (fig. 3). Cations substituted for Al^{+3} and Si^{+4} cause a net negative layer charge. The negative layer charge of montmorillonite is due mainly to substitution of divalent Mg^{+2} ions for trivalent Al^{+3} ions in the octahedral sheet (fig. 3). The negative layer charge of beidellite is due mainly to substitution of trivalent Al^{+3} for quadrivalent Si^{+4} ions in the tetrahedral sheets. The negative layer charge of smectites is balanced by positively charged interlayer cations, most commonly Na^+ and Ca^{+2}, which are exchangeable and commonly hydrated. The layers are said to be expandable because water or other substances readily penetrate between the layers. Two organic liquids commonly used to expand smectites to known thicknesses are ethylene glycol, which produces a 17-angstrom (A) layer thickness, and glycerol, which produces an 18-A layer thickenss. The characteristic feature of illite layers is that they are nonexpanding and have a fixed layer thickness of 10 A. This is because illite layers have a net negative layer charge that is balanced predominantly by interlayer K^+ cations. The K^+ cations are no hydrated, and they fit snugly into the silica rings of adjacent layers. Bonding of K^+ to the rings of oxygen anions prevents penetration of water between the illite

TABLE 1. — *Typical mineralogical composition, in percent, of the Pierre Shale and equivalent rocks*

SHALE

West

Clay minerals	50-65
Clay composition:	
Mixed-layer	50-100
Illite	0-20
Chlorite	0-5
Kaolinite	0-20
Quartz	20-30
Plagioclase	5-10
K-feldspar and other minerals	([1])

East

Clay minerals	75
Clay composition:	
Mixed-layer	75
Illite	15
Chlorite	5
Kaolinite	5
Quartz	15-20
Plagioclase, K-feldspar and other minerals	([1])

BENTONITE

Clay minerals	80-100
Clay composition:	
Smectite	100
Quartz	0-5
Plagioclase	0-10
Biotite	0-10

[1]A minor amount.

layers. The layer charge of illite, like that of beidellite, is predominantly in the tetrahedral layers, and the charge is somewhat larger than in the smectites.

Throughout this paper, layers of mixed-layer clay are referred to as illite-type or montmorillonite-type. The hyphenated "type" terminology is used to alert the reader to two things. First, the layers are parts of a mixed-layer clay. Second, strictly speaking, what is being referred to is not a clay layer as normally thought of, but rather the interlayer space and the nearest halves of the two adjacent layers. The identity of the layer is determined by the behavior of the interlayer area, which in turn is determined primarily by the makeup of the adjacent layers. In mixed-layer clay, a classical layer must commonly be asymmetrical. For example, in figure 3, the upper half of the layer cross section together with the nonexpanding interlayer space having K+ ions and part of the adjacent layer above (not shown) would behave like and could be said to be an illite-type layer, whereas the lower half of the layer cross section and corresponding adjacent parts below would behave like and could be said to be either montmorillonite- or smectite-type.

Interlayering of different types of clay minerals in mixed-layer clay may be random or regular, and partly regular types also are possible.

Random interlayering implies no detectable influence of one layer on adjacent neighbors; in other words, the probability of one type of layer being adjacent to another is the same as its abundance in the mixed-layer crystal. Basal X-ray diffraction peaks of randomly interlayered clay normally lie (migrate) between d-spacing positions of the types of layers involved, depending upon the proportion of the layers. However the 17-A and 10-A d-spacings of glycolated smectite and of illite do not migrate, although higher basal-order reflections do. X-ray peaks of mixed-layer clay are commonly designated by the basal order of the mineral layers between which they are migrating; for example, the peak resulting from the third basal order of smectite-type layers and the second basal order of illite-type layers is herein designated as an S_{003}/I_{002} reflection. Randomly interlayered illite-smectite is the most common type of clay in the Pierre Shale.

Regular or ordered interlayering implies a periodicity in the sequence of layers; in other words, one type of layer tends to follow a different type, and tends not to be adjacent to layers like itself. Any degree of regularity theoretically may occur, from none (random) to the maximum permitted by the proportion of layers. However, regularity is easily

EXPLANATION

O O^{-2} ● Si^{+4}

⊞ OH$^-$ O Al^{+3}

( ) Interlayer cation

- - - Boundary of unit cell

( ) K$^+$ in illite

} SiO$_4$ tetrahedra

} AlO$_4$(OH)$_2$ octahedra

} SiO$_4$ tetrahedra

( ) Na$^+$ and Ca^{+2} in smectite
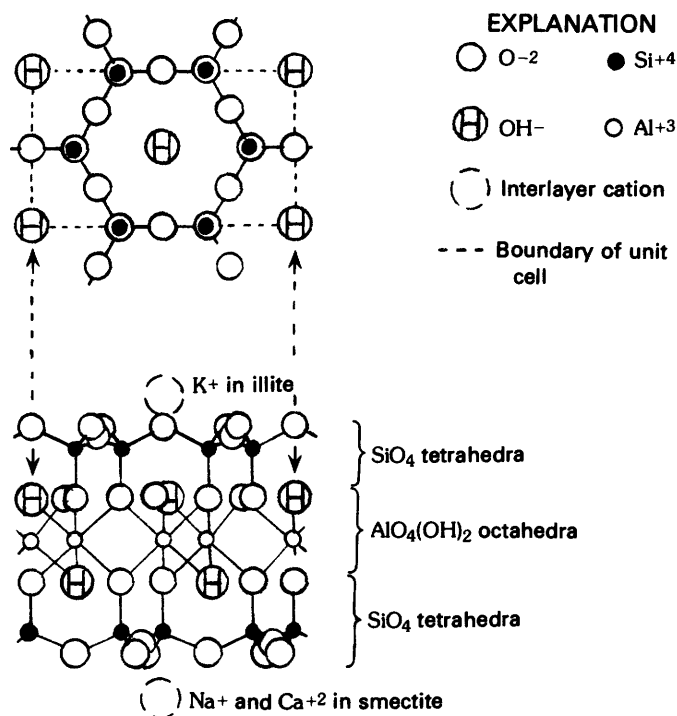
FIGURE 3.— Schematic structure of an aluminum smectite or illite layer, adapted from Bragg (1937, p. 206). Above is a plan view of a silica sheet showing one complete ring of linked silica tetrahedra and parts of others, with a hydroxyl at the center of the rings. Below is a layer cross section showing two outside silica sheets sharing apical oxygen ions with a middle sheet of alumina octahedra. Certain O^{-2} ions that otherwise would be superimposed have been slightly displaced. Al^{+3} substitutes for Si^{+4} in beidellite and illite tetrahedra; Mg^{+2} substitutes for Al^{+3} in montmorillonite octahedra.

recognized only when the degree of regularity is high. Complete regularity commonly occurs only when the two types of layers involved are equally abundant. Such regular interlayering produces a superorder reflection at a d-spacing that is the sum of the thicknesses of the two layers, and this superorder is accompanied by a rational sequence of basal reflections. For example, 10-A and 17-A ordered interlayers produce a basal sequence of 27-A, 13.5-A, 9-A, 6.75-A, ... peaks. Completely regular mixed layering is rare in the Pierre Shale and usually involves chlorite-type layers which are not considered in this report.

Still another kind of partly regular interlayering has been described by Reynolds (1967) and Reynolds and Hower (1970). Probably the most common such interlayering involves "an illite-montmorillonite superlattice (IM), randomly interstratified with additional illite" (Reynolds and Hower, 1970, p. 26); in other words, no two smectite layers (or expanding interlayer areas) are adjacent to each other. The characteristic feature of such clay is that, unlike randomly interlayered types, it produces an X-ray peak that, as the proportions of layers change, migrates in the area between 10 A and 17 A—commonly near 12-13 A. Such clay is abundant in some equivalents of the Pierre Shale, and in this report such clay is said to have IS-ordered interlayering. The IS in this paper, rather than the IM of Reynolds and Hower, reflects the use in this paper of smectite rather than montmorillonite as the general term for expandable clay.

Readers needing a more detailed explanation of mixed layering in clay minerals are referred to MacEwan, Amil, and Brown (1961) and to the papers of Reynolds and Hower mentioned above.

INTERPRETATION OF X-RAY DIFFRACTION TRACES OF MIXED-LAYER CLAY

X-ray diffraction procedures used for quantitative evaluation of the mineralogy of the Pierre Shale (Schultz, 1964) are fairly standard for most minerals. Procedures used for mixed-layer expandable clays are in part unconventional and have been changed from the earlier work. The new method for evaluation of mixed-layer clays is described in detail below and is compared with the old method. The methods are illustrated by sets of X-ray diffraction traces for four samples in figure 4. The new method involves a two-step breakdown of the mixed-layer clay. The first step, which distinguishes proportions of illite-type and smectite-type layers, is illustrated in figure 4 $A-D$, and is described in the next section of the report. The second step, which divides smectite into beidellite- and montmorillonite-type layers is illustrated in figure 4 $A'-D'$ and is described in the second-following section. Both steps involve a conventional peak-migration method for evaluation of proportions of layers as well as an alternative unconventional peak-height method that can be applied to many samples for which peak migration cannot be used.

ILLITE-SMECTITE

Almost all expandable clay from shale in the Pierre Shale shows evidence of interlaying with nonexpandable illite-type layers. Completely expandable smectite (not shown in fig. 4) is common only in bentonite. One of the more completely expanding mixed-layer clays from a shale is illustrated in figure 4A. Treated with ethylene glycol, the first basal reflection at 17 A differs little from that of a completely expanding smectite from a bentonite bed, but the higher order reflections are fairly broad and slightly shifted from the ideal d-spacings (S_{002}, S_{003}, fig. 4). As the proportion of nonexpanding layers increases (fig. 4B), the higher order basal reflections shift or migrate farther toward the d-spacing positions of the nonexpanding illite-type layers (I_{001}, I_{002}), but the first basal reflection remains near 17 A, merely becoming broader and less intense, until it almost completely disappears (fig. 4C).

Clays like those in figure 4A-C are randomly interlayered. Clays having appreciably more illite-type layers than the one shown in figure 4C invariably have IS-ordered interlayering. As previously defined. IS-ordered illite-smectite diffracts X-rays in the approximately 11.5-14-A range that is not possible for randomly interlayered illite-smectite. Most IS-ordered clay from the Pierre Shale shows no super order reflection that is characteristic of completely ordered mixed-layer clay. However, a few do give a small reflection from glycolated material that is almost invariably near 31 A. The 31-A d-spacing, however, is nowhere near a rational multiple of the much stronger basal reflection between 11.5 A and 14A.

All four clay samples in figure 4 A-D produce well-defined reflections near 10 A and 5 A when heated to 300° C. Therefore, all are mixed-layer combinations of only two kinds of layers. One kind is nonexpanding illite, having an unvarying layer thickness of 10 A. The other kind is expanding smectite, which contracts to a thickness of approximately 9.6 A when heated. The 10-A- and 9.6-A-layer thicknesses are so nearly similar that they produce a fairly sharp X-ray reflection not noticeably displaced from the 10-A position (I_{001}, fig. 4), but the second order is noticeably displaced from 5 A (I_{002}).

The most useful migration curve for determining proportions of illite- and smectite-type layers is that involving the S_{003} and I_{002} d-spacings for glycolated material. As will be explained later in connection with figure 6, the S_{003}/I_{002} reflection indicates approximately 20, 45, 60 and 75 percent nonexpanding illite-type layers, respectively, for the samples of figure 4 $A-D$ ("new" method). However, owing to the weak intensity of the reflection and some interference from other minerals, only about one-tenth of the total number of samples could be analyzed by peak migration such as was
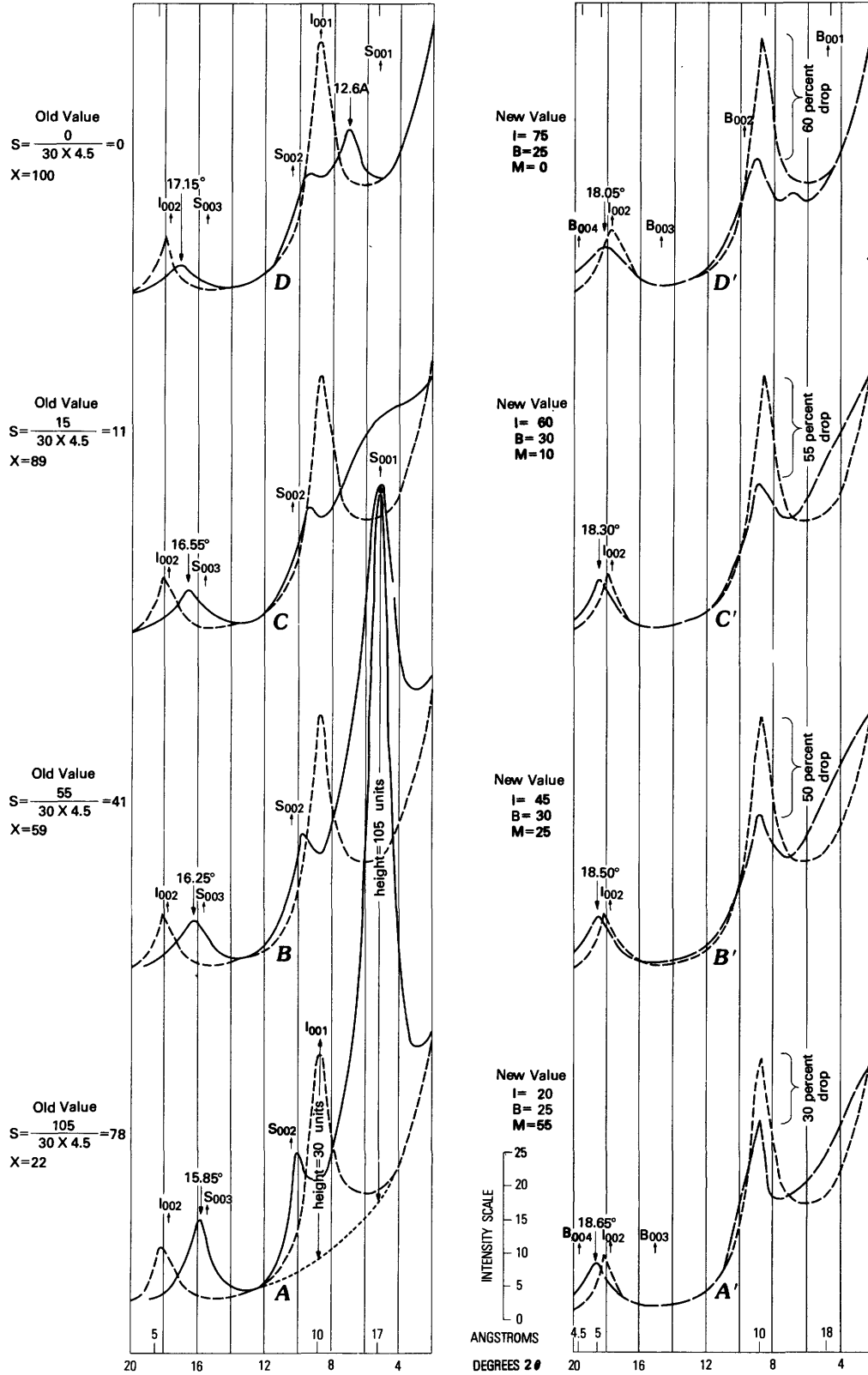
FIGURE 4.—X-ray diffraction traces of four clay samples that illustrate the range of composition of mixed-layer illite-smectite in rocks of Pierre age and the new and old methods of expressing proportions of layers. Curves A'-D' are of the same four clays as A-D, but are Li+ treated. Other treatments are: solid line, ethylene glycol; long-dashed line, glycerol; and short-dashed line, heated. Short arrows show ideal 001 peak positions of smectite (S), illite (I), beidellite (B), and montmorillonite (M); X is mixed-layer clay (see text); long arrows show 2θ positions or angstrom (A) values of observed peaks. CuKα radiation.

done with the exceptionally pure and well-oriented clays illustrated in figure 4.

During the early part of the Pierre Shale study, owing to the limited usefulness of peak migration, a peak-height method previously described (Schultz, 1964) was used to indicate the amount of expandable clay. This "old" peak-height method (fig. 4) divided what is now called mixed-layer clay into two components. One component, which would give a 17-A reflection of the observed relative height, was called montmorillonite (in the group sense—S in fig. 4); the other component, which was assumed not to diffract at the 17-A position, was called mixed-layer clay (X in fig. 4). The basis for the separation was the observation that, for 40-millimeter long oriented aggregate mounts and a 1° beam slit, completely expanding aluminum smectite gave a 17-A reflection about 4½ times the height of the 10-A reflection after heating. The absolute height of the reflections depended greatly upon the degree of preferred orientation, but the ratio of the 17-A peak height to the 10-A peak height from the same sample mount was fairly reproducible. In figure 4A, heights of the 17-A and 10-A reflections in arbitrary units are 105 and 30, respectively. A clay having a 30-unit peak height when heated, if it were entirely expanding smectite, should give a 135-unit (30 X 4½) peak height at 17 A when solvated with ethylene glycol. The observed 105-unit peak height is 78 percent of the expected height, so 78 percent of the expanding clay was attributed to smectite (S) and the remaining 22 percent to mixed-layer clay (X). Values for smectite (S) and mixed-layer clay (X) are similarly calculated by the "old" method for figure 4 B-D.

A reasonably consistent relationship developed, as the Pierre study progressed, between the old peak-height method and the proportion of illite- and smectite-type layers that could be interpreted from peak migration. As shown in figure 5, the 17:10 A ratio decreases from about 4.5 for completely expanding smectite to zero where illite-type layers make up 60-65 percent of the layers. Thus, in samples where illite and smectite are the only two components of the mixed-layer clay, as is the case with most rocks of Pierre age, the 17:10-A ratio can be used in conjunction with figure 5 to estimate the approximate proportion of the two different layers. The estimate from the new peak-height method is more realistic than that from the old method, because rarely does any unmixed smectite occur in shale of the Pierre. Most samples do contain essentially unmixed illite or mica, which gives a 10-A reflection after all sample treatments. An adjustment for such illite must be made in the 10-A peak intensity (Schultz, 1964, fig. 3, table 2) before the peak height ratios (fig. 5) are used.

ILLITE-BEIDELLITE-MONTMORILLONITE

Beidellite, as pointed out in connection with figure 3, differs from montmorillonite in that the layer charge of beidellite is mainly in the tetrahedral layers owing to
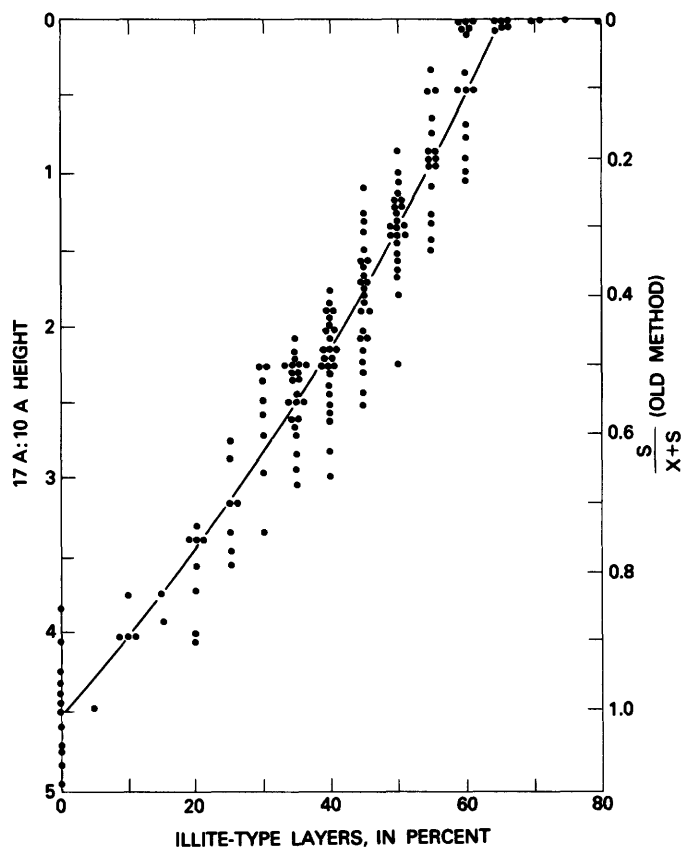
FIGURE 5. Relationship between the proportion of smectite (S) and mixed-layer clay (X) interpreted from peak heights (Schultz, 1964) and the percentage of illite-type layers interpreted from peak migration $(S_{003}/I_{002},$ fig. 4). Plotted points are individual samples. Solid line is curve used to interpret the percentage of illite-type layers. A, angstrom.

Al^{+3}-for-Si^{+4} substitution, whereas the layer charge of montmorillonite is mainly in the octahedral layers owing mostly to Mg^{+2}-for-Al^{+3} substitution. The Greene-Kelly (1955) lithium test uses this charge-site difference to differentiate between beidellite and montmorillonite by making only the latter nonexpanding. The process is herein called a Li^+-200° C-glycerol treatment. Exchangeable cations are replaced with Li^+ by treatment with $3N$ LiCl. Overnight heating at 200 ° C volatilizes interlayer water, and the layer thickness decreases to about 10 A. If the layer is montmorillonite-type, the small Li^+ ions enter vacant cation sites in the octahedral layer (fig. 3) and neutralize the negative layer charge caused by Mg^{+2}-for-Al^{+3} substitution. Thus, the uncharged layer becomes nonexpanding and retains a 10-A thickness when treated with glycerol. Beidellite, similarly treated, remains expanding because its layer charge is in the tetrahedral layer which contains no vacant cation sites for the Li^+ ions to enter.

Proportions of beidellite- and montmorillonite-type layers can be qualitatively evaluated by visually comparing X-ray traces before and after the Li^+-200° C treated clay is

reexpanded by glycerol (fig. 4 A'-D') with traces of the same clay not treated . with Li+. If no reexpansion of the Li+-treated clay occurred, the 10-A reflection (fig. 4 A'-D') before and after glycerol treatment would be unchanged, and all smectite layers would be interpreted as montmorillonite. If the trace of the glycerol-treated clay were essentially the same as that of the natural clay expanded with ethylene glycol (fig. 4 A'-D'), then smectite layers are interpreted as beidellite. In the latter case (fig. 4D and 4D') the traces shown are not actually identical, because clays expanded by glycerol and ethylene glycol produce slightly different spacing—about 18 A and 17 A, respectively. (In practice, the Li+-treated clays were compared with Mg+2-glycerol-treated samples routinely run for identification of vermiculite. These are not shown in figure 4.) Commonly, results are somewhere in between(fig. 4 A'-C'), with an appreciable drop in the intensity of the 10-A reflection after glycerol treatment and a rise in the baseline but no development of an 18-A reflection comparable to the 17-A reflection of the ethylene glycol-treated clay. Apparently both types of layers are present.

The proportion of beidellite-type layers is conventionally evaluated from the position of the 001 reflections of the Li-200°C-glycerol-treated clay. Greene-Kelly (1955) used the second beidellite reflection (fig. 4D', B_{002}) and its shift toward the approximately 9.6-A position of collapsed montmorillonite. For the Pierre Shale, use of this refelction was generally not possible because the angular shift was small, and free illite at 10 A interfered; a shift of the fourth beidellite reflection (fig. 4D', B_{004}) toward higher angles was more useful. Also, Greene-Kelly used the lithium test for two-component interlayering of beidellite- and montmorillonite-type layers. For the Pierre Shale, a third component, the illite-type layers, must be taken into account.

Proportions of illite-, beidellite-, and montmorillonite-type layers are interpreted from the triangular diagram in figure 6. The numbered heavy lines within the triangle refer to the angular position of the peak in the 18°2θ region for Li+-200°C-glycerol-treated material, for example, at 18.65° for figure 4A'. The corners of the triangle correspond to the biedellite (B_{004}) spacing of 4.5 A at 19.73° 2θ, the second basal spacing of collapsed montmorillonite of 4.8 A at 18.5° 2θ, and the second basal spacing of illite (I_{002}) of 5.0 A at 17.74° 2θ. The scale to the right of the triangle from 15.6° to 17.7° 2θ is the migration curve between the 5.7 A (S_{003}) of smectite solvated with ethylene glycol at 15.6° 2θ and the 5.0 A (I_{002}) of illite at 17.74° 2θ that is used to determine the proportion of illite layers in figures 4A-D. For example, in figure 4A, the S_{003}/I_{002} reflection at 15.85° 2θ corresponds in figure 6 to 20 percent illite—this is where the 20 percent illite in the new interpretation in figure 4A comes from. Then, the 18.65°2θ position from the

Li-200°C-glycerol treated sample (fig. 4A') intersects the 20-percent-illite line in figure 6 at the letter A. From A the composition lines project to 25 percent beidellite and 55 percent montmorillonite, as recorded for the new composition in figure 4A. All proportions have been rounded to the nearest 5 percent. The S_{003}/I_{002} migration curve on the right side of figure 6 is adapted from one calculated for randomly interlayered clay (MacEwan, Amil, and Brown, 1961, p. 417), and, as pointed out by Reynolds and Hower (1970, p. 33), the S_{003}/I_{002} migration curve is almost identical for IS-ordered and randomly interlayered illite-smectite.

The problem with the beidellite-montmorillonite interpretation, as with the illite-smectite interpretation, is that most samples give X-ray traces not nearly so good as those in figure 4A'-D', and the relevant reflections cannot be measured. Here again, as data accumulated from the Pierre Shale study, a rough relationship was noticed between the proportion of beidellite-type layers that remained expandable as interpreted from figure 6 and the change in intensity of the 10-A reflection before and after glycerol treatment. This change is labeled as a 30-percent drop in figure 4A' and 50-, 55- and 60-percent drops in figure 4B'-D'. This relationship is shown in figure 7. The decrease in intensity appears to depend not only on the proportion of reexpandable beidellite-type layers but also on the proportion of illite-type layers. For mixed-layer clays having few illite-type layers, the percent decrease in height of the 10-A reflection is approximately equal to the inferred percent of beidellite-type layers (for other smectites see Schultz, 1969 fig. 2). If illite-type layers are dominant, however, the percent decrease in the 10-A peak height is equal to nearly double the percent beidellite-type layers. The lines relating the three factors in figure 7 are very approximate—even more so than the peak-height relationship in figure 5—but the height relations have made possible the estimation of proportions of illite-, montmorillonite-, and beidellite-type layers in mixed layer clays from most samples of Pierre Shale.

The following example illustrates the peak-height method for figure 4B and 4B'. The 17:10-A height ratio of 55:30=1.83 would indicate, in figure 5, 44 percent illite-type layers, rounded to 45 percent. This illite value together with the 50-percent peak drop from the Li+ test (fig. 4B') gives slightly more than 30 percent beidellite-type layers (fig. 7) which, when rounded to 30 percent, leaves 25 percent montmorillonite-type layers. The good agreement with proportions derived from migration curves (fig. 4B, "new value") is by no means universal, but values usually agree within 5 or 10 percent. The critical requisites for application of relative peak heights to the interpretation of mixed-layer clays are that the oriented aggregate must not be broken up during solvation or heating and that essentially all the layers must be either illite- or smectite-type having a basal d-spacing near 10 A when heated.

PEAK POSITIONS OF IS-ORDERED CLAY

Unlike the 17-A reflection for randomly mixed-layer illite-smectite (fig. 4A-C), the first basal reflection for glycol-treated IS-ordered clay does vary over a considerable range, from about 11.5 A to very broad reflections at about 14 A. Figure 8 shows the relationship between proportions of illite-type layers from 11 samples for which the S_{003}/I_{002} curve on the right side of figure 6 could be used and the d-spacing of the first reflection. The range of d-spacings observed is considerably greater than that shown by calculated diffraction profiles of maximum IS-ordered material described by Reynolds and Hower (1970, fig. 5, table 3). The d-spacings of about 13 A observed for 70 percent illite-type layers are close to that calculated by Reynolds and Hower. However, several observed d-spacings of about 14A probably indicate that IS-ordered clay having less than 70 percent illite-type layers in the Pierre Shale tends to have less than maximum ordering. Conversely, many
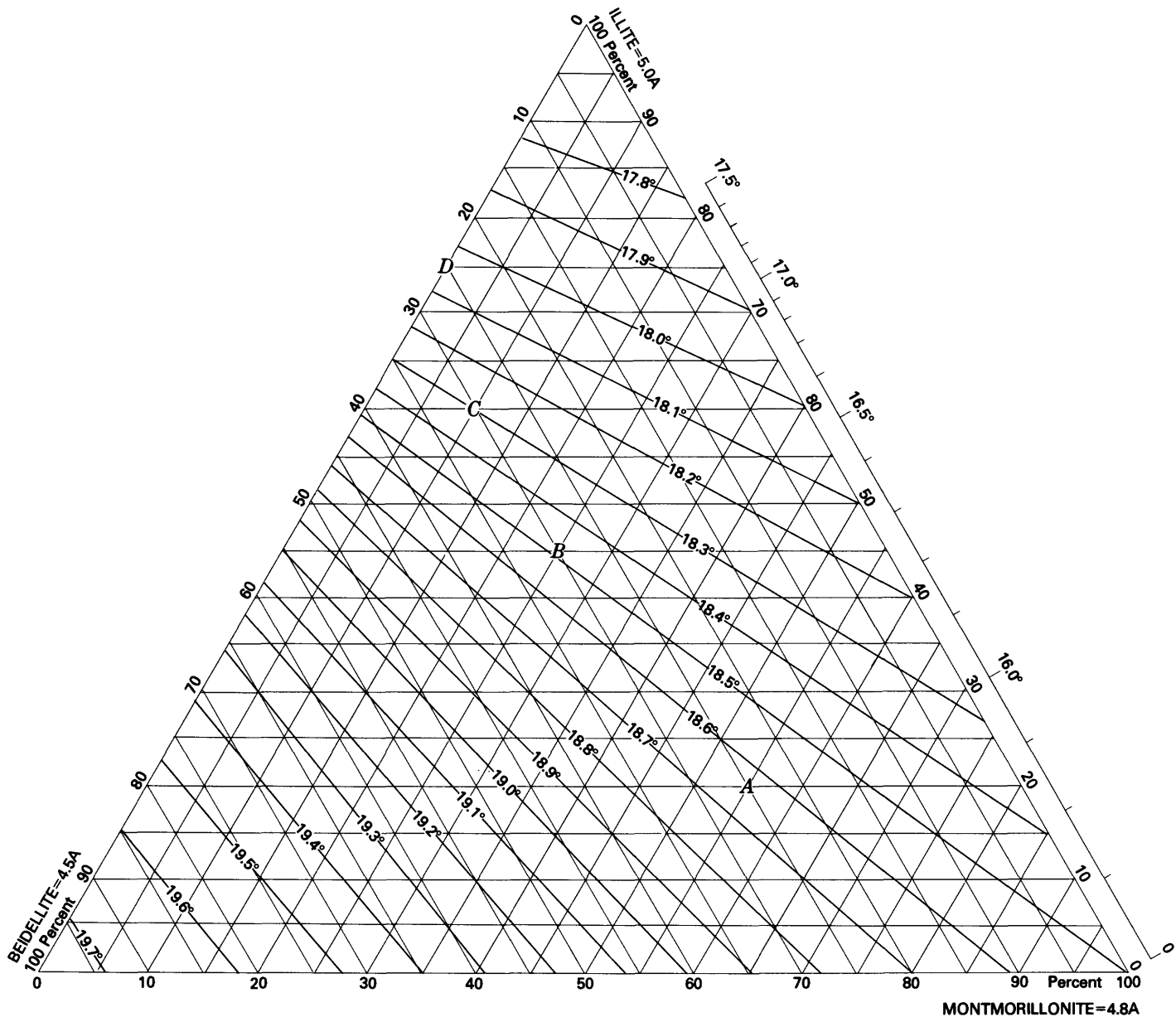
FIGURE 6. — Diagram used to interpret proportions of illite: beidellite: montmorillonite layers in mixed-layer clay. The heavy lines within the triangle are the 2θ positions of the B_{004}/I_{002} reflections (fig. 4A'-D'),and the points at which these lines intersect the legs of the triangle are from migration curves (MacEwan, Amil, and Brown, 1961, p. 417) adapted for an 18-A primary d-spacing appropriate for glycerol. The scale next to the right-hand leg of the triangle is for the S_{003}/I_{002} reflection (fig. 4A-D) adapted for the 17-A primary d-spacing appropriate for ethylene glycol. Letters A-D within the triangle indicate composition of samples on figure 4. CuK$_\alpha$radiation; °, degrees 2θ; A, angstrom.
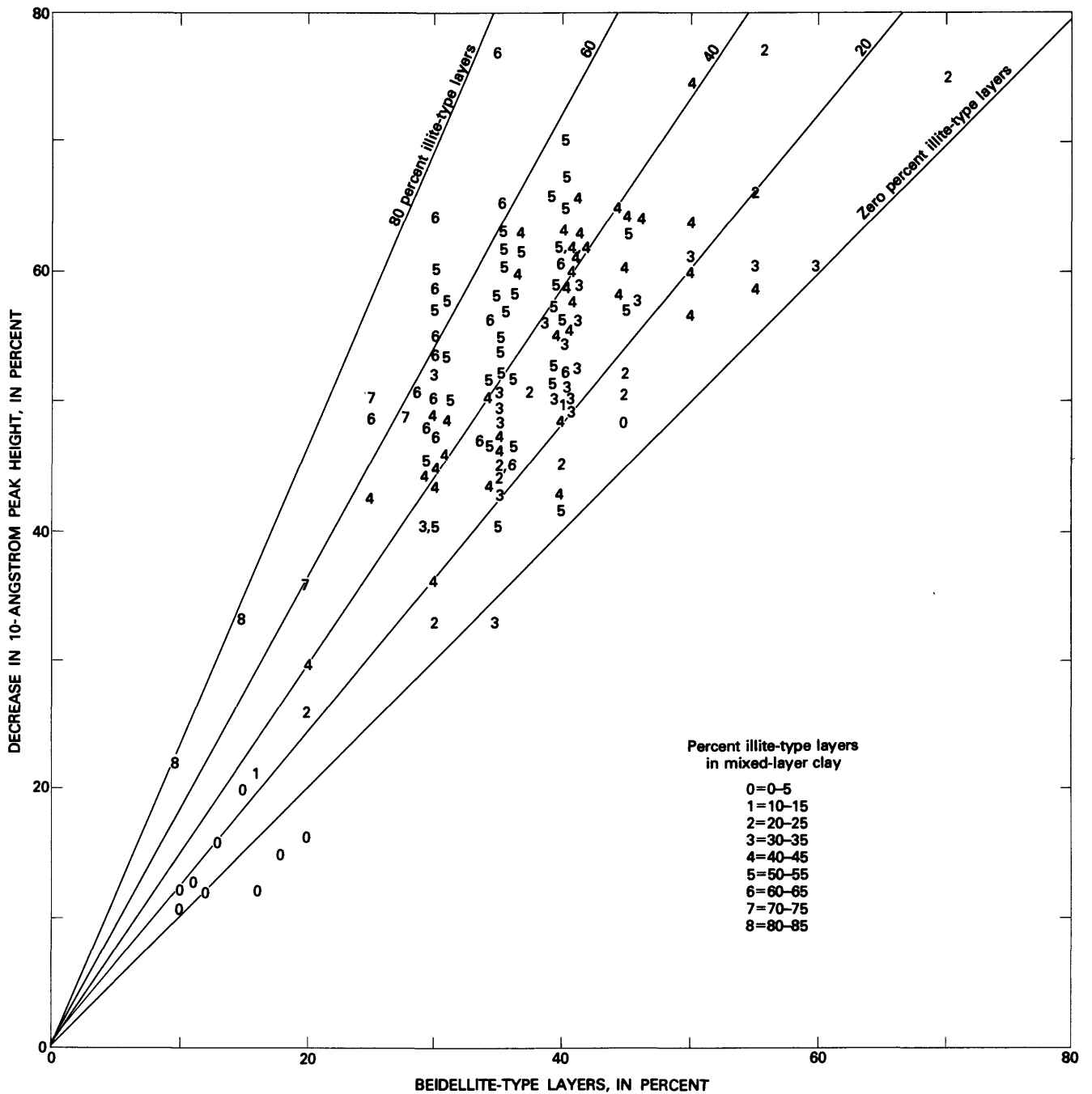
FIGURE 7. — Relationship between the proportion of beidellite- and illite-type layers in mixed-layer clay determined from migration curves and the change in peak height after glycerol treatment of Li^+-saturated and heated clay. Illite-type layers rounded to nearest 5 percent.

observed d-spacings of about 12 A or less indicate that when there is appreciably more than 70 percent illite-type layers, superlattices larger than IS may be present, though no patterns like that for ideal ISII ordering (IMII ordering of Reynolds and Hower, 1970, fig. 7) were observed. Figure 8 is the d-spacing curve used to evaluate the proportion of illite-type layers in IS-ordered clay in the Pierre Shale where only the first basal reflection could be measured.

COMMON PROPORTIONS OF ILLITE: BEIDELLITE: MONTMORILLONITE

Proportions of the three common types of layers in samples of mixed-layer clay from individual samples of the main Pieere Shale study are shown in figure 9. Beidellite

content is relatively uniform, averaging about 35 percent and deviating little more than 10 or 15 percent from the average. In most shales the proportions of illite-type layers vary more widely, from 10 or 15 percent to 60 percent; more than 60 percent illite-type layers occurs mostly in samples having IS-ordered mixed-layering from the Dearborn River locality (fig. 2, loc. 2). Montmorillonite is generally complementary to the proportion of illite-type layers. Almost all smectite having no illite-type layers is from bentonite, and conversely, few of the approximately 200 bentonite samples examined contained detectable illite.

Beidellite layers are slightly more abundant in nonmarine than in marine rock, but the difference is slight. Excluding shale from Dearborn River, which has been altered, mixed-layer clays in marine rock are more illitic, but again the difference is slight.

CHEMISTRY OF MIXED-LAYER CLAYS

One objective of the Pierre Shale study was to determine whether sediments deposited in different environments, such as marine and nonmarine, could be distinguished by their chemistry or mineralogy. The mixed-layer illite-smectite was of particular interest in this regard because it is the most abundant component in rocks of Pierre age. Also, because of its fine grain size and large surface area, the mixed-layer clay might be expected to be particularly sensitive to changes in chemical environment. Two methods were used to determine the chemical makeup of the mixed-layer clay: (1) chemical analysis of the whole rock and then correcting for other mineral constituents (Schultz, 1964), and (2) chemical analysis of the purified mixed-layer clay component. The first method was used on 223 samples, for which chemical analyses are the basic data for much of the main Pierre Shale report. However, as minerals other than mixed-layer clay amounted to half or more of most samples, the structural formulas calculated for the clay may involve considerable error. The formulas calculated are neverthelass believed to be useful because any systematic errors that may be involved apply equally to marine and nonmarine samples; thus, a valid comparison of these two groups can still be made. The second method was used on only 15 purified samples, but the calculated structural formulas are much more accurate.

STRUCTURAL FORMULAS CALCULATED
FROM WHOLE-ROCK SAMPLES

The transformation of a chemical analysis of a mineral to a structural formulas (table 2) involves showing where each chemical element is thought to occur in the structure of the mineral (fig. 3). Of the 223 chemical analyses in the main Pierre Shale report, structural formulas for mixed-layer clay that seemed fairly reasonable could be calculated from 219 analyses. These include 191 from shale, 22 from bentonite, and 6 from marl. Formulas for shale and bentonite are considered separately below, but formulas for marl are not
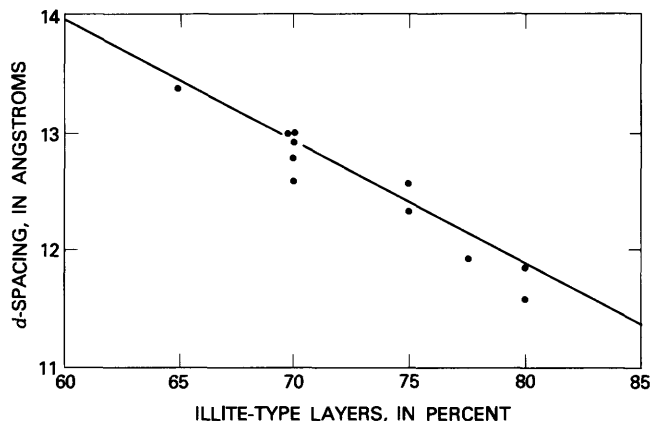
FIGURE 8.—Illite content of 111S-ordered mixed-layer clay samples determined from S_{003}/I_{002} (fig. 6) related to d-spacing of the first basal reflection of the clay treated with ethylene glycol. The solid line was used to interpret the percentage of illite-like layers when the S_{003}/I_{002} reflection was indistinct. $CuK\alpha$ radiation.

considered here because of the small number of samples and the small amount of clay that they contain.

SHALE

The range of composition of mixed-layer clay in marine and nonmarine shale is shown in figure 10, and averages are given in the upper part of table 2. The general similarity between mixed-layer clay in marine and nonmarine rocks is as expected from their mineralogical similarity (fig. 9). One of the bigger differences is the presence of more K^+ ions in the nonmarine rocks. This difference is not in agreement with similar proportions of illite-type layers in marine and nonmarine rocks indicated in figure 9. Average K^+ content for nonmarine rocks, exclusive of the nine chemically analysed samples from the Dearborn River locality (loc. 2), is 0.65. This average exceeds the 0.59 K^+ average for marine rocks even though the average content of illite-type layers, exclusive of the Dearborn River locality samples (fig.9), is about 5 percent less than for marine rocks (fig. 9). These differences are small, and the lack of agreement between the K^+ ion and content of illite-type layers probably indicates that the differences are not significant. Certainly, in view of the wide variation in proportions of illite layers shown in figure 9 and K^+ shown in figure 10 within both marine and nonmarine samples, neither the amount of illite-type layers nor the amount of K^+ in the mixed-layer clay would seem to be a reliable indicator of environment of deposition.

Tetrahedral Al^{+3} is generally higher in nonmarine rocks than in marine rocks. This difference is not due exclusively to abundant illite-type layers in samples from the Dearborn River locality—without these, average tetrahedral Al^{+3} is still 0.52. The higher tetrahedral Al^{+3} for nonmarine rocks is in accord with their somewhat higher beidellite content (fig.9). The difference appears to be real but much too small to serve as a reliable environmental indicator (fig. 10).

Two aspects of the structural formulas calculated from whole-rock analyses seemed unusual. First, the sum of the octahedral cations is less than the ideal 4.00 per unit cell for more than 80 percent of the samples (fig. 10), and second, the average of 0.44 tetrahedral Al^{+3} (table 2) seems too low for clays in most of which illite- and beidellite-type layers predominate. Both of these features could be caused by under-correction for quartz, a possibility that will be considered later.

BENTONITE

The structual formulas for smectite in bentonite differs in generally expected ways from those for mixed-layer clay in shale of Pierre age (table 2). As previously mentioned, smectite in nearly all bentonite samples in the Pierre Shale and in all of the 22 bentonite samples in table 2 are not interlayered with illite-type layers, and mortmorillonite layers predominate over beidellite. Therefore interlayer K^+ ions are few, and tetrahedral Al^{+3}, which is low in montmorillonite, is low in the bentonite. The total interlayer

charge, averaging 0.94 for the bentonite samples, is only about two-thirds that for the shale samples. The amount of iron in the octahedral layer is about half that in shale, and the amount of magnesium is nearly the same. As the amount of minerals other than smectite is small in bentonite, averaging about 10 percent, the correction for other minerals is small, and the average structural formula for bentonite is a more reliable one than for shale. Note, for example, that the sum of the octahedral cations is very close to the ideal 4.00 per unit cell.

STRUCTURAL FORMULAS CALCULATED FROM PURIFIED MIXED-LAYER CLAY

Chemical analyses of mixed-layer illite-smectite concentrated from 15 selected samples of the Pierre Shale and equivalent rocks are given in table 3 together with calculated structural formulas. The samples were selected to give a representative range of proportions of illite-, beidellite-, and montmorillonite-type layers in marine and nonmarine
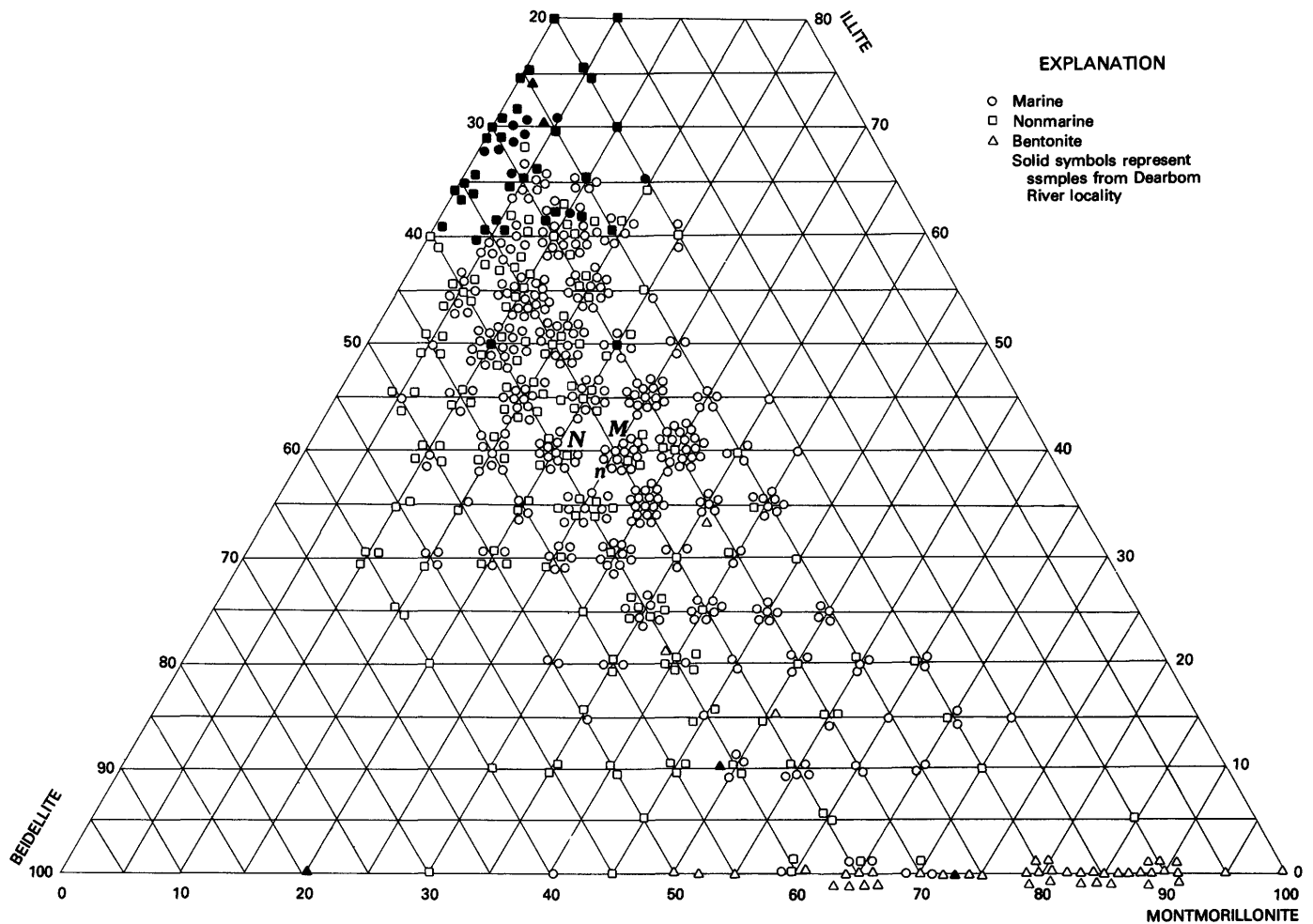
FIGURE 9. — Proportions of layers in mixed-layer illite-smectite in the Pierre Shale and equivalent rocks. Letters M, N, and n are, respectively, the means for marine, nonmarine, and nonmarine exclusive of rocks from the Dearborn River locality (loc. 2). Values, in percent, are at the 5 percent intersections about which the symbols cluster.

TABLE 2. — *Average structural formulas of mixed-layer illite-smectite clay in the Pierre Shale and equivalent rocks, in cations per $O_{20}(OH)_4$*

Cations	Interlayer							Octahedral					Tetrahedral	
	K^+	Na^+	Ca^{+2}	Mg^{+2}	Al	H^+	Total charge	Al^{+3}	Fe^{+3}	Fe^{+2}	Mg^{+2}	Sum	Al^{+3}	Si^{+4}
Calculated from chemical analyses of whole-rock samples														
Shale samples:														
191 total	0.63	0.42	0.09	0.01	0.01	0.01	1.29	2.62	0.68	0.11	0.51	3.92	0.44	7.56
134 marine	.59	.42	.09	.01	.01	.01	1.25	2.64	.68	.11	.51	3.94	.41	7.59
57 nonmarine ..	.69	.41	.08	.01	.00	.02	1.30	2.57	.71	.13	.54	3.95	.55	7.45
Bentonite samples:														
22 total	.09	.40	.12	.07	.02	.01	.94	3.00	.35	.04	.59	3.99	.20	7.80
Calculated before fractionation of 15 shale samples below														
15 shale samples	0.66	0.38	0.13	0.00	0.00	0.00	1.30	2.60	0.69	0.10	0.48	3.87	0.47	7.53
Calculated from chemical analyses of purified < 0.25 μ samples (table 3)														
Shale samples:														
15 total	0.58	0.58	0.02	0.00	0.00	0.00	1.20	2.80	0.53	0.15	0.58	4.06	0.64	7.36
8 marine	.52	.58	.02	.00	.00	.00	1.14	2.81	.50	.15	.62	4.08	.60	7.40
7 nonmarine ...	.63	.58	.02	.00	.00	.00	1.25	2.79	.56	.16	.54	4.05	.68	7.32
Nonmarine less 2 Dearborn River samples	.47	.68	.02	.00	.00	.00	1.19	2.78	.62	.16	.49	4.05	.69	7.31

rocks, and are arranged in table 3 from left to right generally in order of increasing percent of illite layers and of decreasing montmorillonite layers. Average formulas for all 15 samples and for the 8 marine and 7 nonmarine samples are given in the lower part of table 2. Total estimated amounts of impurities are 0-18 percent and average 7 percent, in contrast with an average of 49 percent for other minerals estimated for the original 15 whole-rock samples.

The mixed-layer clay in the purified samples is not identical with that in the whole-rock samples because they represent only those clay particles smaller than 0.25 micrometer (μ). According to X-ray analyses, the $< 0.25\mu$ purified mixed-layer clays tend to be slightly less illitic and more montmorillonitic than mixed-layer clay in the samples as a whole, with average illite:beidellite:montmorillonite proportions of 43:32:25 and 47:37:16, respectively.
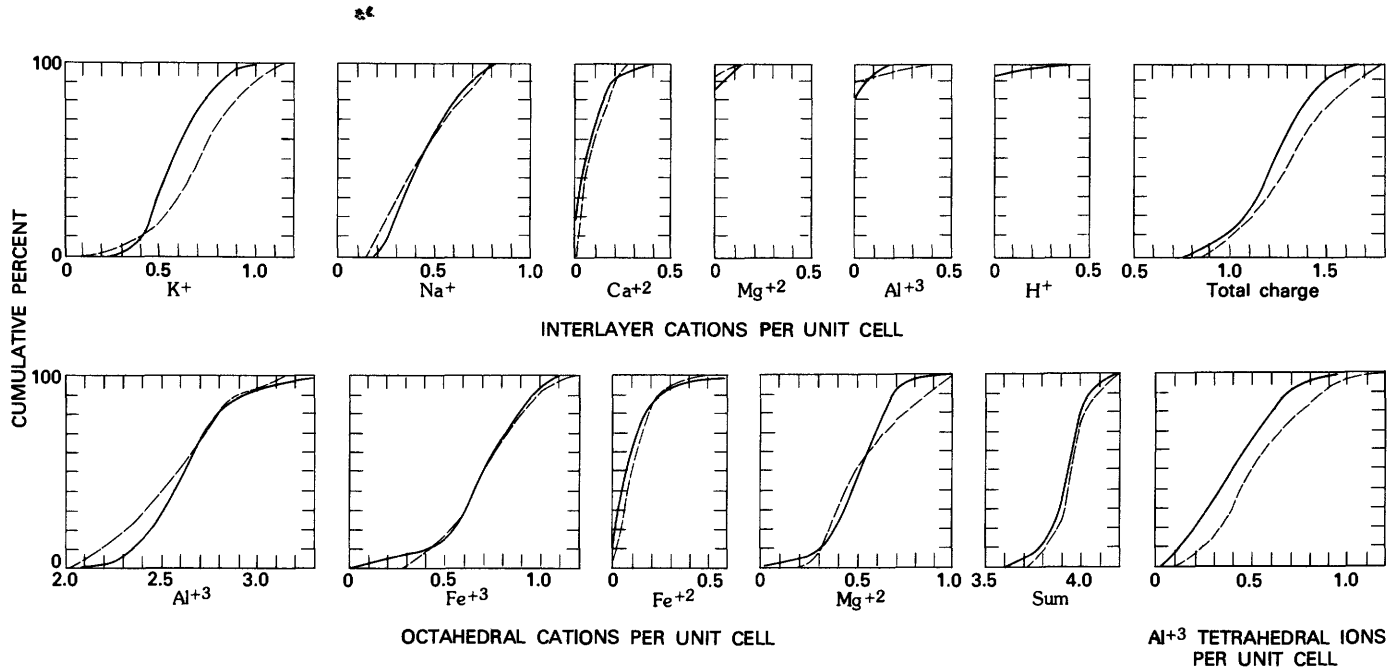
FIGURE 10.—Cation abundance in structural formulas calculated per full unit cell, ideally $O_{20}(OH)_4$. Cumulative curves are for 134 marine (solid line) and 57 nonmarine (dashed line) shales and siltstones.

GEOCHEMISTRY OF THE PIERRE SHALE AND EQUIVALENT ROCKS

TABLE 3.—*Chemical analyses and structural formulas for 15 purified samples of mixed-layer illite-smectite from the Pierre Shale and equivalent rocks*

[Samples were Na-saturated and purified of free iron oxides by Na-dithionate-citrate treatment (Jackson, 1958, p.168) and concentrated by size-fractionation below 0.25μ. Samples are arranged generally from most montmorillonitic on the left to most illitic on the right; illite:beidellite:montmorillonite ratios are in table 5. M, marine; N, nonmarine; < less than. Analyses by L. Artis, S. Botts, G. Chloe, J. Glenn, N. Smith, and D. Taylor]

| Sample No.	259550	259578	159766	159812	159763	259543	159727	159803	159825	159778	159781	159787	259574	159834	159835
Locality No. (fig. 2)	23	16	7	9	7	22	13	5	1	6	6	8	18	2	2
Depositional environment	M	M	N	N	M	M	M	N	N	M	N	M	M	N	N
Chemical analyses, in percent															
SiO_2	60.2	55.2	54.9	52.3	50.7	53.3	51.7	49.8	49.1	52.5	50.0	50.4	50.9	52.2	52.3
Al_2O_3	16.1	19.0	18.9	20.2	22.4	18.7	21.7	20.5	20.6	21.0	22.8	23.0	24.6	23.3	19.1
Fe_2O_3	5.2	4.6	4.4	5.1	4.3	6.5	4.5	6.4	7.5	3.8	4.7	4.1	2.7	3.3	4.5
FeO	.72	1.1	1.6	1.1	1.7	1.0	1.0	1.3	1.2	1.3	1.4	1.1	1.4	1.3	1.9
MgO	2.4	2.8	2.3	2.5	3.1	2.6	2.6	2.4	1.9	3.2	2.1	2.6	2.6	2.6	3.6
CaO	.08	.08	.13	.00	.14	.13	.11	.12	.22	.26	.12	.23	.04	.00	.16
Na_2O	1.9	2.3	2.1	2.3	2.1	2.0	2.0	2.5	2.6	1.7	2.2	1.7	1.4	1.5	1.0
K_2O	2.2	2.0	2.6	2.3	3.0	3.0	2.6	2.3	2.4	3.8	3.4	3.2	4.4	5.3	6.2
H_2O	5.6	7.1	7.0	7.6	6.2	6.3	6.7	7.9	8.0	5.9	6.7	6.0	4.5	5.0	4.4
H_2O^+	4.9	5.4	5.6	5.6	5.8	5.7	6.3	5.2	5.5	6.0	5.6	6.7	6.6	5.0	5.9
TiO_2	.50	.48	.66	.52	.66	.56	.64	1.2	.78	.54	1.0	.70	.44	.13	.47
CO_2	.08	<.05	<.05	.09	<.05	.11	<.05	.05	<.05	.12	.08	.10	<.05	.05	.08
Impurities corrected for, in percent															
Quartz	1	1	4	1	1	1	1	0	0	1	0	0	0	0	0
Cristobalite	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Kaolinite	0	1	2	0	4	1	4	0	0	2	3	3	5	1	0
Illite	2	3	8	2	9	3	8	0	0	5	0	10	13	0	0
Interlayer cations per $O_{20}(OH)_4$															
K^+	0.42	0.34	0.43	0.41	0.50	0.53	0.43	0.43	0.45	0.68	0.64	0.53	0.77	0.95	1.13
Na^+	.59	.66	.68	.66	.68	.58	.64	.71	.73	.51	.63	.55	.46	.40	.27
Ca^{+2}	.01	.01	.02	.00	.02	.02	.02	.02	.03	.04	.02	.04	.01	.00	.03
Total charge	1.03	1.02	1.15	1.07	1.22	1.15	1.11	1.18	1.24	1.27	1.31	1.16	1.25	1.35	1.46
Octahedral cations per $O_{20}(OH)_4$															
Al^{+3}	2.69	2.77	2.74	2.83	2.76	2.60	2.84	2.72	2.67	2.79	2.91	2.94	3.05	3.01	2.62
Fe^{+3}	.62	.50	.51	.56	.49	.72	.51	.70	.82	.42	.52	.46	.28	.34	.48
Fe^{+2}	.10	.13	.21	.13	.22	.12	.13	.16	.15	.16	.17	.14	.19	.15	.14
Mg^{+2}	.57	.60	.53	.54	.72	.57	.60	.52	.41	.71	.46	.60	.60	.54	.76
Total	3.98	4.00	3.99	4.06	4.19	4.01	4.08	4.10	4.05	4.08	4.06	4.14	4.12	4.04	4.00
Tetrahedral cations per $O_{20}(OH)_4$															
Al^{+3}	0.26	0.32	0.38	0.59	0.84	0.48	0.64	0.78	0.86	0.62	0.84	0.78	0.82	0.77	0.57
Si^{+4}	7.74	7.68	7.62	7.41	7.16	7.52	7.36	7.22	7.14	7.38	7.16	7.22	7.18	7.23	7.43

Therefore, the chemical differences shown on table 2 between the 15 samples before and after fractionation do not necessarily represent error. The higher K^+ content for the 15 whole-rock samples clearly reflects more illite-type layers. The lower total interlayer change for the fractionated sample is in accord with thier lower illite and higher montmorillonite content. The high Na^+- and low Ca^{+2}-ion content of the purified samples results from the Na^+-citrate-dithionate treatment intended to reduce and remove free ferric iron oxides, because the treatment also replaces Ca^{+2} cations with Na^+. The higher Fe^{+2} and lower Fe^{+3} contents of the purified samples probably indicates that some Fe^{+3} in the mixed-layer structure was reduced to Fe^{+2}

by the dithionate treatment, but the lower total Fe of the <0.25μ fraction of 0.68 as compared with 0.79 before fractionation may indicate that free iron oxide on the order of 0.5 percent is present in most samples and has been calculated incorrectly into structural formulas of mixed-layer clays in whole-rock samples. These iron differences apparently do not indicate that the more montmorillonitic fractionated clays are iron poor, because no such trend is evident in table 3.

Two differences between the structural formulas from the 15 <0.25μ fractions and from the 191 whole-rock samples indicate errors in correction for impurities in the latter (table 2). These differences for the 0.25μ clays are the higher

content of tetrahedral Al^{+3}, averaging 0.64, and the higher sum of octahedral cations, averaging 4.06. As previously pointed out, what seem to be unrealistically low values calculated from whole samples of shale could result from systematic underestimation of quartz. The fact that all of the 15 formulas show total octahedral cations very close to or above the ideal 4.00 per unit cell (table 3) indicates that the quartz corrections applied to whole-rock samples were, in fact, too low. An average of 24 percent quartz was corrected for when the 191 structural formulas for marine and nonmarine shale were calculated (table 2). If, instead, 26 percent quartz were corrected for, then the tetrahedral part becomes ($Al_{0.62}$ $Si_{7.36}$), and the octahedral part of the structural formula becomes ($Al_{2.62}$ $Fe^{+3}_{0.72}$ $Fe^{+2}_{0.12}$ $Mg_{0.54}$), having a sum of 4.00 cations. The main difference between this formula and that for the 0.25μ mixed-layer clay is the higher iron in formulas computed from the whole-rock sample, which apparently reflects removal of free iron oxide from the purified < 0.25μ samples.

In several other respects, however, the formulas for the fractionated samples support conclusions derived from the structural formulas calculated from whole-rock samples (table 2). Differences in total layer charge, iron content, and tetrahedral Al^{+3} between the mixed-layer clays and smectites in bentonite are confirmed. Small differences in average $K+$ of marine and nonmarine clays are also shown by the < 0.25μ clays, but are due to the two exceptionally illitic clays from Dearborn River. Finally, the seven fractionated nonmarine clays, like the unfractionated clays, tend to have more tetrahedral Al^{+3} and less octahedral Al^{+3} than the marine clays, but proportions of Mg^{+2} are reversed. All of the differences are much too small for use as indicators of environment of deposition. The most remarkable feature of the mixed-layer clay in the marine and nonmarine rocks appears to be its overall compositional similarity.

FORMULAS INFERRED FOR INDIVIDUAL ILLITE-, BEIDELLITE-, AND MONTMORILLONITE-TYPE LAYERS

Three features of the structural formulas of the 15 mixed-layer clays (table 3) should be related to proportions of illite:beidellite:montmorillonite: (1) interlayer K^+ ions should be concentrated in illite; (2) total layer charge balanced by interlayer cations should be higher in illite than in montmorillonite; and (3) the amount of tetrahedral Al^{+3}

should be low in montmorillonite and high in beidellite and illite. In figure 11 these three measures are plotted for the 15 purified samples (table 3), together with the average values
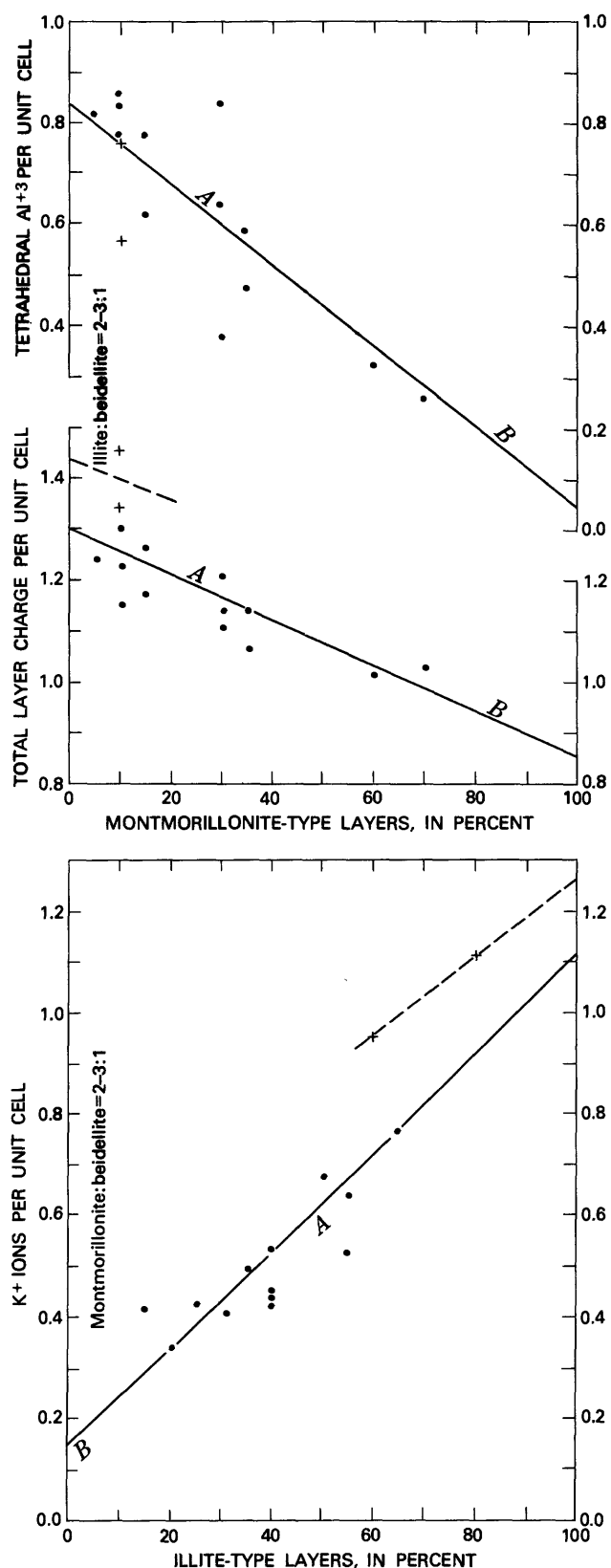
FIGURE 11.—Tetrahedral Al^{+3}, total layer charge, and interlayer K^+ ions of structural formulas related to proportions of illite:beidellite:montmorillonite. A and B are averages, respectively, of 15 purified samples (table 3) and of 22 bentonite samples (table 2). Individual purified samples (table 3) are plotted as points except Dearborn River locality samples plotted as +. Solid lines are drawn through averages for shales so as to come as close as possible to plotted positions of individual samples, especially the 13 mixed-layer samples that are randomly interstratified. Dashed lines indicate appreciable differences between Dearborn River (loc. 2) samples and the other samples.

for all 15 shale samples and for the 22 bentonite samples in table 2. The bentonite samples have an average proportion of 18 percent mortmorillonite layers.

Average structural formulas for individual layers of the mixed-layer clay given in table 4 are in part based on three generally accepted premises and a fourth one taken from table 3: (1) the total of tetrahedral Al^{+3} and Si^{+4} is 8.0; (2) the total of octahedral cations is about 4.0, but may vary slightly from this—perhaps by 0.1 or 0.2 at the most; (3) the layer charge of montmorillonite is mostly in the octahedral layer, whereas the layer charge of beidellite and illite is mostly in the tetrahedral layer (fig. 3); and (4) the population of the octahedral layer of Fe^{+3}, Fe^{+2}, and Mg^{+2} is essentially the same for all three layers, as indicated by lack of consistent variation of values from the mixed-layer clays having a high proportion of montmorillonite layers to those having a high proportion of illite layers (table 3). Concerning this fourth point, montmorillonite-rich bentonites are low in iron (table 2), but this low iron content seems not to apply to montmorillonite layers in shales as shown by montmorillonite-rich clays in samples 259550 and 259578 (table 3).

Variable features of the structural formulas in table 4 are interpreted from figure 11 as follows: Intersections of the average lines with 0 and 100 percent on the left and right sides of the graphs, respectively, indicate the probable composition of the end members. The zero-percent intersection includes two types of layers, the probable proportions of which are indicated just inside the zero line. Total layer charge and tetrahedral Al^{+3} projected to zero montmorillonite represent the average for illite and beidellite. Assuming about two to three times as many illitic as beidellitic layers (fig. 9), the 1.3 average total charge is allotted 1.4 to illite and 1.0 to beidellite; the 0.8-0.9 average tetrahedral Al^{+3} is allotted 1.0 to illite and 0.6 to beidellite. For 100 percent montmorillonite the average tetrahedral Al^{+3} must be near zero, probably no higher than 0.1; the average total layer charge must be 0.8 or 0.9; values of 0.1 and 0.8 are assigned (table 4) so as to balance the layer charge. The average line for K^+ ions clearly does not project to zero for zero illite, indicating that 0.1 or 0.2 K^+ ions must be present before a detectable number of nonexpanding illite-type layers develop. The average K^+ for 100 percent illite-type layers projects to about 1.1 or 1.2; the latter number is used in table 4 so as to reach a total interlayer charge of 1.4 without assuming too many cations that are normally exchangeable. Also, for the illite in table 4 extra octahedral Al^{+3} is assumed, thereby increasing the total of octahedral cations to 4.1 and reducing octahedral layer charge to -0.4; otherwise, the total charge of -1.7 (-0.7 octahedral and -1.0 tetrahedral) could be balanced only by an unreasonably large K^+ ion level that is not reached even in the IS-ordered clays from the Dearborn River locality. The K^+ ion and total interlayer charge in illite-type layers from Dearborn appear to be about 0.2 greater than in a unit cell of

TABLE 4.—Average structural formulas of layers in mixed-layer illite-smectite from the Pierre Shale and equivalent rocks inferred from tables 2 and 3, and figure 11

[X, exchangeable cations]

Illite ....$(K_{1.2}^{+1} X_{0.2}^{+1})$ $(Al_{2.9}^{+3} Fe_{0.5}^{+3} Fe_{0.1}^{+2} Mg_{0.6}^{+2})$ $(Al_{1.0}^{+3} Si_{7.0}^{+4})O_{20}^{-2}(OH)_4$

Total cations .	1.4	4.1	8.0
Total charge ..	+1.4	-.4	-1.0

Beidellite ....$(K_{0.2}^{+1} X_{0.8}^{+1})$ $(Al_{2.9}^{+3} Fe_{0.5}^{+3} Fe_{0.1}^{+2} Mg_{0.6}^{+2})$ $(Al_{0.6}^{+3} Si_{7.4}^{+4})O_{20}^{-2}(OH)_4$

Total cations .	1.0	4.1	8.0
Total charge ..	+1.0	-.4	-.6

Montmorillonite $(K_{0.1}^{+1} X_{0.7}^{+1})$ $(Al_{2.8}^{+3} Fe_{0.5}^{+3} Fe_{0.i}^{+2} Mg_{0.6}^{+2})$ $(Al_{0.1}^{+3} Si_{7.9}^{+4})O_{20}^{-2}(OH)_4$

Total cations .	.8	4.0	8.0
Total charge ..	-.8	-.7	- 1

illite-type layers in normal, randomly mixed-layered clay. A total of 4.1 octahedral cations is similarly assumed for beidellite so as to decrease the octahedral-layer charge from -0.7 to -0.4 units per unit cell and keep it below the tetrahedral-layer charge of -0.6 as is required by definition.

STRUCTURAL OH

Structural water, OH^-, makes up four of the anions in an ideal unit cell of smectite or illite (table 2) and occurs in the octahedral layers ideally at the center of the silica rings at sites not shared with silica tetrahedrons (fig. 3). Structural OH^- has been investigated by two techniques: (1) Differential Thermal Analysis (DTA), which measures heat that is either absorbed or given off as chemical reactions or structural changes occur on heating; and (2) Thermal Gravimetric Analysis (TGA), which measures changes in weight of the sample on heating.

Differential thermal curves typical of most shale and bentonite of Pierre age are illustrated by the two traces in figure 12. The endothermic reactions around 150°- 200° C are due to volatilization of adsorbed and interlayer water. Reations between 550° and 750° C are due to loss of structural $OH-$ from the clay-mineral layers, where two OH^- molecules combine to form a volatile H_2O molecule and a residual O^{-2} ion.Reactions between 850°to 1000°C are due to final breakdown of the layer structures of the clay and formation of new minerals. The loss of structural $OH-$ is the reaction of interest here.

Bentonite (fig. 12) typically shows a dehydroxylation endotherm having its major peak between 650° and 750° C. Such relatively high temperatures are generally considered to be characteristic of montmorillonite, which is, of course, the major constituent of bentonite. Shale of Pierre age, except for a few samples from the Dearborn River locality (table 5, samples 159834 and 159835), invariably has its major dehydroxylation endotherm between 550° and 600° C with or without a small shoulder between 650° and 700° C.
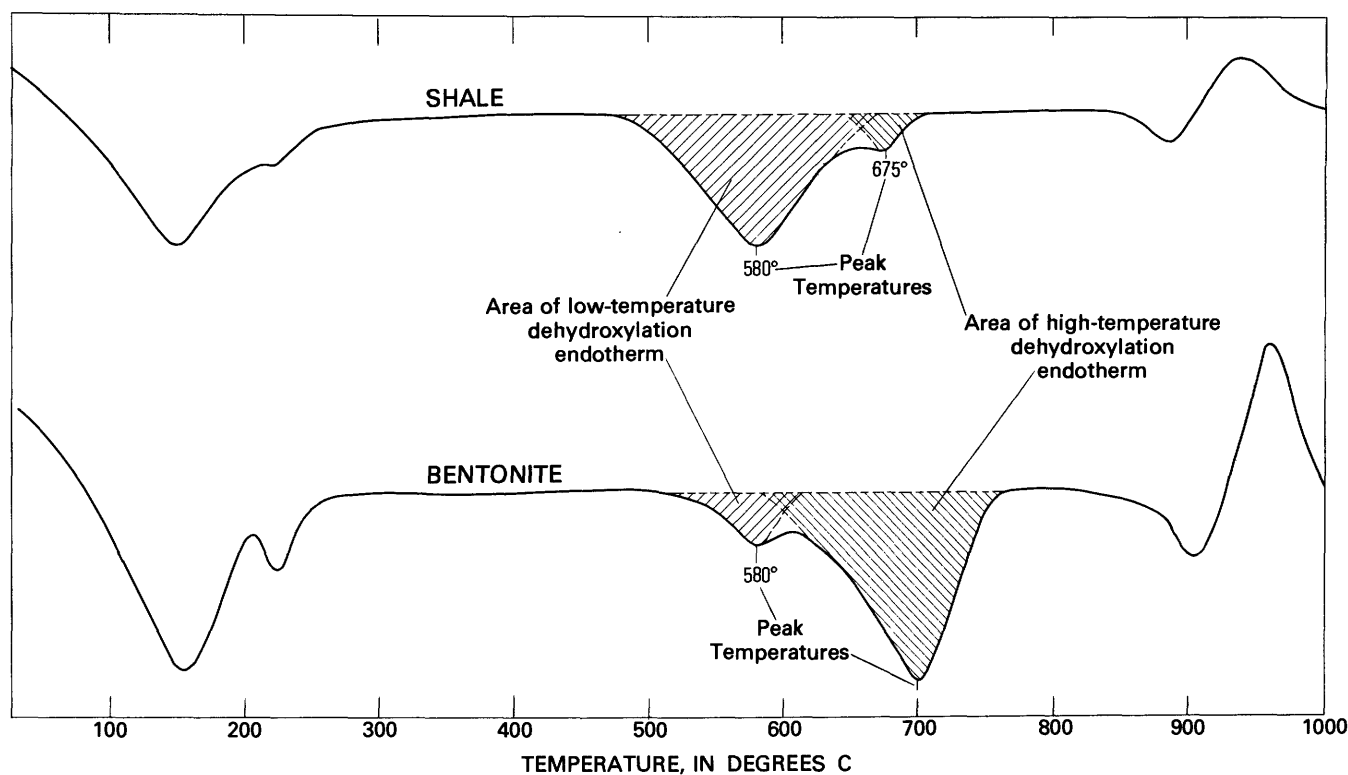
FIGURE 12. — Differential thermal analysis curves typical of shale and bentonite of Pierre age. Patterns between curves and dashed lines indicate how peak areas in tables 5-8 were interpreted.

Only those samples in which montmorillonite-type layers are dominant, like 259550 and 259578 in table 5, gave an appreciable but still subordinate high-temperature endotherm. Initially the lower dehydroxylation temperature for the shale was thought to result from abundant Al^{+3}-for-Si^{+4} substitution such as is characteristic of illite and beidellite. However, this explanation seemed inadequate for some of the more montmorillonitic samples, and initial calculations of structural formulas for smectitic clay in many Pierre Shale samples (fig. 10) did not indicate very high tetrahedral Al^{+3}.

The just-mentioned conflict led to a study of Greene-Kelly's (1955) lithium test as a means for differentiating between beidellite and montmorillonite in the Pierre Shale and in aluminous smectites generally (Schultz, 1969). From this study it was concluded that the lithium test is reliable. A second conclusion was that tetrahedral Al^{+3}, though generally related to dehydroxylation temperature, is not the primary cause for major variations. Instead, the primary cause of variation indicated by thermal gravimetric analyses of 21 smectites was the amount of structural OH^-. If the amount of structural OH^- is ideal, and the OH^- is presumably all in ideal positions in the octahedral layer at the center of silica rings (fig. 3), then the smectite dehydroxylates at high temperatures and gives major DTA peaks between 650° and 750° C, regardless of the tetrahedral or octahedral location of the layer charge. Conversely,

nonideal amounts or possibly nonideal distribution of structural OH^- cause appreciably lower temperatures of dehydroxylation, and major DTA peaks occur between 550° and 600° C.

TABLE 5.—*Dehydroxylation peak temperature and size and amount of deviation from ideal structural water in 15 purified mixed-layer illite-smectites from the Pierre Shale and equivalent rocks*

Sample No.	Locality no. (fig. 2)	Illite: beidellite: montmorillonite ratios	DTA[1] peak temperature in °C and area (in²)		TGA[2] structural water as deviation from ideal 4.0(OH) in percent
			low	high	
259550	23	15:15:70	585(1.6)	690(1.2)	-0.4
259578	16	20:20:60	600(1.7)	685(1.0)	-.55
159766	7	25:45:30	600(2.3)	685(0.1)	-.4
159812	9	30:35:35	590(2.3)	690(0.1)	+.2
159763	7	35:35:30	585(2.4)	675(0.1)	-.1
259543	22	40:25:35	590(2.4)	675(0.1)	-.1
159727	13	40:30:30	560(2.4)	665(0.3)	+.4
159803	5	40:45:15	565(2.2)	660(0.2)	+.5
159825.........	1	40:50:10	600(2.3)	690(0.1)	-.3
159778	6	50:35:15	590(2.3)	700(0.1)	+.3
159781	6	55:35:10	570(2.2)	600(0.2)	-.4
159787	8	55:35:10	575(2.3)	None	-.2
259574	18	65:30:5	565(2.5)	None	-.3
159834	2	[3]60:30:10	610(3.1)	None	-.2
159835	2	[3]80:10:10	630(3.2)	None	-.0

[1]Differential Thermal Analysis (fig. 12).
[2]Thermal Gravimetric Analysis, by F. O. Simon.
[3]IS-ordered mixed layering.

The only mixed-layer clays investigated from the Pierre Shale and equivalents that are of purity comparable with the 21 smectites (Schultz, 1969) are the 15 samples in table 3. Thermal gravimetric analyses (TGA) of these 15 clays were made on the same apparatus by the same operator at the same time as for the 21 smectites and were interpreted using the same methods (Schultz, 1969, fig. 5). The measured amount of high-temperature structural water was corrected for the amounts of kaolinite and quartz or cristobalite shown in table 3. Any illite impurities were assumed to have the same OH^- content as the mixed-layer clays, and no correction was made. For example, in the first sample in table 5, 259550, the measured structural OH^- was 4.08 percent of the ignited weight of the sample. This OH^- occurs in 89 percent of the sample, as 11 percent is quartz and cristobalite (table 3). Therefore the amount of OH^- in pure clay would be 4.08÷0.89=4.57 percent. If a clay with the structural formula calculated for sample 259550 contained the ideal $4(OH)^-$ per unit cell, the structural OH^- should be 4.95 percent of the ignited weight. The sample therefore contains 4.95-4.57=0.38 percent less than the ideal structural water, rounded to -0.4 percent in table 5.

The estimated maximum error in measuring the TGA curves is 0.1 percent of the weight of the sample at both the low and high ends of the temperature range (about 300° and 1000° C, respectively) for loss of OH^-, or a total of 0.2 percent if the errors are in opposite directions. For 9 of the 15 illite-smectites (table 5) measured OH^- deviates more than 0.2 percent from ideal. The other six samples could still have an ideal amount but nonideal distribution of OH^-, or, in view of the possible error of measurement, the actual OH^- content of all but the last sample could deviate more than 0.2 percent from ideal but still be measured as within 0.1 to 0.2 percent of ideal if errors of measurement at about 300° and at 1000° C were both nearly maximum and in opposite directions.

One unusual feature of the data in table 5 is the dehydroxylation peak temperatures of the last two samples—610° and 630° C—which are in the 600°-650° C range between the normal low- and high-temperature dehydroxylation endotherms. Both are IS-ordered mixed-layered clays from Dearborn River (loc. 2). Possible significance of these intermediate temperatures is considered in the next section of this report.

ILLITIC MIXED-LAYER CLAY
IN BENTONITE

Although clay in most bentonite of Pierre age is highly montmorillonitic and contains no detectable illite layers, six exceptions were found in the main study of the Pierre Shale and its equaivalents (fig.9). These six are compared with nearby shales in table 6. Three of the bentonites are from the Dearborn River (loc. 2) section, and for the exceptionally thick 3-foot bentonite bed from the Telegraph Creek

Formation, two analyses are given—one for the middle and the other (Ba, not shown in fig. 9) from the basal 6 inches. The latter is of particular interest because it contains the most illitic mixed-layer clay found in the Pierre Shale. All five of the mixed-layer clays from both bentonites and shales from the Telegraph Creek and Eagle Formations are highly illitic and have IS-ordered mixed layering. Three of the five samples, like the two from claystones at the Dearborn River locality in table 5 (loc. 2), have their main dehydroxylation endotherm peak in the normally vacant 600°-650° C range, and the shale from the Telegraph Creek Formation with its peak at 640° C is so close to the 650°-750° C range for smectites having ideal structural OH^- as to suggest that development of IS-ordered mixed-layering may also involve ordering of OH^-. Such an interpretation is in accord with the nearly ideal OH^- content measured for the two Dearborn River samples in table 5. However, the dehydroxylation temperatures of the bentonite sample (Ba) containing 85 percent illite and of the Eagle bentonite (table 6) are not especially high, so that any tendency toward ordering of OH^- in IS-ordered clay is not consistent. Still another noteworthy feature shown by the rocks at the Dearborn River locality (table 6) is the composition of an argillized sill in the lower part of the Two Medicine Formation. It is composed predominantly of a mixed-layer clay very similar to much of that in most of the shale and bentonite. Several other altered sills or welded tuffs in the lower part of the section also contain similar clays, though in smaller amounts. The occurrence of IS-ordered clay in materials so different as shale, bentonite, and an altered igneous sill indicates that the clay is a locally developed phenomenon.

Not all of the clay from the Dearborn River locality has IS-ordered mixed layering, especially in the upper part of the section. A good example is the bentonite sample from the St. Mary River Formation (table 6) that has barely detectable 10-percent illite-type layers. The nearest shale is much more illitic but is not IS-ordered. These samples occur only about 500 feet stratigraphically above the other samples at the Dearborn River locality (table 6) and show that development of ordering in mixed-layer clay can vary greatly over short distances.

The three bentonite samples in table 6 from the Columbus (loc. 6) and Shawmut (loc. 5) localities all contain mixed-layer clays that are considerably less illitic than those in nearby shales, and all are randomly interlayered. Yet even though the range of proportions of illite-type layers in the three bentonite samples, 15-35 percent, is within the range of illite-type layers in clays from shale (table 5), the bentonite samples give high-temperature dehydroxylation endotherms from 675° to 700° C that are bigger, mostly much bigger, than the low-temperature endotherms. Shale associated with the three bentonite samples shows almost no high-temperature dehydroxylation. This tendency for illitic mixed-layer clays in bentonite to retain the high-temperature endotherm characteristic of the usual

montmorillonite in bentonite is further shown by the fairly large endotherms at 670° and 705° C for the Eagle and Telegraph Creek bentonite samples at the Dearborn River locality. Only the most highly illitic part of the Telegraph Creek bentonite shows no appreciable high-temperature dehydroxylation endotherm.

A noteworthy feature of the two illitic bentonite samples from the Columbus locality (loc. 6, table 6) is that the one from the Bearpaw Shale is more illitic than the one from the Bearpaw Shale is more illitic than the one from the Claggett Shale, which is 300 feet stratigraphically lower. Other bentonite beds at both the Columbus and Shawmut (loc. 5) localities contain normal clays composed only of smectite.

DEPTH DIAGENESIS

Studies by Powers (1959), Burst (1959), and Weaver (1960), among others, and more recently by Perry and Hower (1970), mostly in connection with Tertiary sediments of the Gulf Coast, have convincingly demonstrated the concept of depth diagenesis of clay minerals. In summary, mostly from the last-mentioned work, depth diagenesis involves conversion of expanding clay (smectite in this report) that is found at shallow depths to less expanding illite-smectite mixed-layer clay at greater depths of burial. Development of nonexpanding layers is first noted at depths on the order of 5,000 feet, above which 80 percent or more of the layers commonly are expanding, and it continues to about 10,000 or 15,000 feet, where only 15-20 percent of the layers are expanding. No further decrease in expanding layers is found at greater depths. At the greater depths mixed-layer clay having from 60 or 65 to 85 percent illite-type layers is IS-ordered; less illitic mixed-layer clay at shallower depths is randomly interstratified. Discrete illite (mica), which is abundant at shallow depth, apparently breaks down at greater depth, thereby supplying K^+ ions that are adsorbed on smectite-type layers converting them to illite-type layers. Diagenesis of the clays actually seems to be dependent more on temperature than depth, the IS-ordered mixed layering first developing at about 100° C. With varying thermal gradient in different areas, the depths at which the changes in mixed layering occur vary over several thousand feet.

TABLE 6.—*Mineralogy and dehydroxylation peak temperatures of samples of bentonite, adjacent shale, and an argillized sill of volcanic rock from the Dearborn River locality (loc. 2) within the Montana disturbed belt and of three bentonite samples from equivalents of the Pierre Shale outside the belt (fig. 2) that contain mixed-layer illite-smectite*

[Ba, sample from base of bentonite; B, bentonite; S, shale]

Locality name and number (fig.2)	Dearborn River 2								Columbus 6				Shawmut 5	
Formation	Telegraph Creek Formation			Eagle Sandstone		Sill	St. Mary River Formation		Claggett Shale		Bearpaw Shale		Claggett Shale	
Rock type	Ba	B	S	B	S		B	S	B	S	B	S	B	S
Proportions of layers in mixed-layer clay, in percent														
Illite	¹85	¹75	¹75	¹70	¹60	¹75	10	60	15	60	35	50	20	55
Beidellite	15	25	20	25	30	20	40	30	35	35	30	40	40	35
Montmorillonite	0	0	5	5	10	5	50	10	50	5	35	10	40	0
Proportions of clay minerals in total clay, in percent														
Mixed-layer	95	100	60	100	72	93	100	100	95	46	99	62	98	69
Illite	0	0	30	0	20	0	0	0	0	37	0	29	0	20
Chlorite	0	0	6	0	3	0	0	0	0	6	0	5	0	4
Kaolinite	5	0	4	0	5	7	0	0	5	11	1	4	2	7
Proportions of minerals in total sample, in percent														
Total clay	100	80	55	70	65	70	85	65	70	45	80	65	100	60
Quartz	0	15	29	15	27	17	2	16	3	32	2	25	1	27
K-feldspar	0	0	0	0	0	0	0	2	0	2	0	0	0	0
Plagioclase	0	4	5	6	5	12	1	20	10	10	12	7	0	4
Calcite	0	1	5	8	0	0	10	1	15	0	0	1	0	0
Dolomite	0	0	7	0	0	0	0	0	0	12	0	0	0	4
Dehydroxylation peak temperature, in °C, and area, in square inches														
Low	590	615	640	580	620	620	585	600	550	580	560	590	550	570
	2.6	1.5	1.6	1.5	1.8	1.3	0.9	1.3	0.2	1.2	0.7	1.1	0.2	1.2
High	690	705	(²)	670	(²)	740	695	(²)	690	(²)	675	750	700	(²)
	0.1	0.5	None	0.7	None	0.5	1.2	None	1.4	None	0.9	0.2	1.8	None

¹IS-ordered mixed layering.
²No high-temperature peak.

No direct information is available on past temperatures in the Pierre Shale. Temperature can only be inferred from average thermal gradients in sediments, commonly 8°-10° C per 1,000 feet, and from inferred amounts of overburden. In the discussion that follows, therefore, depth of burial rather than temperature is the primary factor considered.

MAIN PIERRE SHALE STUDY

Variation in illite-smectite proportions in the Pierre Shale and its equivalents is almost identical with that in sediments of the Gulf Coast, both in proportions of layers and in development of IS-ordered layering in clay having more than about 60 percent illite-type layers. The temptation is great, therefore, to attribute variations in illite-smectite proportions in the Pierre Shale to depth diagenesis. Hower and Hall (1970) came to just such a conclusion in central Montana. In the Two Medicine Formation in the general area around the Dearborn River locality (fig. 2, loc. 2) they found the same IS-ordered illite-smectite as was found in this study; a little farther to the east on the Sweetgrass arch, in the general area of locality 3 (fig. 2), they found only randomly mixed-layer illite-smectite. Hower and Hall attributed the more illitic clays near the Dearborn River locality to greater depth-of-burial than on the Sweetgrass arch. More recently, Hoffman (1976) and Hoffman, Hower, and Aronson (1976) have attributed diagenesis of clays around the Dearborn River locality and elsewhere in the Montana disturbed belt (fig. 2) to burial under thrust sheets of the belt, and they have used the clays to interpret the temperatures involved (100°-200° C) and the time of thrusting (Late Cretaceous to Paleocene).

Clearly, the clays at the Dearborn River locality have responded authigenically to some sort of elevated pressure-temperature equilibrium akin to depth diagenesis. However, as explained below, there are three general difficulties with depth diagenesis as the sole explanation of variation in the illite-smectite ratio in the Pierre Shale and equivalents as a whole. First, no general relation exists between the illite-smectite ratio and stratigraphic position, geographic location, or inferred depth of burial that is consistent with pervasive depth diagenesis. Second, except at Dearborn River, the clay in bentonite is so different from that in nearby shale as to indicate little or no diagenesis in either. Third, the abundance discrete illite and the proportion of illite-type layers in mixed-layer clay of individual samples are not compatible with the former altering into the latter.

Past depth of burial of the sampled parts of the Pierre Shale can only be estimated, as the overburden has been removed from outcropping sediments. Generally, the thickness of overlying beds is thought to decrease from west to east, at least from the center of the basin to the Missouri River, much as the thickness of the Pierre Shale itself decreases through this interval (fig. 1). The maximum overburden that can be inferred with confidence is about

12,000 feet in the middle of the Pierre basin of deposition, in the southern part of the Powder River basin, reconstructed as follows:

Age	Formation	Thickness, in feet
Miocene	Arikaree	1,000
Oligocene	White River	1,000
Eocene	Wasatch	2,400
Paleocene	Fort Union	4,500
Late Cretaceous	Lance	3,200
Total		12,100

Overburden along the Missouri River probably was never more than a few thousand feet. Changes in thickness of overburden westward from the Powder River basin are less certain, but the great thickness of lower Tertiary sedimentary rocks listed above are not known to extend as far west as the Dearborn River area.

Variation in porosity of Pierre Shale agrees only partly with the burial depths inferred above. As overburden amounts increased, sediments generally and shales in particular were compacted by the squeezing out of water, and porosity decreased. The general change in expected porosity as depth increases is shown in figure 13, and porosities of shale samples calculated from bulk and grain densities from the main report of the Pierre Shale and equivalent strata are averaged for localities in figure 14. As expected, porosity is greatest in the east. An average porosity of about 25 percent in the Missouri River area corresponds to an overburden of only one or two thousand feet. Porosities of 15-20 percent in the middle of the basin
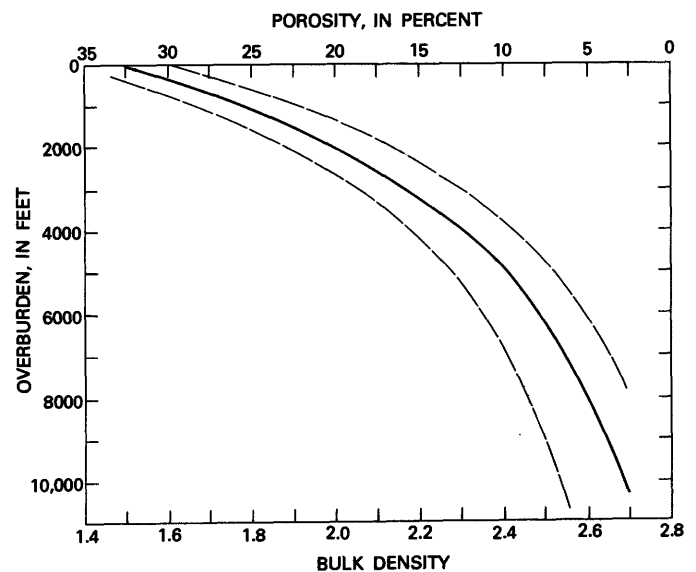

FIGURE 13.—Change in bulk density and porosity of shale as depth of burial increases. Solid line is an average from Athy (1930), Hedberg (1936), Johnson (1950), Dickinson (1953), and B. K. Proshlyakov as cited in Maxwell (1964, p. 698). Dashed lines indicate range of values.
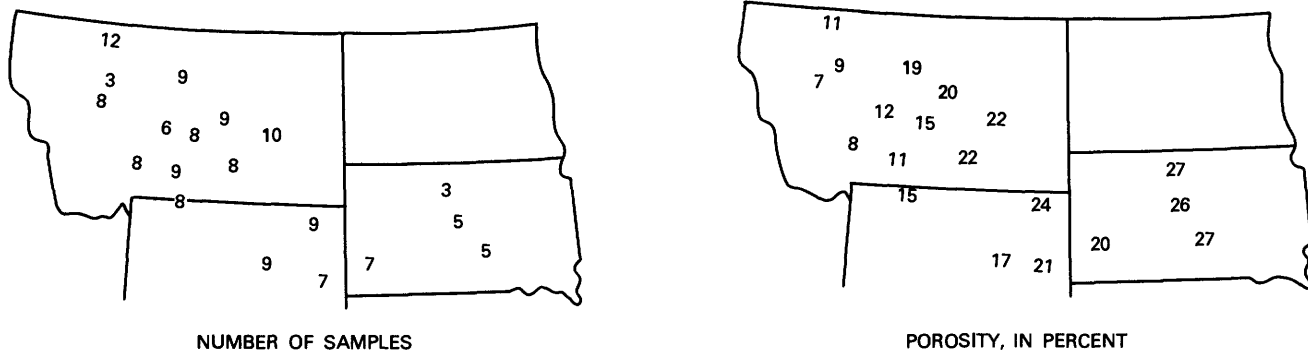
NUMBER OF SAMPLES

POROSITY, IN PERCENT

FIGURE 14. — Average porosity of samples from generalized localities of the main study of the Pierre Shale and equivalent strata (fig. 2). Localities 19, 20, and 21 are combined and localities 11, 12, and 24-26 are omitted because only two or fewer values were determined.

correspond to an overburden of only a few thousand feet—much less than the overburden inferred above for the Powder River basin. Porosities of 5-10 percent, corresponding to overburdens on the order of 10,000 feet that are necessary for depth diagenesis to IS-ordered clay, occur only in the westernmost localities. The average porosity at the Dearborn River locality (loc. 2) of 7 percent is the lowest measured but is not much different from the average porosity at other western localities such as Livingston or Augusta-Choteau (fig. 2, locs. 1, 3), where mixed-layer clay is randomly interlayered.

Average illite content of mixed-layer clay in the upper three and the lower three fossil zones of the Pierre Shale and equivalent rocks as used in the main Pierre Shale report is shown for individual localities in figure 15. Except for the

highly illitic mixed-layer clay at the Dearborn River locality (loc. 2), averaging 65 and 67 percent illite-type layers in the upper and lower parts of the Pierre, there are no conspicuous regional trends. Nor is mixed-layer clay in the southern part of the Powder River basin, like the 31 and 47 percent illite in the upper and lower parts at the Salt Creek locality (loc. 10), much different from average. The most consistenly illitic mixed-layer clay, averaging 50 percent or more of the layers, comes from the lower part of the Pierre Shale in the Missouri River area, but here the overburden, estimated both from reconstruction and from porosity, was minimal. Although mixed-layer clay in the lower part of the Pierre Shale and equivalents is generally more illitic than in the upper part (fig. 15), within individual sections adjacent samples may differ greatly. In the Missouri River area the highly illitic

Upper part, Pierre Shale and equivalents

Lower part, Pierre Shale and equivalents

NUMBER OF SAMPLES
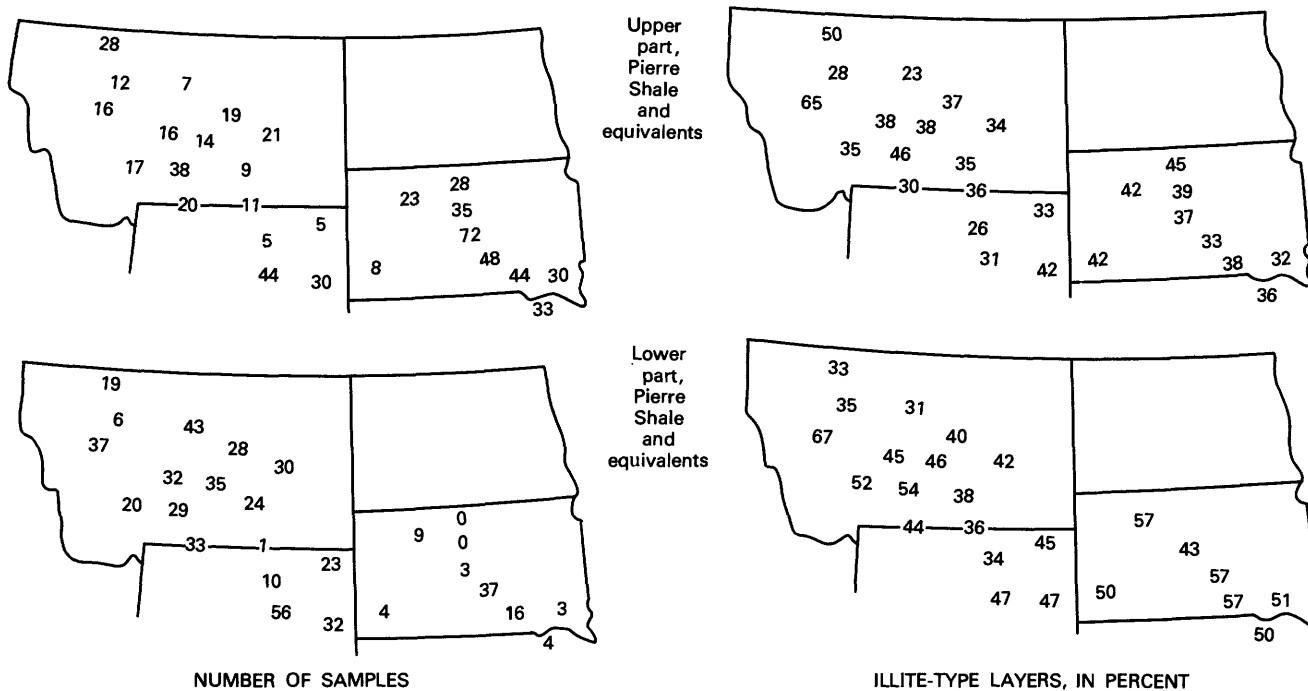
ILLITE-TYPE LAYERS, IN PERCENT

FIGURE 15. — Average proportion of illite-type layers in mixed-layer illite-smectite from generalized localities of the main study of the Pierre Shale and equivalent strata (fig. 2).

character of the mixed-layer clay in the lower part of the Pierre is so consistent that this characteristic has been used as one compositional criterion for correlation of beds (Schultz, 1965); yet the change to less illitic clays in the upper part of the Pierre is abrupt, taking place over a few feet, rather than a gradual change over hundreds of feet as would be expected from depth diagenesis.

Finally, there is the question of whether discrete illite originally deposited in the Pierre Shale and equivalents has dissolved and furnished K^+ ions to diagenetically alter expandable smectite-type layers to nonexpanding illite-type layers of mixed-layer clay. If so, discrete illite should have a negative correlation with the proportion of illite-type layers in mixed-layer clay. Instead, the opposite relation is observed. In marine rocks discrete illite has a correlation coefficient of +0.47 with the proportion of illite-type layers. In nonmarine rocks this correlation, +0.07, is also positive. but the magnitude of the coefficient is not significant. The much lower coefficient in nonmarine rocks is due in considerable part to samples from the Dearborn River locality (loc. 2), which contain exceptionally illitic mixed-layer clay but very little discrete illite. Discrete illite in the Pierre Shale is thought to be almost entirely of nonvolcanic origin. Whether the scarcity of discrete illite at the Dearborn River locality is due to its solution during diagenesis or to the scarcity of nonvolcanic detritus is not certain. The locality is very near the volcanic source (figs. 1, 2), so a high proportion of volcanic detritus is expectable. In any case, the general tendency in most samples, other than those from the Dearborn River locality, for discrete illite to occur with the more illitic mixed-layer clay is incompatible with pervasive depth diagensis in most of the Pierre Shale and its equivalents.

Thus, with the exception of the Dearborn River locality, the variations in the illite:smectite ratio that might be expected from depth diagenesis are not observed. The strongest argument for in-place development of the highly illitic IS-ordered mixed-layer clay at the Dearborn River locality is that such clay occurs not only in claystone but also in bentonite, which presumably once had the usual montmorillonitic composition characteristic of most bentonite. Conversely, in most of the Pierre Shale and its equivalents, the great difference between the highly montmorillonitic clay of bentonite and the illitic mixed-layer clay in shale seems an equally strong argument against depth diagenesis.

COMPLEMENTARY STUDIES

The bentonite-shale relationship at the Dearborn River locality (loc. 2) is illustrated by only a few bentonite samples from the main study of the Pierre Shale (table 6). Also evidence of past burial depths is uncertain and partly contradictory, particularly as to relative amounts of overburden in the central and western parts of the basin. Complementary studies made to help clarify the problems of overburden thickness and significance of bentonite are described in the following sections of this report.

CUTTINGS FROM DEEP WELLS

The well cuttings used in this study came from depths that are known within a few tens of feet. These depths give a minimum unequivocal depth of burial. Cuttings from three wells near the axis of the Powder River basin (* in fig. 2) were obtained from American Stratigraphic Co., Casper, Wyo. The cuttings all came from the lower part of the Pierre Shale from depths of 10,000-12,350 feet. All three wells started in the Wasatch Formation, so that actual past overburden thicknesses must have been greater than the well depths (see unnumbered table in the section "Main Pierre Shale study") and generally in the range affected by depth diagenesis.

The average mineralogy of the 12 samples of shale cuttings analyzed is given in table 7. Also given for comparison is the average mineralogy of stratigraphically equivalent samples at the nearest outcrop sampled, about 20 miles to the west on the Salt Creek anticline (fig. 2, loc. 10). The average compositions of the shale are nearly identical. This similarity indicates either that the outcrop samples were once buried at depths similar to the cuttings and have been similarly altered by depth diagenesis or that neither the outcrop samples nor the well cuttings were so affected.

TABLE 7.—*Mineralogy and dehydroxylation peak temperatures of shale and bentonite cuttings of Pierre age at depths of 10,000 feet or more in the Powder River basin and of samples from stratigraphically equivalent rocks from the nearest outcrops at the Salt Creek locality (loc. 10, fig. 2)*

[<. less than]

	Well cuttings		Salt Creek	
	Bentonite	Shale	Bentonite	Shale
Number of samples	10	12	3	4
Proportions of layers in mixed-layer clay, in percent				
Illite	35	50	0	45
Beidellite	35	35	10	35
Montmorillonite	30	15	90	20
Proportions of clay minerals in total clay, in percent				
Mixed-layer	100	60	100	60
Illite	0	25	0	25
Chlorite	0	7	0	5
Kaolinite	<1	8	0	10
Proportions of minerals in total sample, in percent				
Total clay	95	55	95	55
Quartz	2	30	0	30
K-feldspar	0	1	0	2
Plagioclase	4	7	1	5
Calcite	1	1	2	3
Dolomite	0	7	0	8
Dehydroxylation peak temperature, in °C, and area, in square inches				
Sample	(^{1})	(^{2})	^{3}159721	^{3}159720
Low	(^{4})	590	(^{4})	575
	None	1.1	None	1.2
High	685	680	715	665
	^{5}0.7	0.3	3.0	0.4

^{1}Composite sample from 10,000-10,030 ft. depth.
^{2}10,000-10,010 ft.
^{3}Individual samples from main Pierre Shale report.
^{4}No low-temperature peak.
^{5}Small dehydroxylation endotherm due to small sample.

The most significant features of the well cuttings were particles of bentonite and the composition of these particles. The light-colored bentonite particles contrast with the much more abundant dark shale particles from which the bentonite samples were separated. The maximum quartz content of any of the 10 bentonite samples was 7 percent and in most it was only 1-2 percent, amounts that are typical of most bentonite but much lower than those of shale analyzed from the Pierre Shale and its equivalents (table 1). None of the bentonites contained chlorite or free illite and two contained small amounts of kaolinite. These also are features typical of bentonite but not of shale. The atypical feature of all 10 samples of bentonite cuttings was the presence of mixed-layer illite-smectite. The proportion of illite-type layers ranged between 20 and 45 percent and was consistently lower than in the accompanying shale particles, though only slightly so in some cases. The mixed-layer composition of the bentonite particles proves that they cannot be drilling mud and must therefore be from bentonite interbedded with the Pierre Shale and its equivalents. Their mixed-layer composition must be caused by depth diagenesis. In contrast, the normal composition of the three bentonite samples from outcrops at the Salt Creek locality (loc. 10) indicates no alteration of the bentonite, and therefore, presumably, no alteration of the shale. The close similarity between mixed-layer clay in the surface shale and in the well cuttings pointed out in the preceding paragraph indicates that neither groups of shale have been appreciably altered by depth diagenesis.

The explanation for the consistently altered condition of bentonite from the Powder River basin well cuttings in contrast to the unaltered bentonite only 20 miles away on the Salt Creek anticline lies in the post-Cretaceous history of the Powder River basin. Conglomerates of Eocene age at the western edge of the basin near Buffalo, Wyo. (Sharp, 1948), contain boulders of metamorphic and igneous rock derived from the core of the Bighorn Mountains to the west (fig. 2). The presence of these boulders shows that the Bighorn Mountains were uplifted and the Powder River basin began to form well before the Eocene Epoch. Therefore, the lower Tertiary sedimentary rocks that make up most of the thick overburden of the Pierre Shale in the center of the basin likely were t. 'inner on the flanks of the basin. As previously pointed out in connection with figures 13 and 14, no more than a few thousand feet of overburden is indicated by porosity of shale at the Salt Creek locality (loc. 10). Such overburden on the edge of the basin was too thin to produce any change in the composition of the bentonite, let alone to produce the abundant illite-type layers of the mixed-layer clay in the shale.

The amount of bentonite cuttings in the well samples was much too small for differential thermal analysis. However, one small sample was composited from three adjacent 10-foot samples from one well and was sandwiched next to the thermocouple between layers of alundum in the sample well of the DTA apparatus. As shown in the lower part of table 7, the sample gave a dehydroxylation endotherm having a single peak at 685° C. Thus, like the few other mixed-layer clays from bentonite in the main study of the Pierre Shale and its equivalents (table 6), it tended to retain the high temperature of dehydroxylation in the 650°-750° C range that is typical of normal unaltered bentonite.

MONTANA DISTURBED BELT

The Montana disturbed belt is a narrow zone of closely spaced thrust faults east of the Rocky Mountain front extending from central Montana well into Canada (Mudge, 1970). Thrusting was from west to east. The only stratigraphic section in this belt that was sampled for the main Pierre Shale study was that at the Dearborn River locality (fig. 2, loc. 2); this is also the only section from which IS-ordered mixed-layer clay was identified, though others (Hower and Hall, 1970; Hoffman, 1976; Hoffman and others, 1976) have identified such clay at many other localities in the disturbed belt. Maiklem and Campbell (1965) described IS-ordered mixed-layered clay from one bentonite and randomly mixed-layered clay from several other bentonite beds from the Pierre-equivalent strata west of Calgary in the Foothill belt of Alberta, Canada, a northern extension of the Montana disturbed belt (fig. 2). To determine just how closely and consistently IS-ordered mixed layering is related to the disturbed belt, other localities from the south end of the disturbed belt near Wolf Creek to Marias Pass about 100 miles to the north were sampled in 1972 on a field trip arranged by John Hower and John Hayes. The localities are given letter designations in figure 2 to distinguish them from the numbered localities of the main study of the Pierre Shale and equivalents.

Mineralogy of the additional samples from the disturbed belt is shown in table 8. At four of the seven localities bentonite beds, as well as shale or claystone, were sampled. Two of these bentonite localities, Marias Pass and Sun River, actually are in the Colorado Shale, below Pierre-equivalent rocks (fig. 1), but their mineralogy still illustrates the alteration of clay in the disturbed belt. At five of the seven localities the mixed-layering is IS-ordered. At Wolf Creek, where the clay in the bentonite is not IS-ordered, it is still highly illitic and is very similar to that in the adjacent claystone. As at the Dearborn River locality (table 6), the mixed-layer clay in the bentonite is nearly as illitic or more so than in the shale. Thus, in the disturbed belt there seems to be no appreciable tendency for bentonite to lag behind shale during alteration.

Only one of the IS-ordered clays listed in table 8, the bentonite from the Sun River locality (loc. S), gives a dehydroxylation peak temperature within the intermediate temperature range of 600°-650° C that seemed to characterize several of the clays at the Dearborn River locality (table 6). Therefore, this feature and any intermediate degree of OH⁻ ordering that it may indicate for IS-ordered clay in the shale or claystone is erratically developed. All four bentonite samples in table 8, however,

TABLE 8.—*Mineralogy and dehydroxylation peak temperatures of shale and bentonite samples from the Montana disturbed belt (fig. 2)*

[B, bentonite; S, shale]

Locality	M		T	C	S		B		D	W	
Rock type	B	S	S	S	B	S	B	S	S	B	S
Proportions of layers in mixed-layer clay, in percent											
Illite	¹70	¹60	55	¹60	¹80	¹70	¹70	¹60	¹60	45	50
Beidellite	25	25	25	35	20	20	25	35	35	35	30
Montmorillonite	5	15	20	5	0	5	5	5	5	20	20
Proportions of clay minerals in total clay, percent											
Mixed-layer	99	67	64	78	99	100	90	70	89	93	85
Illite	0	28	28	14	0	0	0	15	0	0	0
Chlorite	0	0	5	5	0	0	0	15	0	0	15
Kaolinite	1	5	3	3	1	0	10	0	11	7	0
Proportions of minerals in total sample, in percent											
Total clay	75	55	45	55	95	75	75	50	70	85	65
Quartz	27	30	18	30	1	18	6	23	20	6	17
K-feldspar	0	0	0	0	0	0	0	1	0	0	0
Plagioclase	2	1	6	5	4	4	6	5	3	10	3
Calcite	0	15	9	0	0	0	12	9	0	0	0
Dolomite	0	0	15	5	0	0	0	12	0	0	0
Dehydroxylation peak temperature, in °C, and area in square inches											
Low	595	570	580	585	605	590	590	580	590	560	560
	0.8	1.3	0.9	1.4	1.4	2.0	1.2	1.2	2.2	1.2	1.5
High	710	680	(²)	(²)	695	690	705	(²)	670	700	660
	1.4	0.1	None	None	1.4	0.2	1.0	None	0.1	1.7	0.1

¹IS-ordered mixed layering.
²No high-temperature peak.

Description of localities

M, Colorado Shale, 2.5 miles east of Marias Pass, in railroad cut north of U.S. Route 2, unsurveyed.
T, St. Mary River Formation, in gully 0.25 miles south of road along Two Medicine River and 4.9 miles southwest of U.S. Route 89, NW¼NE¼ sec. 26, T. 31 N., R. 10 W.
C, Two Medicine Formation, 18 miles west of Choteau along Bellview Road, NE¼ sec. 24, T. 24 N., R. 8 W.
S, Colorado Shale, in gully just south of bridge over Sun River, NE¼SW¼ sec. 36, T. 22 N., R. 9 W.
B, Two Medicine Formation, 100 yards east of Bowmans Corner, NE¼NW¼ sec. 30, T. 18 N., R. 4 W.
D, Eagle Sandstone, 1 mile south of Dearborn River bridge on U.S. Route 287, SW¼ sec. 34, T. 17 N., R. 4 W.
W, Two medicine Formation, in town of Wolf Creek south of U.S. Route 91 across from Union Oil Co. gas station, NE¼ sec. 2, T. 14 N., R. 4 W.

have a large component of their dehydroxylation endotherms peaking between 650° and 750° C, so that this characteristic and the ordering of OH⁻ that it implies is retained from the original montmorillonitic bentonite.

The data in tables 6 and 8 clearly show that alteration of expanding clays and IS-ordered mixed layering is related in some way to the Montana disturbed belt. The exact relationship, however, is not clear. Stacking of thrust sheets to achieve the required overburden would seem an obvious explanation in a zone of thrust faults. Such an explanation is particularly appealing at the Marias Pass locality (loc. M), which is well into the disturbed belt, where one can see in the mountain face just to the north a thick section of Precambrian metasedimentary rocks thrust eastward over the Cretaceous rocks. However, as at the Dearborn River locality (loc. 2), most of the sample localities are on the eastern side of the disturbed belt where only Cretaceous strata are involved, deformation is mostly open folding, and

the thrusts tend to be small (Mudge, 1970). Furthermore, porosity measurements (fig. 14) indicate no great difference in overburden between the Dearborn River locality within the distrubed belt and the Augusta-Choteau locality (loc. 3, fig. 2) about 15 miles to the north and just outside the disturbed belt. Yet, mixed-layer clays from the Augusta-Choteau locality, having avarages of 28 and 35 percent illite-type layers, are among the least illitic found (fig. 15). Initially, alteration of the IS-ordered clays at the Dearborn River locality was thought possibly to be related to heat from small intrusive sills in the section or to heat from the younger Upper Cretaceous Adel Mountain Volcanics of Lyons (1944) that occur less than 10 miles to the east and that may have once covered the Dearborn River locality. However, such volcanic rocks are not present near the northern localities sampled within the disturbed belt.

SUMMARY AND INTERPRETATION

Mixed-layer illite-smectite is the most abundant constituent of the Pierre Shale and its equivalents. The lithium test is used to differentiate smectite layers into montmorillonite and beidellite. X-ray methods have been developed for use of relative peak heights where conventional peak-migration methods cannot be used, so that the threefold breakdown of mixed-layer clay into illite-, beidellite-, and montmorillonite-type layers can be made for most samples. Within the mixed-layer clay, beidellite makes up about a third of the layers, commonly ranging from 25 to 45 percent. Proportions of illite-type layers range much more widely between samples, commonly from 20 to 80 percent, but rarely few or no such layers are present. Montmorillonite is generally complementary to the amount of illite, commonly from 0 to 60 percent of the layers. Mixed-layer clay containing as much as about 60 percent illite-type layers is randomly interlayered; when it contains more illite-type layers it is IS-ordered. Such ordered interlayering occurs only in the Montana disturbed belt. The ranges and average proportions of layers differ little between marine and nonmarine rock.

Smectitic clay in bentonite differs from that in shale in that it rarely is interlayered with illite-type layers. Montmorillonite usually makes up 60-90 percent of the layers, the remainder being beidellite. The only consistent exceptions to the usual composition of bentonite in the Pierre equivalents are in the Montana disturbed belt, where many bentonite beds contain IS-ordered clay, and in deep wells from the Powder River basin, where bentonite contains less illitic, randomly interlayered illite-smectites. Only three other illitic bentonite samples were noted out of about 200 analyzed.

The mixed-layer clay in the Pierre Shale and its equivalents has an average structural formula of $K^+_{0.6}Na^+_{0.4}Ca^{+2}_{0.1}(Al^{+3}_{2.8}Fe^{+3}_{0.5}Fe^{+2}_{0.1}Mg^{+2}_{0.6})(Al^{+3}_{0.6}Si^{+4}_{7.4})O^{-2}_{20}(OH)^-_4$, which differs little between marine and nonmarine rocks. From chemical analyses of purified mixed-layer clays, structural formulas have been inferred for illite, beidellite,

and montmorillonite layers (table 4) that show expectable differences in K+, total layer charge and tetrahedral Al+3. Illite-type layers in IS-ordered clay seem to have a slightly higher K+ content and total layer charge than in other mixed-layer clays. The average structural formula for smectite in bentonites of $K_{0.1}^{+}X_{0.8}^{+}(Al_{3.0}^{+3}Fe_{0.3}^{+3}Fe_{0.1}^{+2}Mg_{0.6}^{+2})$ $(Al_{0.2}^{+3}Si_{7.8}^{+4})O_{20}^{-2}(OH)_4^{-}$ (X represents exchangeable cations) differs consistently from that of mixed-layer clay in shale in that the structural formula has much lower K+, lower total layer charge originating mostly in the octahedral layer, less iron, and little tetrahedral Al+3. Montmorillonite layers in mixed-layer clays in shales are similar to those in bentonites except that they do not seem to have the low iron content.

Smectite clay in bentonite also differs from that in shale in that it contains an ideal 4(OH)⁻ per unit cell as measured thermogravimetrically, whereas the OH⁻ in shale is not of ideal amount or is not ideally located within the layer. The ideal 4(OH)⁻ of bentonitic montmorillonite is volatilized at relatively high temperatures giving dehydroxylation peaks between 650° and 750° C, whereas the nonideal OH⁻ of shale gives dehydroxylation peaks between 550° and 600° C. The lower temperature is dominant even in mixed-layer clays from shale having 60-70 percent montmorillonite-type layers. On the other hand, the uncommon illitic mixed-layer clay found in some bentonite beds tends to retain the high temperature of dehydroxylation characteristic of bentonite, even in highly illitic IS-ordered clay. IS-ordered clay in shale has either a low temperature of dehydroxylation or, in some clay, an intermediate temperature between 600° and 650° C, which may indicate a tendency toward OH⁻ ordering. This intermediate dehydroxylation is, however, very inconsistently developed.

Depth diagenesis or some type of diagenetic alteration can be shown to have consistently affected only the IS-ordered mixed-layer clay from the Montana disturbed belt, where such regularly interlayered clay occurs in most shale or claystone, bentonite, and even argillized igneous instrusive rock. In contrast, the less illitic randomly interlayered clay in shale outside the disturbed belt generally cannot be shown to have developed by depth diagenesis; instead, most such interlayered clay must have developed before rather than after deposition.

The most highly illitic mixed-layer clay in rocks of Pierre age outside the disturbed belt occurs most consistently on the east side of the basin of deposition along the Missouri River. Past overburden amounts here, both as reconstructed from thicknesses of younger rocks at their nearest outcrops and as inferred from porosities of the shale, were minimal and were much less than necessary to alter the mixed-layer clay in the shale. Bentonite in the Missouri River area contains smectite with no illite-type interlayers, and it also obviously has not been altered by depth diagenesis. Farther to the west, but still east of the Montana disturbed belt, a few

bentonite samples do contain somewhat illitic mixed-layer clay that apparently results from depth diagenesis. Mixed-layer clay in shale closely associated with these somewhat illitic bentonite beds is consistently much more illitic than that in the bentonite. The possibility was considered that the onset of alteration in the bentonite lagged appreciably behind alteration in the shale, because montmorillonite in bentonite, which has a mostly octahedral layer charge, might logically be expected to alter with more difficulty to illite, which has a mostly tetrahedral layer charge, than would the more beidellitic and illitic mixed-layer clay in the shale. Such a lag, however, seems unimportant. First, mixed-layer clay in shale along the Missouri River is as illitic or more so than that in shale associated with the somewhat illitic bentonite beds. Therefore, as the clays in shale and bentonite on the Missouri River are unaltered, there is no logical reason to infer that similarly illitic mixed-layer clay in shale farther west is altered either, just because nearby bentonite is somewhat altered. In addition, a comparison of mixed-layer clay from the Wolf Creek locality (loc. W, table 8) with that in the three pairs of samples from the Columbus and Shawmut localities (locs. 6 and 5, table 6) shows that illitization of the bentonite at the Wolf Creek locality closely approaches the proportion of illite-type layers in the shale, and yet any illitization of the shale has not advanced beyond that in the shale at the Columbus or Shawmut localities. Therefore, the depth-temperature conditions that produced the lower degree of illitization of bentonite at the Columbus and Shawmut localities cannot logically be inferred to have increased the proportion of illite-type layers there in the shale. Apparently bentonite does not lag appreciably behind shale in depth diagenesis. Therefore the montmorillonitic composition of most bentonite in rocks of Pierre age indicates not only a lack of depth diagenesis of the bentonite but also no possible alteration by depth diagenesis of the associated shale.

The extent to which depth diagenesis is believed to have modified the mineralogy of the mixed-layer clays in the Pierre Shale and equivalent strata is summarized in figure 16. Mixed-layer clays originally deposited commonly contained 20-60 percent illite-type layers, a composition that is retained in most of the Pierre Shale and equivalents (fig. 16A); accompanying bentonite contains no illite-type layers. At a few isolated outcrops, overburden thicknesses on the order of 10,000 feet and resulting high temperatures have caused development of some illite-type layers in smectites of bentonite (fig. 16B), but only minor additional development of illite-type layers has occurred in the shale in the originally least illitic mixed-layer clay. Examples are the bentonite at the Columbus and Shawmut localities (locs. 6 and 5, table 6), some of the least illitic bentonite from the Powder River basin wells (table 7), and the upper part of the Dearborn River locality (table 8, St. Mary River Formation). Still more rarely, diagenetic development might have advanced to form nearly half illite-type layers in the bentonite (fig.
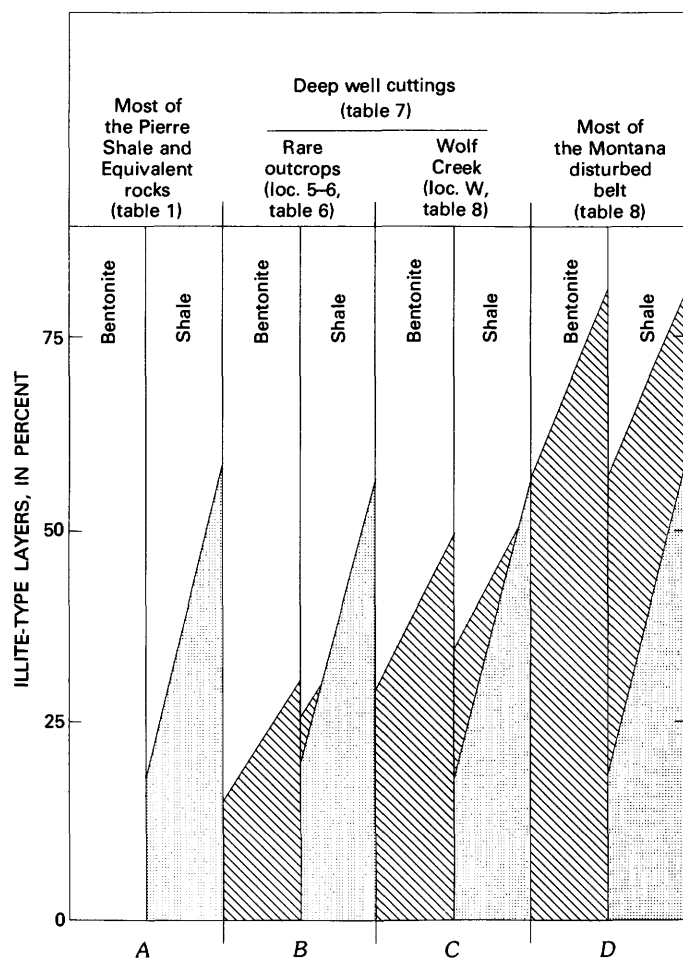
FIGURE 16.—Common proportions of illite-type layers in mixed-layer clay originally deposited (stippled pattern) and that developed by depth diagenesis (lined pattern) in the Pierre Shale and equivalent strata. Interlayering is random except in the Montana disturbed belt where it is mostly IS-ordered.

16C) and increased the proportion of illite-type layers in all mixed-layer clays in the shale that originally had appreciably fewer illite-type layers. Examples are the bentonite and shale from the Wolf Creek locality (loc. W, table 8) and possibly some of the more illitic bentonite from the Powder River basin wells that are almost as illitic as mixed-layer clays in accompanying shale. Even here, however, newly developed illite-type layers in the shale probably are far subordinate to the original illite-type layers. Only in the Montana disturbed belt (fig. 16D) do authigenically developed illite-type layers unequivocally and appreciably augment the original illite-type layers.

If illite in the mixed-layer clays and its wide range of proportions throughout much of the rocks of Pierre age is not due to depth diagenesis, what has caused it? If both the mixed-layer illite-smectite of the shale and the smectite of the bentonite are altered volcanic debris, as seems to be the case, why are they so different?

The closest relationship between any one factor and the 'illite: smectite ration of the mixed-layer clays in the Pierre Shale and its equivalents seems to be the rapidity of burial or the length of contact with weathering conditions at the land surface or with seawater before burial. Clay deposited slowly so that it was in contact with surface conditions for long periods of time tends to contain highly illitic mixed-layer clay. For example, the shale in the lower part of the Pierre Shale along the Missouri River is relatively thin and must have been deposited much more slowly than the much thicker shale in the upper part or in stratigraphically equivalent shale farther west (fig. 1). As previously mentioned in connection with figure 15, this lower shale from the Missouri River area contains some of the most consistently illitic mixed-layer clay in the Pierre Shale. The high proportion of illite-type layers cannot have been caused by depth diagenesis, because past overburden was minimal. Therefore, long contact of mixed-layer clay with seawater before burial may have resulted in fixation of K^+ on some of the more highly charged beidellite-type layers, converting them to illite-type layers. The amount of rock thus altered, however, was too small to increase the average proportion of illite-type layers in marine rock as a whole, as the average is not appreciably different from that in nonmarine rock (fig. 9). Conversely, mixed-layer clays having few illite-type layers consistently occur in altered tuffaceous rocks in which the clay occurs as rounded sand-size aggregates that originally were grains of volcanic glass. These aggregates disintegrate readily in water and could not have been transported and deposited in their present condition. Instead, they must have been deposited as grains of volcanic glass that were altered to clay after deposition. Thus, the highly montmorillonitic clays in such tuffs probably had little contact with surface conditions. The ultimate example would be bentonite, which is composed almost entirely of wind-transported volcanic glass that altered to montmorillonite after burial.

Dacitic volcanic ash, such as that from which bentonite and most smectitic clay in the Pierre Shale and its equivalents formed, commonly contains about 60-65 percent SiO_2 and about 16 percent Al_2O_3, whereas the clays contain only about 50 percent SiO_2 and 18-20 percent Al_2O. The alteration thus releases a considerable excess of SiO_2. In bentonite beds, buried under a layer of mud when alteration occurs, the excess SiO_2 cannot be readily flushed away. Because of the excess SiO_2, Al^{+3} could not compete effectively with Si^{+4} for cation positions in tetrahedral sheets of the forming montmorillonite layers, and the layer charge was limited almost entirely to the octahedral sheet, owing to Mg^{+2}-for-Al^{+3} substitution. Apparently the homogeneous uniform composition of the silica sheets limited OH^- almost entirely to ideal cation positions at the center of the silica rings (fig. 3).

Most of the volcanic debris, particularly the larger fragments, probably did not travel nearly so far as the fine glass particles that formed the bentonites, but fell instead in land areas near the volcanoes. Long periods, perhaps thousands of years, separated the volcanic eruptions; during this time the terrestrial debris was subjected to alteration considerably different from that of the bentonite beds—to weathering agents like rain, sun, and organic acids from plants. Circulation of water probably was fairly open so that much of the excess silica could be washed away. Furthermore, the coarse volcanic debris probably cooled slower than the bentonite ash, so that crystallization advanced to a sodic plagioclase-quartz stage, compared with a calcic plagioclase-biotite stage indicated by the phenocrysts in bentonite (Schultz, and others 1978).

For either or both of the above reasons—(1) leaching of silica and (2) crystallization of quartz—the altering volcanic debris must not have had nearly as great a silica excess as the altering bentonite. Consequently, Al^{+3} could compete with Si^{+4} for cation positions in the tetrahedral sheets, and the newly forming smectitic clay tended to be more beidellitic than in the bentonites. Because of this inhomogeneous composition of the silica sheets, OH^- distribution also tended to be erratic and nonideal. Furthermore, the net layer charge on the octahedral layer due to Mg^{+2}-for-Al^{+3} substitution tended to be as large as that of the clay in bentonite; this octahedral charge, combined with the additonal tetrahedral charge, apparently was large enough to fix many of the K^+ ions released during alteration of the tuff, and illite-type layers developed.

Weathering of most tuffaceous debris probably started where it initially fell. Much of this weathered debris was eroded and redeposited downstream where it was again weathered. Several such cycles of erosion, redeposition, and weathering probably occurred before the altered volcanic sediment—mostly mixed-layer clay—reached the sea. In the marine environment, some additional development of illite-type layers may have occurred locally owing to fixation of K^+ during periods of exceptionally slow deposition. However, judged from the similarity of mixed-layer clays in most of the Pierre Shale and equivalent nonmarine rocks, most of the mixed-layer clay was little altered in the marine environment. Only locally within most of the area studied has overburden been sufficient to alter the clays originally deposited in Cretaceous time. Diagenetic alteration has been pervasive only in the Montana disturbed belt, in most of which the piling up of thrust sheets and elevated temperatures owing to the augmented overburden seem to account for the alteration. However, highly illitic IS-ordered clay in some areas on the edge of the distrubed belt, where thrusting is minor, may indicate that factors other than overburden may also have been important; perhaps something like shearing stress or elevated thermal gradients due to nearby igneous activity had an effect.

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