

# THE ILLITES FROM SOME NORTHERN OHIO SHALES

*By*

BRUCE W. NELSON<sup>1</sup>

University of Illinois, Urbana, Illinois

## ABSTRACT

The Middle Paleozoic shales of northern Ohio contain a well-crystallized variety of illite as their main constituent. Powder diagrams relate the illite to the two-layer monoclinic muscovite crystallization. The low asymmetry of the 10 Å reflection indicates that interlayering of non-mica or hydrated-mica units is small. The relative intensities of the basal reflections show that the illites approach the ideal muscovite composition but have about one-fourth the octahedral aluminum replaced by iron and are deficient about one-half or less the interlayer potassium. The interlayer positions are essentially anhydrous. One-dimensional Fourier syntheses made before and after thermal treatment of the illites indicate that intensity changes of the basal reflections due to thermal treatment are related to electron density changes confined to the octahedral layer. Dehydroxylation begins at moderately low temperatures and continues until an anhydride structure is formed.

## INTRODUCTION

The lower Mississippian and upper Devonian shales of northern Ohio include gray, black, and red shales, and intermediate varieties, all of which constitute the major lithology of the Appalachian rocks extending from northwestern Pennsylvania to central northern Ohio. The different lithologic varieties contain clay mineral assemblages of quartz, illite, chlorite, and kaolinite, whose proportions vary systematically in terms of geological factors. An illitic mineral is present in all the rocks, and an attempt has been made below to characterize it in terms of x-ray diffraction diagrams and response to thermal treatment. An account of the geological relations of the different clay mineral assemblages will be given separately in the geological literature.

## GENERAL FEATURES

The illite component in the clay mineral assemblages from all of the northern Ohio rocks is very similar. Small differences exist in the degree of asymmetry of the 10.0 Å diffraction maximum and in the response to thermal treatment. Characteristic powder data are given in Table 1. These data show that the illite is allied to the two-layer monoclinic muscovite crystallization, the 025, 115, and 116̄ reflections being particularly diagnostic (Grim, Bradley, and Brown, 1951, p. 166). Some diffraction diagrams show fewer or more diffuse reflections than those recorded in Table 1, but the differences appear to result from poor resolution of the two-layer monoclinic reflections. There is no evidence that either the three-layer trigonal or the one-layer monoclinic muscovite polymorphs (Levinson, 1955) occur in these shales. The preceding statements and those to

<sup>1</sup> Now in the Department of Geological Sciences, Virginia Polytechnic Institute, Blacksburg, Virginia.

TABLE I.—POWDER DATA FOR SHALE ILLITE<sup>1</sup>

Indices	d kX	Relative intensity
002	9.98	s
004	5.00	m
110	4.47	vs
111	4.26	w
022	4.13	w
113	3.90	w
023	3.72	mw
114	3.51	mw
024, 006	3.35	vs
114	3.22	w
025	3.01	mw
115	2.87	w
116	2.79	yw
202	2.57	vs
133, 202	2.45	w
204, 133	2.38	m
221	2.25	w
223	2.20	w
206, 043	2.13	mw
0010	2.00	m
208	1.71	w
2010, 312	1.66	w
	1.65	
	1.54	
060	1.50	vw
337	1.378	ms
335	1.338	w br
400	1.288	w br

<sup>1</sup> The data given for shale illite are representative of those obtained with  $\text{CuK}\alpha$  radiation from the illites in all samples of the northern Ohio shales. Patterns vary in the diffuseness and number of diffraction lines.

Intensities are: very strong, vs; strong, s; moderately strong, ms; moderate, m; moderately weak, mw; weak, w; very weak, vw; and broad lines, br.

follow are based upon analyses of  $<1 \mu$  material separated from the mechanically disaggregated shale by sedimentation. In view of the number and character of the reflections recorded in the x-ray diffraction diagrams and the observed intensities of the basal reflections recorded in Table 2 it seems justifiable to consider these illites as well crystallized.

Most illites are characterized by more or less asymmetrical 10 A diffraction maxima that are caused by supplementary diffraction effects on the low-angle flank of the 10 A reflection. The asymmetry is thought to result from the interlayering of non-mica (chlorite, montmorillonite, etc.) or hydrated-mica units with mica layers of the normal type. Illites from the northern Ohio shales differ among themselves in the extent to which asymmetry is observed. Such differences have been measured quantitatively by slow-speed scanning with a General

Electric XRD-3 diffractometer. A scanning rate of  $0.2^\circ 2\theta$  per minute was used, and the recorded profiles were corrected for the difference in Lorentz and polarization factors existing over the angular range considered by adjustments at every tenth of a degree  $2\theta$  after the method of Bradley (1954, p. 331). The method gives true diffraction profiles of the 10 Å maximum. The illite profiles were all compared with a profile obtained under the same conditions from powdered muscovite, which was used as a standard. The asymmetry is defined as the difference in degrees  $2\theta$  between the observed peak of the 10 Å maximum and the mean peak position measured at one-fourth maximum intensity. Filtered  $\text{CuK}\alpha$  radiation was employed.

TABLE 2.—INTENSITY DATA AND CALCULATED STRUCTURE FACTORS FOR ILLITES<sup>1</sup>

00l	25° C			350° C			600° C		
	I	F	$\frac{100 X}{F/F_{006}}$	I	F	$\frac{100 X}{F/F_{006}}$	I	F	$\frac{100 X}{F/F_{006}}$
BS 3									
002	4760	3.76	56.6	5400	4.00	57.5			
004	635	-2.81	-42.3	755	-3.06	-44.0			
006	1515	6.64	100.0	1665	6.96	100.0			
008	50	1.66	25.0	55	1.74	25.0			
00, 10	405	-6.10	-92.0	405	-6.10	-87.7			
00, 12	8	1.07	16.1	8	1.07	15.4			
00, 14	15	1.78	26.2	17	1.89	27.2			
00, 16	15	2.06	31.1	19	2.32	33.4			
TC-B-2									
002	1470	2.09	51.3	1415	2.05	49.1	1170	1.86	30.7
004	190	-1.54	-37.7	225	-1.67	-40.0	375	-2.16	-35.5
006	570	4.07	100.0	600	4.18	100.0	1270	6.08	100.0
008	25	1.17	28.8	20	1.05	25.1	70	1.96	32.2
00, 10	125	-3.39	-83.3	110	-3.18	-76.2	85	-2.80	-46.0
00, 12	—	—	—	5	0.847	20.3	8	1.07	17.6
00, 14	9	1.38	33.8	8	1.30	31.0	12	1.59	26.1
00, 16	9	1.60	39.3	10	1.69	40.4	12	1.85	30.4
HT-B-2									
002	885	1.62	53.7	1080	1.79	55.8	675	1.42	34.6
004	80	-0.996	-35.2	130	-1.27	-39.6	150	-1.36	-33.4
006	275	2.83	100.0	355	3.21	100.0	575	4.09	100.0
008	15	0.907	32.1	15	0.907	28.3	35	1.39	33.9
00, 10	60	-2.35	-83.1	65	-2.44	-76.1	40	-1.92	-46.9
00, 12	—	—	—	8	1.07	33.4	10	1.20	29.3
00, 14	5	1.02	36.2	8	1.30	40.4	8	1.30	31.7
00, 16	8	1.51	53.3	5	1.19	37.1	8	1.51	36.9

<sup>1</sup> Intensities are given in counts above background for the natural material, natural material heat treated at 350° C for 24 hours, and natural material heat treated at 600° C for 24 hours.

Structure factors are given after correction of the observed intensities for Lorentz and polarization effects assuming diffraction follows powder laws.

Ratios of structure factors with respect to the (006) factor are also given.

Data from oriented clay mineral aggregates with particle size less than one micron. Diffractometer recording,  $\text{CuK}\alpha$  radiation, Ni filter.

The standard muscovite profile has zero asymmetry and the peak and mean peak position fell at  $8.80^\circ 2\theta$ . The asymmetry of the illite maxima varied from 0.07 to 0.36. A shift of the peak position toward lower angles accompanies increasing asymmetry. A gray shale illite from a quartz-illite-chlorite-kaolinite assemblage had its peak at  $8.82^\circ$  and the asymmetry of 0.07. A dark-gray shale illite from a quartz-illite-chlorite assemblage had its peak at  $8.74^\circ$  and an asymmetry of 0.19. A gray shale illite from a quartz-illite-chlorite-calcite assemblage had its peak at  $8.60^\circ$  and the asymmetry of 0.36. These figures indicate the degree of departure from muscovite character exhibited by the northern Ohio shale illites. In general this departure is relatively small, and if the asymmetry is due to interlayering effects these must be relatively nonextensive. Interlayering of hydrated-mica units in some illites and chlorite units in others causes the peak asymmetry, as judged from the results of thermal treatment. Interlayering of chlorite units is the major cause of the higher peak asymmetries recorded.

### STRUCTURE FACTORS FOR THE BASAL REFLECTIONS

More detailed analysis of the character of the illites depends upon quantitative intensity data and their reduction to structure factors for individual reflections, of which the different orders of the basal reflections are most useful. Intensities were obtained from slow-speed diffractometer records of well-oriented clay mineral aggregates. In many cases eight basal orders were recorded, and representative data are given in Table 2. The reduction of the intensity data to structure factors is somewhat of a problem, because the conditions under which diffraction occurs from an oriented aggregate are not those which would normally satisfy the classical formulas. The situation has been resolved in the following way.

In film patterns of oriented clay aggregates the concentration of intensity of diffracted radiation for successive orders of the basal reflection appears to obey powder laws more closely than the classical formula for diffraction from an extended single crystal face. Neglect of the absorption correction led Brown (1951, p. 269) to a partial justification of the single-crystal formula when considering oriented-aggregate diffraction in the Debye-Scherrer method, but since the absorption correction is independent of angle in the focusing diffractometer the single-crystal formula should not be used to correct data obtained under these conditions. In spite of some reservations which must be held for the effects of orientation, it seems best under the circumstances to correct the observed intensity data according to the powder formula. Neglect of extinction and temperature corrections aids the compromise. Relative structure factors, therefore, are given in Table 2, and these were calculated from the following expression:

$$F \sim [I(1 + \cos^2 2\theta) / \sin \theta \cos 2\theta]^{\frac{1}{2}}$$

The data in Table 2 allow a more detailed characterization of the shale illites.

### COMPOSITION OF THE ILLITES

It would be desirable to know precisely the chemical composition of the shale illites, and certain generalizations are possible within the limitations of the

data. The relative values of structure factors calculated for the different basal orders do not depart drastically from those found by Jackson and West (1930), but there are some differences that could be real or could result from the manner in which the raw data were reduced. Ordinarily it would not be practical to go beyond the previous statement, but recently Brown (1955) has calculated the effect of compositional variations in the muscovite lattice on the theoretical structure factors and it is possible to show some correlations with his results.

Structure factors for the natural shale illites differ from those calculated for the ideal muscovite composition in the greater value of the second order as compared with the fourth and sixth orders and in the lower value of the fourth order as compared with the second and sixth orders. The calculated values compare very favorably indeed with those given by Brown (1955, p. 660) when one-half the interlayer potassium is replaced by water and one-fourth of the octahedral aluminum is replaced by iron. In this case Brown's summations yield  $F$ 's of 48 (002), -41 (004), and 102 (006), which should be compared with Table 2. Somewhat better agreement could be obtained by assuming a slightly higher iron content. If the interlayer sites are not occupied by water where potassium is deficient, it is necessary to assume that more than half of the interlayer potassium is present. These conclusions are supported to some degree by the Fourier syntheses given in the following section, but it is not possible to carry the analysis any further. Since the raw intensity data have been reduced to structure factors as efficiently as possible, it has been assumed that differences observed between the illite structure factors and those previously calculated for ideal muscovite compositions may be at least partly real. The northern Ohio shale illites, therefore, are probably 50 percent deficient in interlayer potassium and contain iron in about 25 percent of the octahedral aluminum positions. The high degree of crystallinity accompanying the potassium deficiency is of interest.

### THE EFFECTS OF THERMAL TREATMENT

Relative intensities of the basal reflections in x-ray diagrams of heated illites differ from those characterizing these minerals in their natural state. In some illites the 10 Å reflection increases in intensity and becomes less asymmetrical after heat treatment at 350° C. Presumably this is due to dehydration and collapse of interlayered hydrated-mica units. In other illites heat treatment causes little change in asymmetry and small changes in relative intensity. Interlayered chlorite units are probably responsible for such behavior. But observed relative intensity changes in other reflections, and possibly those above, perhaps are not so obviously explained. After heat treatment at higher temperatures more pronounced relative intensity changes occur, as has been observed previously (Bradley and Grim, 1951). The major changes in the basal reflections are a relative decrease in intensity of the second-order reflection and an increase in the fourth-order and sixth-order reflections. The effects of thermal treatment on the Ohio shale illites were studied by one-dimensional Fourier syntheses. Structure factors were calculated from basal reflection intensities of illites in their natural state, illites heated at 350° C, and illites heated at 600° C. The oriented clay aggregates of the natural materials were heated in a muffle furnace for 24 hours at constant temperatures of 350° C and 600° C. Representative data are given in Table 2 and the Fourier syntheses are reproduced in Figures 1, 2, and 3.

For comparison the Fourier synthesis of muscovite given by Jackson and West (1930) has been recalculated on the basis of eight orders of the basal reflection. The synthesis is shown in Figure 1a. Figure 1b shows the synthesis of an illite that approaches muscovite character. The most apparent difference is in the relatively low electron density at the interlayer position, and this perhaps reflects a potassium deficiency. The octahedral cation density in the illite synthesis may be somewhat greater relative to the anion density than that in the muscovite synthesis and, if this difference is significant, could reflect the replacement of aluminum by small amounts of iron. In other respects the syntheses are similar. The dotted curve in Figure 1b is the synthesis of the same illite heat treated at 350° C. The structure has been modified very little in spite of important intensity changes in the basal reflections shown in Table 2.

Figure 2 shows syntheses for two different illites and the curves in Figures 1b, 2a, and 2b represent the range of characteristics. The general features in the syntheses of the natural illites are very similar, while the syntheses of the illites

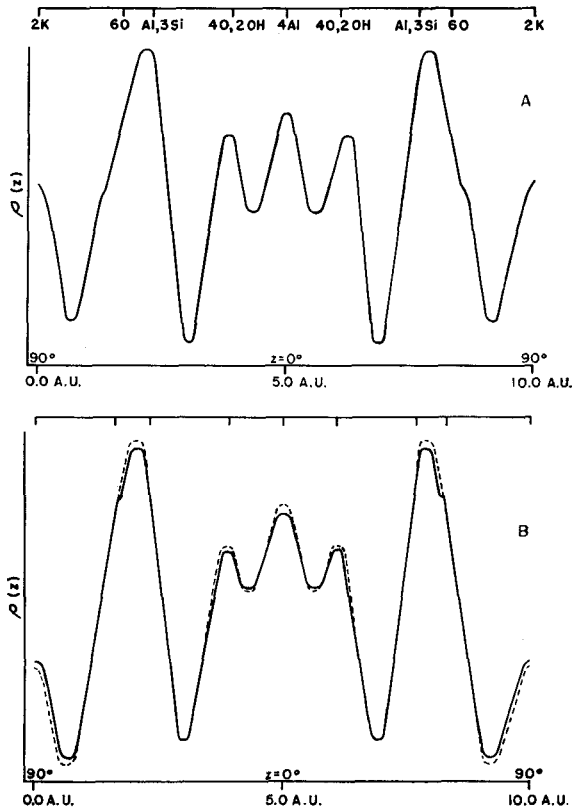


FIGURE 1. — Fourier syntheses. (a) Jackson and West muscovite (from eight basal orders). (b) BS-3 illite: Natural material (—); heated at 350° C (---).

heat treated at 350° C exhibit increasingly marked effects. In Figure 2a heat treatment has resolved the octahedral positions owing to increased electron density at the cation site and decreased electron density at the anion site. The tetrahedral positions are relatively unaffected. In Figure 2b the changes in electron density distribution within the octahedral layer are more clearly shown, and these are accompanied by changes in the synthesis that reflect an increased separation between the tetrahedral layers of the structure. The interlayer electron density changes very little.

Perhaps the most notable feature of the low-temperature syntheses is that they reveal changes that are more fully developed in the illites heated at higher temperatures and shown by the syntheses in Figure 3. The changes in the basal reflection intensities observed in illites heat treated at 350° C, therefore, should be interpreted in terms of changes in structure completed at higher temperatures. The northern Ohio shale illites seem to differ in the degree to which such structural changes can occur at a given temperature. The differences cannot be correlated thus far with geological factors.

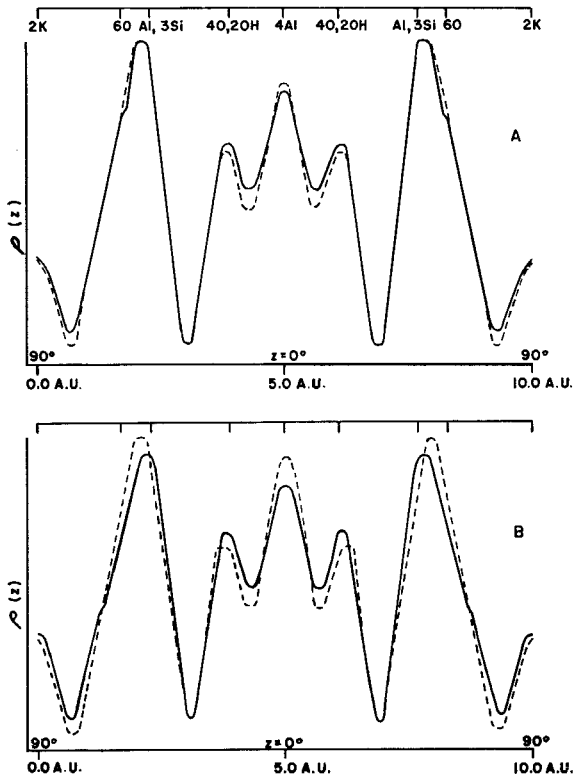


FIGURE 2.—Fourier syntheses. (a) TC-B-2 illite: Natural material (—); heated at 350° C (---). (b) HT-B-2 illite: Natural material (—); heated at 350° C (---).

Figure 3 shows syntheses of two illites that have been heat treated at 600° C for 24 hours. In Figure 3a the synthesis of the natural material is repeated so that the magnitude of the electron density shifts can be seen. These results are representative of all the illites heated at high temperatures. The most remarkable feature of these syntheses is the redistribution of electron density in the octahedral layer. The anion sites are much reduced in density, while the cation site shows a remarkable increase in density. Bradley and Grim (1951, p. 183) suggested that a modified anhydride structure was formed in heated dioctahedral illites. The proposed structure involved a rearrangement of the octahedrally coordinated anions by a shift toward the octahedral cation position and expulsion of one-sixth of the octahedral oxygens in the form of water. The process has been referred to as dehydroxylation. The Fourier syntheses shown in Figure 3 fully support Bradley and Grim's high-temperature anhydride structure.

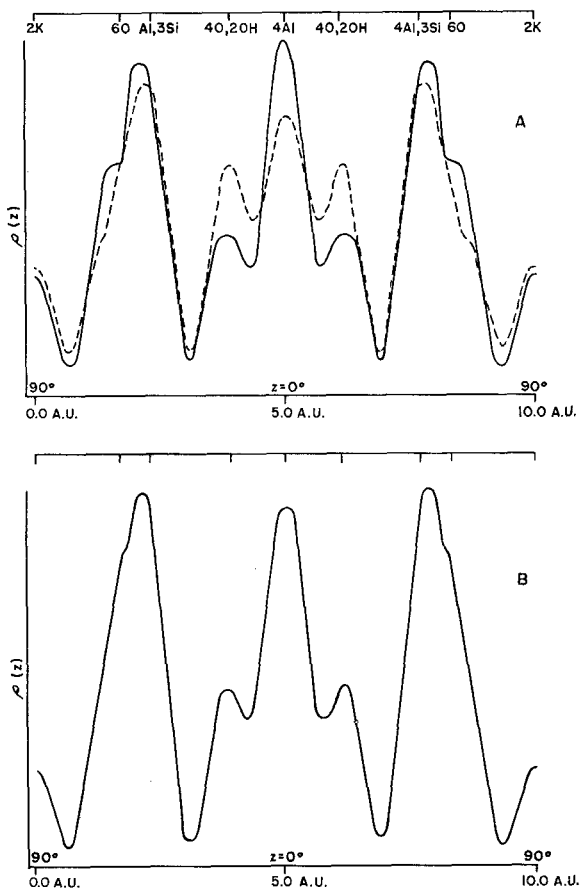


FIGURE 3.—Fourier syntheses. (a) HT-B-2 illite: Heated at 600° C (—); natural material (---). (b) TC-B-2 illite: Heated at 600° C.



In Figure 3 as in the previous syntheses the change in electron density at the interlayer position as a result of the thermal treatment is small. If the syntheses show a real potassium deficiency in the interlayer position, a further decrease in density should result from the thermal treatments if the deficient potassium is replaced by water. Since no decrease occurs it is suggestive that these sites are deficient in potassium only and no, or little, water occupies the interlayer positions. The interlayer positions, therefore, are essentially anhydrous. This feature may be the cause of the high degree of crystallinity observed and may distinguish these shale illites from what would be called less well-crystallized varieties.

This completes the characterization of illites that occur in the northern Ohio shales. An attempt has been made to show how a detailed analysis of the x-ray diffraction characteristics of these minerals can supply significant information that would not be possible by conventional analysis of natural mixed clay-mineral assemblages.

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