

GENESIS OF CLAY MINERALS IN SOME PENNSYLVANIAN SHALES OF INDIANA AND ILLINOIS

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ABSTRACT

Shales of marine, brackish-water, and nonmarine origin, collected from cyclothem of Pennsylvanian age, were analyzed chemically and mineralogically. Clay mineral identifications were accomplished using x-ray diffraction and differential thermal analysis techniques. Summations of the structure amplitudes of the individual clay minerals formed a basis for semi-quantitative ratios between illite and kaolinite-chlorite. Illite was found to be enriched in the marine shales. The origin of the authigenic clay minerals in the shales is discussed from two aspects. The first and probably the more correct uses the thesis that the ultimate clay mineral is built up from a skeletal aluminum-silicate structure; the second discusses the origin of the clay minerals from a purely colloidal point of view. Trace element determinations, pH values, and pipette analyses are also included as a part of this study.

INTRODUCTION AND ACKNOWLEDGMENTS

One of the primary duties of a geologist is to reconstruct the environments in which minerals or rocks have developed. The clay minerals should be excellent indicators of environment because of their sensitivity to slight changes in the composition, temperature, and pH of their surroundings (Frederickson, 1952, p. 6). Kaolinite usually develops in an acidic environment or in a neutral environment where intense leaching processes prevail. Montmorillonite forms in the presence of certain alkalis and alkaline earths. Illites are the dominant clay minerals in marine sediments (Grim, 1953, p. 348-353). An understanding of the environment or environments that favor the development of chlorite must await additional data.

The purpose of this paper is to present some data on the clay minerals found in Pennsylvanian shales deposited in marine and nonmarine environments. In addition to the clay mineral analyses, chemical analyses and a few trace element determinations of these shales are included in order that a better understanding of the genesis of the clay minerals in environments of slightly differing characteristics may be attained.

Chemical analyses were made by Mr. Maynard E. Collier, Chemist, Department of Geology, Indiana University. Trace elements were determined spectrographically by Mr. Richard K. Leininger and Mr. S. Ross Taylor, Geochemist and Spectrographer respectively of the Indiana Geo-

logical Survey. Mr. John M. Smith aided in the preparation of the samples for chemical analyses and x-ray study. Mr. Kenneth R. Vance made the pipette analyses and pH determinations used in this study. Mr. Richard K. Leininger and Mr. S. Ross Taylor offered valuable advice on the interpretation of the chemical analyses. Dr. Harold W. Wanless, Department of Geology, University of Illinois, suggested several localities in western Illinois where suitable shale samples could be collected. The author is indebted to Dr. Ralph E. Grim, Department of Geology, University of Illinois, and Dr. William F. Bradley, Illinois Geological Survey, for their criticisms of this paper, but the author assumes sole responsibility for its contents. Dr. Thomas G. Perry, Department of Geology, Indiana University, kindly read the manuscript.

STRATIGRAPHY, ENVIRONMENTS, AND LITHOLOGIES OF SOME PENNSYLVANIAN SHALES

The Pennsylvanian coal measures of the Eastern Interior Basin display

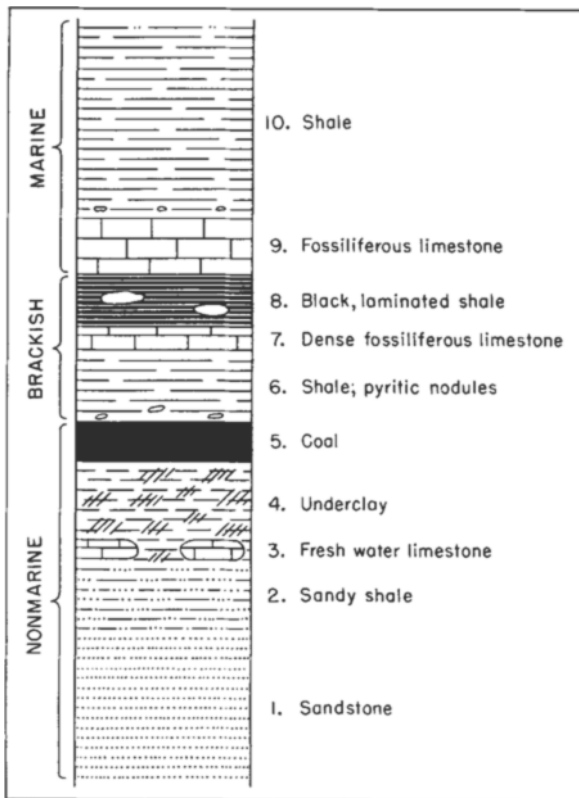


FIGURE 1. — Pennsylvanian repetitive cycle in western Illinois (after Weller).

a remarkable succession of cyclical deposits. Correlations have been based on cyclothem in this basin (Wanless, 1931, p. 179-193).

Weller (1930, p. 97-135) described a repetitive cycle in western Illinois which consisted of ten members (Fig. 1). The basal member is a quartzose or subgraywacke sand that commonly lies unconformably upon the upper member of the previous cyclothem. The basal sandstone grades upward through a sandy shale to a clay shale that contains a fresh-water limestone at the top, which in turn is succeeded by underclay and coal. These lower five members are considered nonmarine deposits.

Above the coal is a thin shale bearing pyrite nodules and which is overlain by a dense, argillaceous limestone. Black, fissile shale containing large concretions overlies this limestone. Above the black shale is a nonargillaceous, fossiliferous limestone which is overlain by a bluish-gray marine



FIGURE 2.—Location of samples (X) in the Pennsylvanian outcrop area of the Eastern Interior Basin.

TABLE 1.—LITHOLOGY AND STRATIGRAPHIC AND GEOGRAPHIC LOCATION OF SAMPLES

Sample No.	Formation or Cyclothem ¹	Description	Location
M5036	Shelburn	Marine: Fine-grained, massive, blue-gray shale.	SW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 22, T. 6 S., R. 11 W., Vanderburgh Co., Indiana
M50113	Linton	Marine: Fine-grained, dense, gray shale.	NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 20, T. 15 N., R. 8 W., Parke Co., Indiana
M5048, 49	Brazil	Marine: Fine-grained, hard, laminated, dark-gray shale. M5048 is fossiliferous.	NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 33, T. 2 S., R. 5 W., Dubois Co., Indiana
M50102, 103	Brazil	Nonmarine: Fine-grained, dark-gray to black shale. Contains pyrite nodules.	NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 25, T. 13 N., R. 7 W., Clay Co., Indiana
M50130	Brazil	Nonmarine: Fine-grained, dark-gray, carbonaceous shale. Contains limonite nodules.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 31, T. 20 N., R. 7 W., Fountain Co., Indiana
M5080, 81	Mansfield	Brackish: Fine-grained, hard, blue-gray shale. Contains pyrite concretions. M5080 contains sandy lenses.	SE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 23, T. 7 N., R. 5 W., Greene Co., Indiana
M5082	Mansfield	Brackish: Fine-grained, laminated, hard, dark-gray, carbonaceous shale.	NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 19, T. 13 N., R. 4 W., Putnam Co., Indiana
M52202	Gimlett ¹	Marine: Fine-grained, blocky, hard, light-gray shale.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 1, T. 8 N., R. 6 E., Peoria Co., Illinois
M52203, 204	Gimlett ¹	Marine: Fine-grained, blocky, dense, dark-gray shale. Contains limestone concretions.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 1, T. 8 N., R. 6 E., Peoria Co., Illinois
M52205	Gimlett ¹	Nonmarine: Medium- to fine-grained, massive, micaceous, sandy, gray shale.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 1, T. 8 N., R. 6 E., Peoria Co., Illinois
M52206	Sparland ¹	Brackish: Black, fissile shale.	NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 1, T. 8 N., R. 6 E., Peoria Co., Illinois

Sample No.	Formation or Cyclothem	Description	Location
M52208	Liverpool ¹	Marine: Fine-grained, blocky, massive, tannish-gray shale.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 5 N., R. 4 E., Fulton Co., Illinois
M52210	Liverpool ¹	Marine: Fine-grained, dense, soft, dark-gray shale.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 5 N., R. 4 E., Fulton Co., Illinois
M52212	Liverpool ¹	Brackish: Fine-grained, dark-gray, fossiliferous shale.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 5 N., R. 4 E., Fulton Co., Illinois
M52215	Liverpool ¹	Brackish: Fine-grained, dark-gray, dense shale.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 4, T. 5 N., R. 3 E., Fulton Co., Illinois
M52218	Liverpool ¹	Nonmarine: Fine-grained, dense, blocky, gray shale.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 31, T. 2 N., R. 1 E., Schuyler Co., Illinois
M52219, 220	Liverpool ¹	Brackish: Fine-grained, hard, gray shale.	SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 31, T. 2 N., R. 1 E., Schuyler Co., Illinois
M52221	Liverpool ¹	Nonmarine: Sandy, micaceous, hard, gray shale.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 19, T. 2 N., R. 1 E., Schuyler Co., Illinois
M52213	Greenbush ¹	Marine: Fine-grained, dense, soft, gray shale.	NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 5 N., R. 4 E., Fulton Co., Illinois
M52217	Bernadotte ¹	Nonmarine: Fine-grained, dense, blocky, sandy, blue-gray shale.	NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 31, T. 2 N., R. 1 E., Schuyler Co., Illinois
M52216	Seville ¹	Nonmarine: Fine-grained, micaceous, laminated, sandy shale.	NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 31, T. 2 N., R. 1 E., Schuyler Co., Illinois

¹ Cyclothem

shale. The members 6 - 8 most probably were deposited in restricted shallow marine or brackish conditions. Members 9 and 10 probably reflect deposition in an environment with open marine circulation.

Members 1, 4, 5, 8, 9, and 10 in Figure 1 are geographically the most persistent units and are, therefore, the most commonly encountered members of the cyclothems in the Eastern Interior Basin. The shale units sampled for this study were Nos. 2, 6, 8, and 10 of Figure 1. Channel type samples of these shale units were collected from Pennsylvanian cyclothems along the western edge of the Eastern Interior Basin in western Illinois and from the Pennsylvanian formations along the eastern edge of the Basin in western Indiana (Fig. 2).

Cyclothems do not contain the same members over large areas but are subject to lateral variations. Wanless and Shepard (1936, p. 1177-1206) described three types of coal cyclothems: (1) the piedmont type characterized by thick, terrestrial clastic sediments, noteworthy development of coal, and subordinate marine beds; (2) the deltaic type of cyclothem, similar to the one shown in Figure 1, predominant in the Eastern Interior Basin; (3) the neritic type of cyclothem characterized by a dominance of marine conditions with alternating marine limestones and shales.

A knowledge of the stratigraphy and sedimentation of cyclothems must be obtained before the results of a study determining the genesis of the clay minerals can be analyzed. The stratigraphic and geographic locations, the lithologies, and the environmental classifications of the Pennsylvanian shales sampled are shown in Table 1.

METHODS OF STUDY

Samples were collected from shales believed to have formed in nonmarine, restricted marine or brackish, and open marine environments. Clay mineral identifications and ratios, chemical analyses, trace element determinations, pH determinations, and pipette analyses were made to determine whether there were significant variations which could be related to the above-mentioned three major environments.

A representative portion of each shale sample was disaggregated and dispersed in distilled water. Sodium hexametaphosphate was added to some suspensions to aid in deflocculation. Particles 2 microns and less in equivalent spherical diameter were siphoned off for x-ray identification and differential thermal analysis.

For x-ray identifications the clay minerals were oriented on glass slides using a technique described by Grim (1934, p. 45-46), and dried at 60°C. A General Electric XRD-3D spectrogoniometer using nickel-filtered copper radiation was employed with settings of 50 kvp and 16 ma.

The differential thermal analysis apparatus is similar to that described by Grim (1951, p. 1031-1053). The heating rate was 12°C/minute and a resistance of 200 ohms was used in the recording circuit. Because adequate descriptions of the DTA method are recorded in the literature (Grim, 1951), a further review of the method is not required.

Trace element determinations were made on a Jarrell-Ash 21-foot grating spectrograph in which a DC arc was used. The samples were mixed with graphite, palladium, and iron oxide. Iron was used as the internal standard. The wavelength range was 3425 to 4675 angstroms.

Na_2O , K_2O , CaO , and Li_2O values were obtained with the aid of a Beckman model DU spectrophotometer having a flame photometer attachment. All other chemical values were determined using standard methods of chemical analysis.

Pipette analyses were run on four samples to determine if any relationships exist between mineral composition and size. Fifty grams of each of the four samples used were diluted up to 1 liter and fractions of less than 1/32, 1/64, 1/128 --- 1/2048 mm size fractions were siphoned off at predetermined intervals using a technique described by Krumbain and Pettijohn (1939, p. 166).

A 30-gram sample was placed in 1000 ml of distilled water and pH determinations were made after the samples had been agitated and disaggregated and allowed to settle for 48 hours. A Beckman model G pH meter with a glass electrode was used for these determinations.

TABLE 2. — CHEMICAL ANALYSES OF SHALES

Sample No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	Li ₂ O	Ig. Loss	Total
M5036 ¹	64.1	16.3	5.9	0.85	0.69	1.90	1.36	2.73	—	4.25	98.79
M5048 ¹	62.0	21.4	5.12	0.87	0.25	0.95	0.27	3.07	<0.005	6.44	100.37
M5049 ¹	59.7	21.2	4.45	0.86	0.25	1.28	0.22	3.11	0.008	9.64	100.72
M50113 ¹	62.8	18.8	4.86	0.84	0.11	1.84	1.12	3.52	0.012	5.33	99.23
M52202 ¹	54.8	18.9	8.38	0.67	1.32	2.27	0.78	3.60	<0.005	9.20	99.92
M52203 ¹	47.9	12.9	3.52	0.56	14.4	1.63	0.63	2.38	0.006	15.9	99.82
M52204 ¹	48.6	14.3	3.18	0.52	13.2	1.53	0.60	2.86	0.006	15.0	99.79
M52208 ¹	59.9	19.6	6.48	0.75	0.09	2.11	1.25	3.26	0.016	6.75	100.21
M52210 ¹	54.3	23.5	5.07	0.80	0.47	2.44	0.76	4.11	0.020	8.03	99.50
M52213 ¹	56.7	21.0	6.85	0.76	—	2.31	1.00	3.80	0.013	7.08	99.51
M5080 ²	61.0	17.8	8.02	0.82	0.54	1.88	0.20	2.83	<0.005	7.37	100.46
M5081 ²	57.6	19.8	7.81	0.78	0.31	2.08	0.18	3.27	—	7.96	99.79
M5082 ²	65.1	17.2	5.30	0.62	0.40	1.03	0.12	2.16	0.021	7.96	99.91
M52206 ²	44.7	20.4	9.18	0.75	2.06	2.07	0.71	3.32	0.017	16.4	99.61
M52212 ²	53.0	20.0	6.19	0.82	2.79	2.24	0.64	3.15	0.014	10.1	98.94
M52215 ²	55.8	18.7	7.28	1.00	2.83	1.65	0.86	2.74	0.017	8.75	99.63
M52219 ²	63.8	16.6	5.69	0.73	0.58	1.77	1.30	2.88	0.010	6.14	99.50
M52220 ²	61.2	14.8	5.69	0.65	2.73	1.69	1.16	2.62	<0.01	8.92	99.47
M50102 ³	59.6	16.2	8.92	1.12	0.47	1.34	0.20	2.78	0.011	8.89	99.53
M50103 ³	55.6	20.3	7.36	0.78	0.090	1.80	0.19	3.26	0.019	10.1	99.50
M50130 ³	59.4	19.1	6.98	0.80	0.18	0.98	0.16	3.06	0.019	9.08	99.76
M52205 ³	63.5	19.2	4.68	0.78	0.18	1.85	1.28	3.12	0.017	5.28	99.89
M52216 ³	71.2	14.8	3.02	0.93	0.02	0.12	0.22	2.86	<0.01	6.14	99.32
M52217 ³	75.4	15.2	0.94	0.95	0.02	0.10	0.17	2.33	<0.01	4.40	99.52
M52218 ³	58.1	20.3	6.63	0.75	0.25	2.31	0.97	3.58	0.015	7.23	100.14
M52221 ³	67.8	15.8	4.31	0.88	0.18	1.69	1.20	2.56	0.014	5.36	99.78

¹ marine

² brackish

³ nonmarine

CHEMICAL ANALYSES

The term *shale* lacks chemical significance because the composition of shales varies with the chemical composition of the materials from which they are derived. The Pennsylvanian shales used for this study were collected from three distinct environments and it was hoped that the chemical analyses could be grouped to show some relationship to the environment.

The chemical analyses of the raw shales are given in Table 2, and they reveal a wide range in the chemical composition of the shales. The SiO_2 values range from 47.9 to 64.1 percent in marine shales, 44.7 to 65.1 percent in brackish-water shales, and 55.6 to 75.4 percent in nonmarine shales. The average value of the SiO_2 in the nonmarine shales is higher than the average value of the SiO_2 in either the brackish or marine shales. In general, the nonmarine shales are more arenaceous than the marine and brackish shales and, consequently, the higher average SiO_2 value was expected.

The Al_2O_3 , Fe_2O_3 , and TiO_2 values do not indicate a significant difference among the shales from the three environments. The CaO values have a lower average value in the nonmarine shales although two CaO values in the marine shales are abnormally high. The amounts of MgO , Na_2O , and K_2O are not particularly diagnostic of an individual environment; however, the values are slightly lower in the nonmarine environment than in the marine. The average of the Li_2O values are slightly higher in nonmarine shales than in marine shales. The ignition losses are too variable in each of the three environments to be diagnostic.

Chemical analyses of these Pennsylvanian shales do not permit the differentiation of marine and nonmarine shales. Work is in progress to apply correction factors such as the percent quartz and calcite to the analyses and to reinterpret them.

A comparison of the average chemical analyses of shales (Rankama and Sahama, 1950, p. 226) with the average analyses of the twenty-six Pennsylvanian shales used in this study shows some interesting differences.

	Average Shale (Rankama & Sahama)	Aver. of all Penn. Shales Collected	Aver. of Marine Shales	Aver. of Brackish-Water Shales	Aver. of Nonmarine Shales
SiO_2	58.84	59.37	57.0	57.8	63.8
Al_2O_3	15.48	18.2	18.8	18.2	17.6
Fe_2O_3	6.77	5.8	5.4	6.9	5.4
TiO_2	0.71	0.79	0.75	0.77	0.87
CaO	3.12	1.71	3.01	1.53	0.17
MgO	2.44	1.64	1.82	1.80	1.27
Na_2O	1.30	0.67	0.79	0.64	0.55
K_2O	3.24	3.03	3.24	2.87	2.94
Li_2O	0.0099	0.011	0.009	0.011	0.014

The Al_2O_3 , CaO , MgO , and Na_2O values of the Pennsylvanian shales are significantly different from the corresponding values of the average shale. The low CaO , MgO , and Na_2O values and the high Al_2O_3 values suggest that many of the shales were deposited in water having a slightly acidic pH; this lends credence to the hypothesis that portions of the Pennsylvanian cyclothems are nonmarine in origin. This is further substantiated by comparing the average chemical analyses of the shales from the three environments with the average shale. The average K_2O value does not differ significantly from that of the average shale; this suggests that potassium is more readily adsorbed and held by aluminum-silicate colloids to form illite than are sodium, calcium, and magnesium.

TRACE ELEMENT DETERMINATIONS

By definition, shales are fine grained and are composed of predominantly colloidal size particles, including quartz (Murray and Gravenor, 1953, p.

TABLE 3. — TRACE ELEMENTS IN SHALES

Sample No	Ga ³⁺	Cr ³⁺	Ni ²⁺	Co ²⁺	V ³⁺	Mn ²⁺	Sc ³⁺	Sr ²⁺	Ba ²⁺
M5036 ¹	+	78	38	18	62	570	<20	110	360
M5048 ¹	+	110	<50	nd	130	180	nd	110	300
M5049 ¹	+	100	nd	nd	<100	180	nd	130	340
M50113 ¹	+	75	54	23	110	290	<20	160	550
M52202 ¹	+	78	nd	nd	140	340	nd	160	570
M52203 ¹	nd	95	nd	nd	130	260	nd	150	200
M52204 ¹	nd	98	nd	nd	140	190	nd	260	260
M52208 ¹	+	80	nd	nd	120	450	<20	110	400
M52210 ¹	+	160	nd	nd	190	520	nd	330	350
M52213 ¹	+	120	nd	nd	140	430	nd	140	330
M5080 ²	+	110	71	24	150	950	24	94	280
M5081 ²	+	120	<50	nd	130	~1000	nd	83	330
M5082 ²	+	120	<50	nd	110	210	nd	50	190
M52206 ²	+	190	160	nd	200	170	nd	47	240
M52212 ²	+	120	nd	nd	200	400	nd	140	410
M52215 ²	+	110	nd	nd	140	380	nd	130	350
M52219 ²	+	66	nd	nd	98	260	<20	75	220
M52220 ²	+	69	<50	<20	110	350	nd	70	250
M50102 ³	+	91	<50	nd	<50	~1200	nd	170	360
M50103 ³	+	120	nd	nd	<50	950	nd	300	440
M50130 ³	+	95	nd	nd	140	650	nd	260	460
M52205 ³	+	78	nd	29	81	290	<20	210	610
M52216 ³	+	85	nd	nd	110	85	nd	100	310
M52217 ³	+	78	nd	nd	88	28	<20	370	410
M52218 ³	+	66	nd	nd	98	230	<20	70	260
M52221 ³	nd	150	nd	nd	200	440	nd	400	550

+ — present but background prevented accurate reading

nd — not detected

¹ marine

² brackish

³ nonmarine

25-28). An important property of colloidal size particles is their ability to bind certain elements or substances by adsorption. Some trace elements are probably adsorbed by the clay minerals and others may fit into the structure. Because shales are composed largely of clay minerals, a few trace elements were determined (Table 3). It was hoped that the determination of these trace elements would indicate that certain of them had an affinity for specific clay minerals or environments. Only a few trace elements could be determined by the method employed, but additional methods are being developed so that many more trace elements can be found in the near future.

An analysis of the trace elements in the raw shales in Table 3 indicates that only three elements showed significant variation in average values when comparing the three environments.

	V ³⁺	Sr ²⁺	Ba ²⁺
Marine	126 ppm	166 ppm	366 ppm
Brackish	142	86	284
Nonmarine	102	235	425

The vanadium content is highest in shales deposited under brackish water conditions; such shales are dark colored and have a higher organic content than the shales from the marine or nonmarine environments. Vanadium is sometimes enriched in shales that have a high organic content (Rankama and Sahama, 1950, p. 601). A possible explanation for the greater vanadium content in the marine shales compared with the nonmarine shales is that vanadium could substitute for ferrous or ferric iron and magnesium in illite which is the most abundant clay mineral in the marine shales.

Nonmarine shales have the highest average values of barium and strontium whereas brackish water shales have the lowest average value of these elements. The strontium to barium ratio in sea water is 260:1 (Rankama and Sahama, 1950, p. 483) whereas barium dominates strontium in Pennsylvanian shales. This anomaly is easily explained because barium is probably preferentially adsorbed by the clays as it has a lower ionic potential than strontium, and the ionic radius of barium (1.34A.) nearly equals the ionic radius of potassium (1.33A.). The reason for the concentration of barium and strontium in the nonmarine shales is not readily explained although the pH of the depositional environment may have contributed to the concentration of these elements.

	Average Shale (Rankama & Sahama)	Aver. of all Penn. Shales Collected	Aver. of Marine Shales	Aver. of Brackish-Water Shales	Aver. of Nonmarine Shales
V	120 ppm	123 ppm	126 ppm	142 ppm	102 ppm
Cr	410 - 680	102	99	113	95
Mn	620	423	341	465	484
Sr	170	162	166	86	235
Ba	460	359	366	284	425

The average values for the trace elements in Pennsylvanian shales are less than the corresponding values of the average shale reported by Rankama and Sahama (1950, p. 226).

The average pH values of the shales collected from each of the three environments show that there is a correlation with the environment of deposition. The average pH of the marine shales is slightly basic and the average pH of the brackish and nonmarine shales is slightly acidic. Much more work has to be done to learn the true significance of pH values before any conclusions can be drawn.

	Average pH value
Marine shale	7.6
Brackish shale	6.4
Nonmarine shale	6.6

PIPETTE ANALYSES

Pipette analyses were run on four samples to determine if a relationship exists between clay mineral ratios and decreasing particle size. The illite to kaolinite and chlorite ratio invariably increases as particle size decreases. In sample M52202 the ratio ranges from 20:1 in the 1/32 mm fraction to 39:1 in the 1/2048 mm fraction. In sample M52203 the ratio varies from 9:1 to 12:1; in sample M52204 from 9:1 to 18:1; and in sample M52205 from 3:1 to 5:1 in the 1/32 mm to the 1/2048 mm fractions, respectively.

CLAY MINERAL COMPOSITION

Pennsylvanian shales collected for this study were composed almost entirely of four minerals; the clay minerals (illite, kaolinite, and chlorite) and colloidal size quartz. The clay minerals, which are of immediate concern, were identified by x-ray and differential thermal analysis techniques. All shales contained these three clay minerals, as well as quartz, but in widely differing proportions. The intensities of the basal plane reflections of the clay minerals, recorded and counted on a Geiger counter x-ray spectrometer, were used in this study to determine the relative proportions of the clay minerals present in the shale.

The reflecting power of the (001) plane of illite, kaolinite, and chlorite plus the (002) plane of chlorite were determined by summation of the structure amplitudes. These calculations showed that the reflecting power of the (001) plane of kaolinite has for all practical purposes three times the reflecting power of the (001) plane of illite and $2\frac{1}{2}$ times the reflecting power of the chlorite (001) plane. Because of atomic substitutions in chlorite and illite, the reflecting powers of the (001) planes were considered as being one-third that of the (001) plane of kaolinite. The (002) plane of chlorite has a reflecting power of approximately one-half that of the (001) plane of kaolinite.

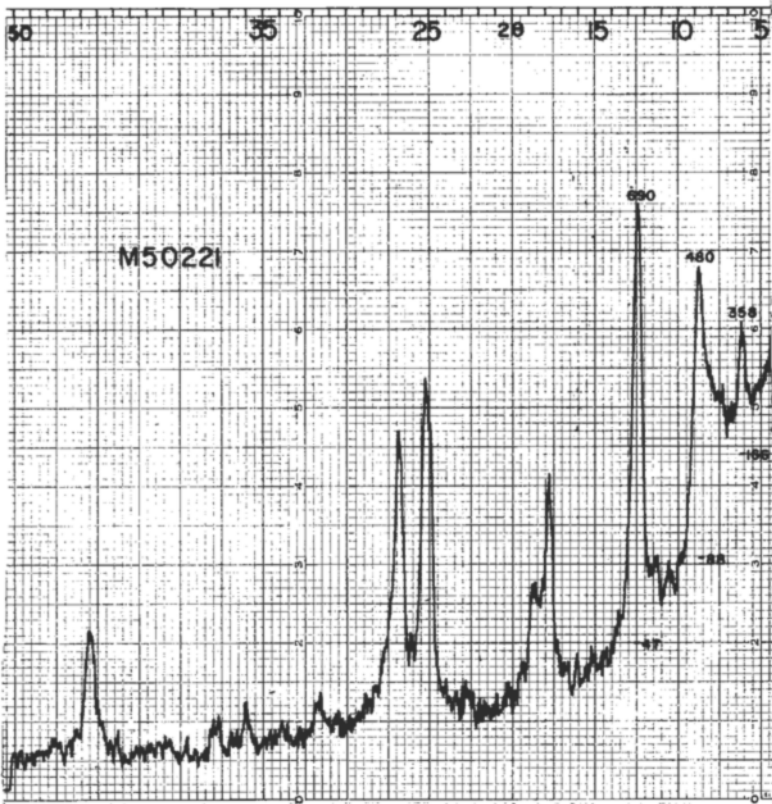


PLATE 1.—X-ray spectrometer trace showing intensities of (001) reflections and background.

Plate 1 shows the intensities of the peaks in counts/sec plus the background count of a Liverpool shale from western Illinois (M50221). This x-ray pattern exemplifies how clay mineral ratios were determined. The intensity counts are shown at the (001) reflection of kaolinite at $12.4^\circ 2\theta$, of illite at $8.8^\circ 2\theta$, and of chlorite at $6.2^\circ 2\theta$. The background intensity was subtracted from the peak intensity giving the true intensity of the reflection. Because the (001) plane of kaolinite has a reflecting power approximately 3 times that of the (001) planes of illite and chlorite, the values of the intensities of the illite and chlorite peaks were each multiplied by 3. The reflecting power of the (001) plane of kaolinite is approximately twice that of the (002) plane of chlorite; thus, one-third of the total intensity at the (001) kaolinite peak is due to the presence of the (002) reflection of chlorite because the (001) kaolinite reflection and the (002) chlorite reflection both appear at the same position. By equating these

corrected values, the clay mineral ratio is approximately 5 illite to 2 kaolinite to 2 chlorite.

The chlorite (001) reflection appears at the same position as some montmorillonite (001) reflections. Chlorite was distinguished from montmorillonite by heating the sample to 300°C which removed the adsorbed water from the basal planes of montmorillonite and changed the (001) reflection to 8.8° 2θ (Brindley, 1951, p. 116; Grim, 1953, p. 98). Montmorillonite was not detected in the Pennsylvanian shales collected for this study.

Chlorite was difficult to distinguish from kaolinite in many samples because the (001) reflection of chlorite was very subdued; under such conditions the appearance of the (001) and (003) reflections of kaolinite can provide helpful information. In some instances the (002) reflection of kaolinite at 25° 2θ showed two distinct peaks or a deflection on the high angle side of this reflection which is caused by the (004) reflection of chlorite. The (003) reflection of kaolinite appears at approximately 37.8° 2θ and is sufficiently intense to rise considerably above the background, but the chlorite (006) reflection which should appear at this same position is absent owing to the structure factor. This means that if the kaolinite (003) reflection is very weak or absent when strong (001) and (002)

TABLE 4. — CLAY MINERAL RATIOS IN SHALES

Sample No.	Illite	Kaolinite	Chlorite
M5036 ¹	4	1	1
M5048 ¹	6	2	1
M5049 ¹	6	2	1
M50113 ¹	6	2	1
M52202 ¹	20	1	1
M52203 ¹	9	1	1
M52204 ¹	9	1	1
M52208 ¹	7	2	2
M52210 ¹	4	1	1
M52213 ¹	4	1	1
M5080 ²	3	1	1
M5081 ²	5	2	1
M5082 ²	5	2	2
M52206 ²	4	1	1
M52212 ²	6	2	1
M52215 ²	3	1	1
M52219 ²	5	1	1
M52220 ²	4	1	1
M50102 ³	2	1	1
M50103 ³	2	1	1
M50130 ³	3	2	2
M52205 ³	3	1	1
M52216 ³	6	2	1
M52217 ³	6	2	1
M52218 ³	7	2	2
M52221 ³	5	2	2

¹ marine

² brackish

³ nonmarine

reflections appear at 12.4° and $25^\circ 2\theta$ respectively, then the strong kaolinite (001) and (002) reflections are primarily due to (002) and (004) reflections of chlorite. When this method of detection was not considered positive, then the sample was heated to 600°C which destroyed the kaolinite reflections and left the chlorite (001) reflection (Grim, 1953, p. 87). The reflections of poorly crystalline chlorites are destroyed at a lower temperature ($400 - 450^\circ\text{C}$) and the kaolinite reflection remains (Grim, personal communication).

Table 4 shows the approximate clay mineral ratios, as determined by the previously described procedure, in the shales from the three environments. The illite to kaolinite-chlorite ratio is highest in marine shales and lowest in nonmarine shales. This relationship is shown diagrammatically in Figure 3. The clay minerals in marine shale, showing a high illite to kaolinite-chlorite ratio, are represented by the x-ray pattern in Plate 2. The clay mineral ratios are more diagnostic of the environments than either the chemical analyses or the trace elements.

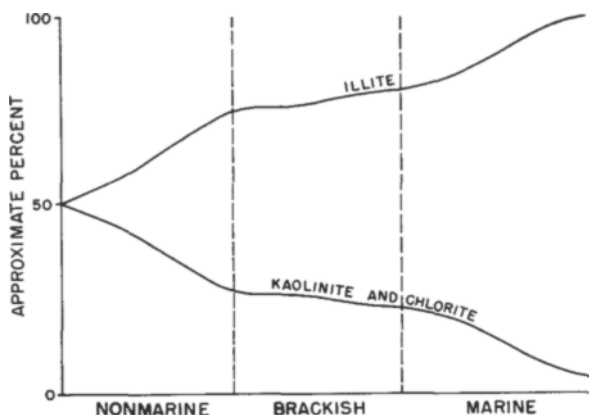


FIGURE 3.—Diagram showing clay mineral ratios in three Pennsylvanian environments.

Differential thermal analysis curves of one sample from each of the three environments are shown in Figure 4. The DTA curve of sample M50102 is typical of the curves of nonmarine shales. The curves of nonmarine shales show a moderate exothermic reaction from 300 to 500°C , which is oxidation of organic material, and a relatively sharp endothermic break at 550°C as well as a prominent exothermic break at 950°C , which are attributed to the presence of a high proportion of kaolinite. The DTA curve of sample M52214 is typical of the curves of brackish-water shales. These shales have more organic material, which gives a larger exothermic break in the 300 to 500°C region. The endothermic break at 550°C and

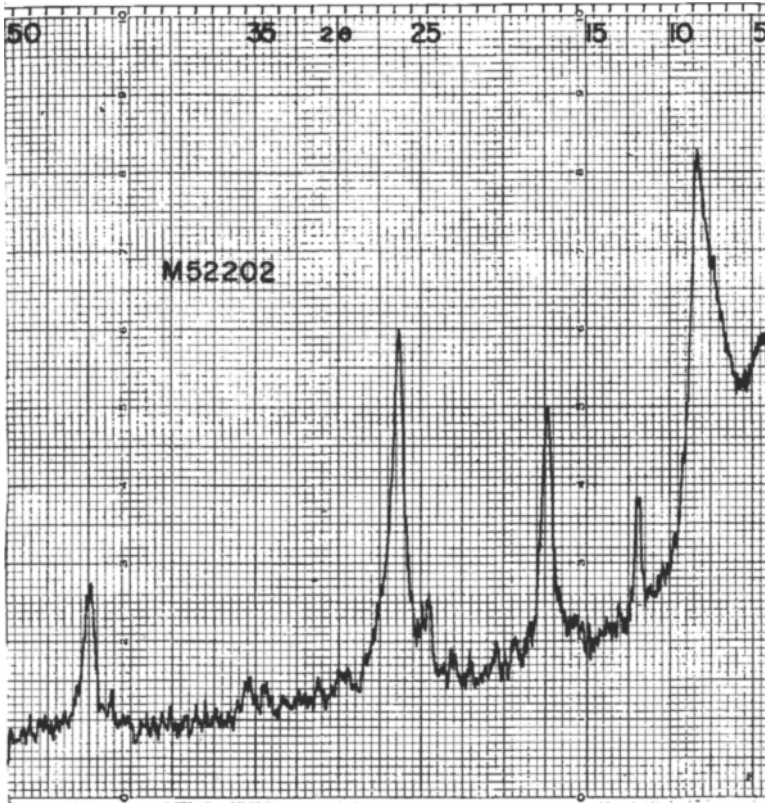


PLATE 2.—X-ray spectrometer trace of marine shale.

the exothermic break at 950°C are smaller than these same breaks on the curve of the nonmarine shale because of the higher proportion of illite. The DTA curve of sample M52202 is typical of marine shales which have a high illite content.

GENESIS OF THE CLAY MINERALS

The genesis of clay minerals in Pennsylvanian shales is a difficult subject to discuss because of the large number of variables which affect their formation. Ries (1927, p. 1-37) discussed two prevalent ideas of the genesis of clay minerals; the "residual clay" and the "transported clay" theories. Hauser (1952, p. 100-106) has emphasized the importance of colloidal phenomena in the genesis of clay minerals. In reality, certain features of the three theories must be invoked to explain the genesis of the clay minerals in the Pennsylvanian shales.

The primary aspect of this question is the chemical and physical conditions of the three environments in which the clay minerals were formed.

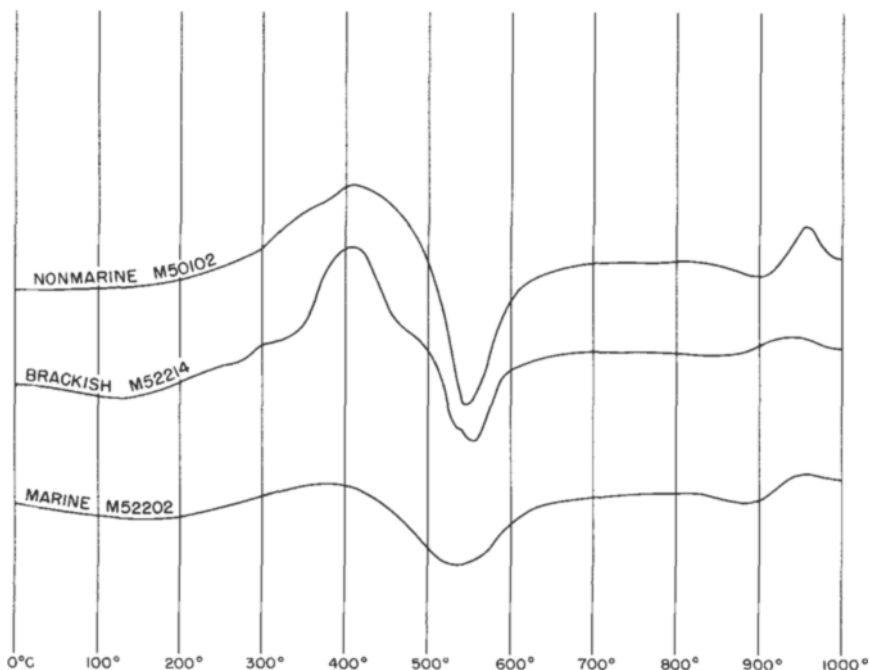


FIGURE 4.—DTA curves of shales from three Pennsylvanian environments.

Nonmarine shales are generally lenticular deposits which grade into shaly sandstone or sandstone. The nonmarine environment was probably characterized by relatively fresh, shallow-water lakes or embayments on the shoreward side of the epicontinental seas which covered the Eastern Interior Basin during Pennsylvanian time. The water probably had a neutral to slightly acidic pH; furthermore, the water in such lakes or embayments remained fresh through current and wave activity, and slightly oxidizing conditions maintained on their bottoms.

The brackish-water environment of Pennsylvanian cyclothems is characterized by dark-gray to black, carbonaceous, locally fossiliferous shales, which are tabular bodies of large areal extent. The waters of this environment were probably quiet, alternately freshening and stagnating owing to stream action and marine inflows and had a pH varying between neutral and acidic, perhaps as low as pH 5 if the organic content of the lagoons was extremely high. Bottom conditions in the brackish-water environment were strongly reducing.

The marine environment of the Pennsylvanian cyclothems is characterized by dense, locally fossiliferous, relatively massive shales, which are geographically widespread. The marine shales probably formed in an environment in which the water was relatively quiet and had a pH of 7.5

to 8. The bottom conditions were probably slightly reducing, as are the present day bottoms of the continental shelves.

Millot (1952, p. 107-114) studied the relations between the environment of deposition and the clay minerals and found that kaolinite was predominant in nonmarine environments and that illite predominated in marine environments. In the Pennsylvanian shales of this study, illite dominates in each environment but its proportion to the other clay minerals increases from nonmarine through the marine environments. The increased ratio of illite to the other clay minerals indicates that the clay minerals in these shales were not entirely detrital, but a relative enrichment of illite is due to the physical and chemical conditions of the environment. Granted that some of the clay minerals in these Pennsylvanian shales are truly detrital, more are probably authigenic. Environmental conditions favored the formation of specific clay minerals; physical and chemical conditions varied, however, in the environments under investigation, as reflected by the variation in the clay mineral ratios.

Authigenic clay minerals are believed to form as a result of two processes. The first and probably the most important is the formation of the clay minerals from a skeletal aluminum silicate sheet structure. The second process involves the growth of the clay minerals from colloids and ions present in the environment. The clay minerals which form in a single environment will be the same whichever process is involved because the physical and chemical conditions of the environment are the controlling factors in each process.

The formation of the specific clay minerals from the skeletal aluminum silicate sheet structure will be discussed first. In crystalline rocks, soils, and sedimentary rocks, weathering processes usually remove the soluble components, the alkalis, and alkaline earths, first. Weathering and transportation break down some crystalline particles to clay size. Some of these particles are clay size or colloidal size aluminum silicate structures from which the soluble ions have been removed. This skeletal aluminum silicate structure has been referred to in the literature as "degraded illite" (Grim, 1953, p. 351) which has an excess negative charge. The structure will utilize certain cations in the structure to build up the clay minerals. Other cations will be adsorbed on the surface of the clay mineral. The physical and chemical conditions of the environment control which cations will be present and thus which clay minerals will form. In the marine environment potassium and magnesium will be taken up by the skeletal aluminum silicate structure to form illite and chlorite respectively.

The ions which are most important in the formation of the clay minerals from the skeletal aluminum silicate structure are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+} . These ions are in true solution in most natural waters. The controlling factor in their deposition is ionic potential (Z/R). Mason (1952, p. 138) stated that the ionic potential of an element determines to a major extent its place of deposition in sedimentary rocks. Elements

having an ionic potential less than 3, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Fe^{2+} , generally remain in solution in natural waters. The hydration of an ion depends on its ionic potential because the greater the charge on the surface of the ion the greater its attraction for hydroxyl groups. Potassium has a very low ionic potential (0.75) and therefore is less hydrated than the other ions, Na, Ca, Mg, and Fe, mentioned above. Consequently, potassium is more readily adsorbed by oppositely charged colloids and other ions having a higher ionic potential. Sodium, a hydrated ion, has an ionic potential of 1.00; therefore, sodium is probably not adsorbed as readily as potassium because the effective ionic radius exceeds that of potassium. The ionic potentials of the other three ions are as follows: Ca^{2+} (1.9); Fe^{2+} (2.4) and Mg^{2+} (2.6); therefore, these ions are most probably highly hydrated. According to the laws of adsorptive capacity of ions proposed by Noll (1931, p. 552), elements which have a high attraction intensity, that is, a low hydration and a high polarizability, will be enriched in argillaceous sediments. Potassium satisfies these requirements and is preferentially adsorbed with regard to Na, Ca, Fe, and Mg.

The second process involves colloids and ions, and a review of the chemical characteristics of the ions or charged colloids which make up the clay minerals is necessary to understand some of the possible reactions which may take place. Roy (1945, p. 393) indicated that silica in natural waters is in true solution, probably as an SiO_3^{2-} ion. Most workers believe that dissolved silica is transported and precipitated as a negatively charged colloid. Aluminum enters into solution at $\text{pH} \ll 4$ and $\text{pH} \gg 9$. Neither of these pH's is common to natural waters; therefore, aluminum must be transported and precipitated as colloidal aluminum hydroxide which carries a positive charge. Ferric hydroxide is precipitated at pH 3 and ferrous hydroxide at pH 7. Ferric hydroxide must be transported and precipitated as a colloid and it can carry either a positive or negative charge, depending on the environment (Mason, 1952, p. 148). Ferrous iron is in ionic solution in an acidic environment and in the colloidal state in a basic environment. Rankama and Sahama (1950, p. 235) state that silica is the most abundant colloid in nature; and, therefore, silica gels deposited in muds and clays cause an excess negative charge which results in the attraction of cations.

Silica is transported in natural waters as a colloid and possibly in true ionic solution. Aluminum is transported as colloidal aluminum hydroxide. These two oppositely charged colloids will be concentrated in depositional basins and flocculate to form a loose colloidal sediment or gel. Potassium and some sodium, calcium, and magnesium ions will be adsorbed by the silica. Clay minerals will form through the ageing of the colloidal gel or mud and only those cations that fit into the clay structure will be retained; the excess silica will form colloidal size quartz, which is present in most argillaceous sediments (Murray and Gravenor, 1953, p. 25).

Grim, Dietz, and Bradley (1949, p. 1785) showed that illite is enriched in Recent sediments of the Pacific Ocean off the California coast. Grim and Johns (1952, personal communication) have shown that stream-transported montmorillonite is transformed to illite and chlorite in a marine environment. The montmorillonite is very poorly crystalline and may represent the first stage in the formation of the clay minerals from silica and alumina colloids.

The physical and chemical factors in the depositional environment control which clay minerals will form. The solubility of silica and alumina are functions of pH because alumina is soluble below pH 4 and above pH 9 and the solubility of silica increases almost linearly with increasing pH. Alkaline waters, therefore, contain relatively more silica than alumina, which promotes the formation of such clay minerals as illite in which the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio is 4:1. In an acidic environment, however, the alumina:silica ratio is significantly lower, and consequently the formation of a clay mineral that has an $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 2:1, such as kaolinite, would be favored. Alkalies and alkaline earths, magnesium excepted, are usually not abundant in a nonmarine environment so that the illite to kaolinite ratio is relatively low. In contrast, alkalies and alkaline earths occur abundantly in a marine environment which results in a relatively high illite to kaolinite ratio. Chlorite is present in about the same proportion in both the marine and nonmarine environments studied so that this mineral is formed in the presence of Mg^{2+} in either environment.

CONCLUSIONS

Chemical analyses of Pennsylvanian shales collected from three different environments showed few variations that could be attributed to environmental factors. Correction factors, such as the subtraction of the percentages of quartz and calcite, may enhance the possibility of obtaining a significant relationship between chemical analyses and environments.

The trace elements V^{3+} , Ba^{2+} , and Sr^{2+} are of variable abundance in the three environments considered. Barium may be partially enriched in illite as a replacement for potassium because barium has a similar ionic size and a low ionization potential.

The average pH value of marine shales is basic but is slightly acidic in the brackish and nonmarine environments.

X-ray studies of the pipette fractions show that the amount of illite increases with decreasing particle size.

Clay mineral analyses by Geiger counter x-ray spectrometer and differential thermal analysis methods reveal that illite is enriched in marine shales.

Some clay minerals in the shales are detrital, but the majority are probably authigenic, as they have formed predominantly from a skeletal aluminum silicate structure and secondarily from silica and alumina colloids. The negatively charged aluminum silicate structure and the colloids

adsorb ions that have a low ionic potential, thereby forming the clay minerals. Potassium has a low ionic potential and, therefore, is readily adsorbed from solution. It must be emphasized that the same clay minerals will form regardless of whether they are derived from the skeletal aluminum silicate structure or from silica and alumina colloids. The physical and chemical factors of the environment determine which clay minerals will form, and consequently illite is enriched in the marine environment.

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DISCUSSION

Charles E. Weaver. — The curve presented indicates that chlorite and kaolinite both decrease from nonmarine to marine environment. Is this curve a total for kaolinite and chlorite or do the curves for both minerals decrease in this manner?

Haydn Murray. — The curve is a total for kaolinite and chlorite but I believe from the x-ray data that kaolinite decreases from the nonmarine to the marine environment while chlorite remains fairly constant in amount in both environments. Owing to the difficulty in detecting kaolinite when chlorite is present, however, the two minerals were combined on the curve.

M. L. Jackson. — How can we assign definite intensity ratios in the absence of a quantitative evaluation of interstratification in "standard materials" and the extensive interstratification in the sample materials? It would seem to me that the x-ray diffraction method is a qualitative and a semiquantitative tool not subject to quantitative interpretations in layer silicates, randomness being what it is along the Z-axis.

Haydn Murray. — Definite intensity ratios are assigned purely on the basis of what appears on the x-ray powder diagram by counting the intensities with a scaler unit. These shales do not have the extensive interstratification of the clay minerals which is prevalent in the recent sediments and in soils. This interstratification was looked for and certainly should be looked for before any attempt is made to assign intensity ratios.

Duncan McConnell. — Although vanadium may be associated with organic matter, and apparently is in petroleum, this element also tends to be associated with phosphate minerals. I should like to inquire whether or not P_2O_5 was determined for these samples.

Furthermore, when dealing with rocks of complex mineral composition, I believe that extreme caution should be used in attempting to reach general geochemical conclusions regarding the association of particular elements with particular minerals. For example, the dark-colored, brackish-water shales may contain one or more phosphate minerals, such as colophane.

Haydn Murray. — P_2O_5 was not determined at the time of the presentation of this paper. It is now being determined and the analyses will appear in a later paper dealing with the geochemistry of some shales.

W. Arthur White. — Did you notice any difference in the crystallinity of the illite from nonmarine and marine environment?

Haydn Murray. — No difference in the crystallinity of the illite from nonmarine and marine was noted.