

Clay Mineralogy of Devonian Shales in the Appalachian Basin

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By JOHN W. HOSTERMAN *and* SALLIE I. WHITLOW

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CLAY MINERALOGY OF DEVONIAN SHALES IN THE APPALACHIAN BASIN

By JOHN W. HOSTERMAN and SALLIE I. WHITLOW

ABSTRACT

A study of the clay mineralogy of Devonian black shales in the Appalachian basin was undertaken to help predict areas of potential gas resources. More than 2,100 samples from 84 drill holes representing 11 shale units were analyzed for clay mineralogy or whole-rock mineralogy or both. Approximately 1,300 samples were from drill cores, and about 800 samples were from drill cuttings. Illite (2M) recrystallized during diagenesis is more or less uniformly present throughout all shale units. Chlorite formed during low-grade metamorphism is least abundant in the younger units and more abundant in the older units. Illite-smectite mixed-layer clay, which supplied the material for the formation of chlorite, is most abundant in the younger units and least abundant in the older units. Illite-chlorite mixed-layer clay occurs in trace amounts in all shale units. Kaolinite, the only unaltered detrital clay mineral, occurs in about 25 to 30 percent of the samples. The source of the kaolinite appears to have been to the east and northeast of the basin of deposition. The color of the shale units is primarily due to organic content; however, for equal amounts of organic carbon, those shales that contain calcite are darker than those that do not.

INTRODUCTION

This report presents mineralogical analyses of 11 Devonian black shale units in the Appalachian basin. More than 2,100 samples from 84 drill holes (pl. 1) were collected and analyzed. Two types of samples were collected, one from drill core and the other from drill cuttings. The samples from drill core were taken at 5-, 10-, 15-, or 20-ft intervals, depending on lithology. The samples from drill cutting represent intervals ranging from 20 to 100 ft. The number of samples taken from each drill hole ranged from 3 to 77, depending on the length of core or cuttings and the sampling interval. Most samples were taken from dark-gray to black shale units, and a few were taken from light-gray silty shale units. Limestone beds were not sampled.

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SAMPLE PREPARATION

Each sample was ground with alcohol in a tungsten-carbide ball mill for 15 to 20 min. A 0.5-g portion of the ground material was pressed, along with 1.5 g of backing material, into a wafer 2 mm thick and 29 mm in diameter. This wafer was placed in an automatic X-ray diffractometer to determine whole-rock mineralogy. The remainder of the ground material was dispersed in deionized water. An ultrasonic horn was then placed in this clay-water mixture for 15 to 20 min. Usually, this treatment dispersed the sample, and flocculation did not occur. If the sample did flocculate, it was placed in a centrifuge and washed with deionized water three or four times. If the sample continued to flocculate after this treatment, a few drops of sodium metaphosphate solution (0.05 g of NaPO_3 dissolved in 1 ml of H_2O) were added to assure dispersal of the sample. The $<2\text{-}\mu\text{m}$ clay fraction, obtained after settling for a given time and to a given depth, was siphoned off and placed on a porous ceramic tile by means of Kinter and Diamond's (1956) vacuum technique.

The samples were analyzed for clay mineralogy on a standard X-ray unit using copper ($\text{CuK}\alpha_1$) radiation and the following optical arrangements: a 1° beam slit, a medium-resolution soller slit, a 0.1° detector slit, a graphite crystal for monochromatic radiation, and a 5° takeoff angle. A goniometer was run at a speed of $1^\circ/2\theta/\text{min}$, and a chart recorder was driven at a speed of 12 in./hr, so that the X-ray diffraction trace was recorded at a rate of $5^\circ/2\theta/\text{in}$. A detector was set on a linear scale of 1,000 counts per second (cps) for full-scale deflection,

and a 2.5-s time constant was used. The resulting X-ray diffraction trace was used to identify and determine the relative abundances of the clay mineral, following Schultz's (1960) method. An electronic planimeter was used to measure selected basal peak areas on the X-ray diffraction traces to obtain the proportions of individual clay minerals.

The samples were analyzed for whole-rock or bulk mineralogy on an automatic X-ray diffractometer using copper radiation and the following optical arrangements: a theta compensating slit, a medium-resolution soller slit, a 0.2-mm receiving slit, a graphite crystal for monochromatic radiation, and a 6° takeoff angle. The goniometer was run at a step-scan speed of 0.5° 2 θ /min; a 1-s time count was made every 0.02° 2 θ . The counts per second were recorded, in digital form, on cassette tapes. The digitized data were transmitted to a computer that compared the data against mineral standards. The minerals were identified and their amounts determined by a computer program using a least-squares method.

Three methods of preparing the clay fraction for X-ray diffraction analysis were tested because it was found that small amounts of kaolinite are difficult to recognize when chlorite is also present. The first method consisted of settling the clay fraction onto a glass slide by using a centrifuge. The second method consisted of settling the clay fraction onto a glass slide by allowing the water to evaporate from the clay-water mixture under room conditions. The third method consisted of placing the clay-water mixture onto a porous ceramic tile and removing the water through the tile by the vacuum method (Kinter and Diamond, 1956). X-ray diffraction traces were made of the top surfaces of all three preparations and of the bottom surfaces (the surface in contact with the support medium) of the first two preparations (methods 1 and 2). An X-ray diffraction trace of the bottom surface of the sample on the porous tile (method 3) could not be made because the sample could not be removed from the tile. However, the following discussion will show that the inability to analyze the bottom surface of the sample by method 3 does not matter.

The three methods result in different mineralogical interpretations (fig. 1). The X-ray diffraction traces of the top surfaces of the samples prepared by methods 1 and 2 (figs. 1A, B) show a single peak at 25° 2 θ , and the intensity of the 9° 2 θ peak is much larger than that of the 12.5° 2 θ peak. The 20.8° 2 θ quartz peak has a low-intensity peak, which indicates that quartz is present in a very minute amount. The X-ray diffraction traces of the bottom surfaces of the samples prepared by methods 1 and 2 (figs. 1D, E) and the top surface of the sample prepared by method 3 (fig. 1C) show a double peak at 25° 2 θ , and the intensities of the 9° 2 θ peak

and the 12.5° 2 θ peak are nearly equal on all three traces. Comparison of the 20.8° 2 θ peak intensities indicates that the quartz on the bottom surfaces is more abundant than that on the top surfaces, a result of differential settling. Another obvious effect of settling seen in methods 1 and 2 is the double peak at 25° 2 θ , which indicates the presence of the (002) peak for kaolinite and the (004) peak for chlorite. Kaolinite, which is coarser grained than chlorite and settles faster than chlorite, is not observed on the top surface. The vacuum method (method 3) of Kinter and Diamond (1956, p. 111) minimizes or eliminates the effects of differential settling.

CLAY MINERALOGY

The clay minerals in Devonian-age shales in the Appalachian basin are illite, chlorite, kaolinite, and two types of mixed-layer clay. X-ray studies by Bates and Strahl (1957) identified illite, kaolinite, and chlorite as the clay minerals in the Chattanooga Shale in Tennessee. All samples analyzed contained considerable illite, some chlorite, and small amounts of mixed-layer clay. Kaolinite is present in about 25 to 30 percent of the samples. The relative amounts of clay minerals in each sample were calculated by using the following techniques. The areas beneath the peaks on the X-ray diffraction traces at 10 Å (8.8° 2 θ), 7 Å (12.6° 2 θ), and 3.5 Å (25° 2 θ) were measured with a planimeter. Proportions of illite and mixed-layer clays are calculated from the area changes of the 10-Å peak. The proportions of chlorite and kaolinite are calculated from a ratio obtained by measuring the areas of the double peak at about 3.5 Å and applying this ratio to the area of 7 Å.

Illite in this report is applied to a dioctahedral muscovite, $(\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)(\text{Mg,Fe})_6\text{O}_{20}$. It contains approximately 12 percent K₂O, 39 percent Al₂O₃, 45 percent SiO₂, and 5 percent H₂O. Illite is the most abundant clay mineral, its relative proportions ranging from 40 to 90 percent. It is recognized on X-ray diffraction traces by a strong first-order basal (001) peak at 10 Å, a weak second-order basal (002) peak at 5 Å, and a strong third-order basal (003) peak at 3.3 Å. Identification of the illite polymorph is difficult because of the presence of other minerals. The 2M polymorph is identified (fig. 2) by the three prism reflections at 3.9, 3.7, and 3.5 Å between 22° and 26° 2 θ . Undoubtedly, 1M and Md polymorphs are also present in varying amounts, but there are no definitive peaks for positive identification. Only the material at the 10-Å position that does not expand when it is treated with ethylene glycol (HOCH₂CH₂OH) is considered illite. The material that expands when it is treated with ethylene glycol

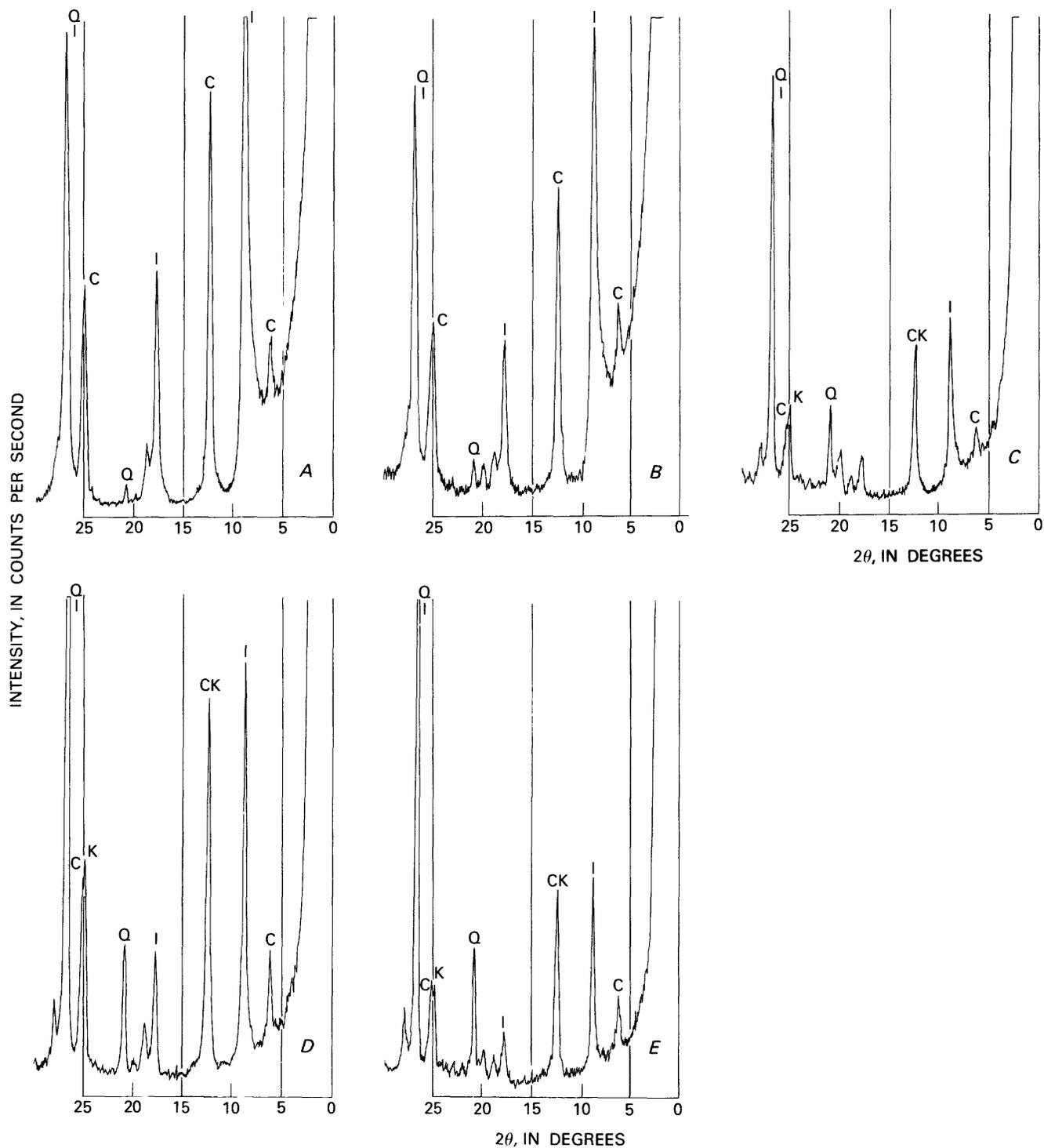


FIGURE 1.—X-ray diffraction traces of one sample prepared by three different methods. The sample is from drill hole 57 (API No. 47-035-21369) in Jackson County, W. Va., at a depth of 3,489 ft. C is chlorite, I is illite, K is kaolinite, and Q is quartz. A, Top surface of settled sample; water removed by centrifuge. B, Top surface of settled sample; water removed by evaporation. C, Top surface of sample on porous ceramic tile; water removed by vacuum. D, Bottom surface of A. E, Bottom surface of B.

and (or) collapses when it is heated to 350 °C is mixed-layer clay.

Mixed-layer clay minerals result from the random interlayering of two or more clay minerals. Illite is one of the major constituents. Two types of mixed-layer clay minerals are present in Devonian black shales. One type, produced by the random interlayering of illite and an expandable mineral such as smectite, is called illite-smectite mixed-layer clay throughout this report. The second type, composed of a random mixture of illite and either a degraded chlorite or a vermiculite, is called illite-chlorite mixed-layer clay throughout this report. Mixed-layer clay minerals are identified by comparing the 10-Å peak area measurements on the X-ray diffraction traces of the clay fractions that have been run untreated, after ethylene glycol saturation and after heating to 350 °C for a minimum of 30 min. Ethylene glycol saturation expands the smectite layers and leaves illite as the only mineral represented by the 10-Å peak area. Therefore, the 10-Å peak area of the untreated sample represents illite and illite-smectite mixed-layer clay. Heating to 350 °C collapses the expandable layers and the vermiculite-type layers to the 10-Å position; therefore, the 10-Å peak area, after heating, represents illite and both types of mixed-layer clay minerals. An estimate can be made, on the basis of area measurement, of the relative proportions of illite, illite-smectite mixed-layer clay, and illite-chlorite mixed-layer clay minerals.

Chlorite $(\text{OH})_8(\text{SiAl})_4(\text{MgFe}_3)(\text{MgAl})_3\text{O}_{10}$ is present in almost all of the Devonian shale samples analyzed for this report. Its average chemical content is 14 percent MgO, 27 percent Fe_2O_3 , 17 percent Al_2O_3 , 30 percent SiO_2 , and 12 percent H_2O . Chlorites in Devonian shales range from a magnesium variety to an iron variety. Chlorite is recognized on the X-ray diffraction trace by its moderate (magnesium) to weak (iron) first-order basal (001) peak at 14 Å, its strong second-order basal (002) peak at 7 Å, its moderate (magnesium) to weak (iron) third-order basal (003) peak at 4.7 Å, and its weak (magnesium) to moderate (iron) fourth-order basal (004) peak at approximately 3.5 Å. Chlorite is not affected by ethylene glycol saturation or heating to 350 °C. Heating to 550 °C, however, produces an increase in the first-order basal (001) peak at 14 Å and a decrease in the second-, third-, and fourth-order basal peaks. Fine-grained chlorite decomposes in warm hydrochloric acid (Brindley, 1961, p. 264), but it may be necessary to keep the temperature at about 80 °C for 16 to 20 hr to achieve complete decomposition, especially if the chlorite is well ordered. The relative chlorite composition in Devonian shales ranges from 0 to 30 percent, the average being between 10 and 15 percent.

Kaolinite $(\text{OH})_2\text{Si}_2\text{Al}_2\text{O}_5$ is the least abundant clay mineral in the Devonian shale samples analyzed. It

contains approximately 40 percent Al_2O_3 , 46 percent SiO_2 , and 14 percent H_2O . Kaolinite is recognized on the X-ray diffraction trace by its strong basal (001) peak at 7 Å and its moderate basal (002) peak at 3.5 Å. Kaolinite is not affected by ethylene glycol saturation or by heating to 350 °C for a minimum of 30 min. Heating kaolinite to about 550 °C destroys its crystalline form; however, the exact temperature at which this destruction takes place is dependent upon the grain size and the degree of crystallinity of the kaolinite. Kaolinite is more immune to attack by warm dilute acids than most other clay minerals, including chlorite, are; however, dissolution rates also vary considerably with grain size and degree of crystallinity. Kaolinite occurs in about 30 percent of the Devonian shale samples analyzed in relative proportions up to a maximum of 20 percent.

The presence of kaolinite in small amounts is extremely difficult to determine when chlorite is present. A slight difference in the *c*-axis dimension of the two minerals is expressed as a doublet at 3.50 Å for the second-order basal (002) peak of kaolinite and at 3.57 Å for the fourth-order (004) peak of chlorite. We depended upon this doublet (at about 25° 2θ) for recognizing the existence of kaolinite because neither heating nor acid treatment can remove one mineral without affecting the other.

NONCLAY MINERALOGY

Minerals other than clay minerals include allogenic minerals that were introduced during deposition of the clay, authigenic minerals that were formed at the time of or shortly after deposition of the clay, and fossil material. The allogenic minerals are quartz, K-feldspar, plagioclase, and biotite. The authigenic minerals are calcite, dolomite, siderite, gypsum, pyrite, marcasite, barite, and traces of galena and chalcopyrite. Minerals derived from fossil material are calcite, dolomite, and apatite. Quartz is present in all shale samples analyzed, and pyrite is present in most samples, especially those high in organic matter. Calcite is present in almost all shales sampled from Pennsylvania and New York. All of the other nonclay minerals, both allogenic and authigenic, occur in very minor amounts throughout the Appalachian basin.

COLOR VALUES AS RELATED TO ORGANIC CONTENT

To investigate the possibility of a relationship between color and organic carbon content, we determined the color of each whole sample by visually comparing the Munsell soil color charts (Munsell Color Company,

1954) with dry pressed-powder wafers. The Munsell color designation is composed of hue (color), value (lightness), and chroma (saturation). A neutral (N) color has no hue or chroma but does have value. The value ranges from 0 (black) to 10 (white) for neutral colors and from 1 to 9 for colors having hue and saturation. Values from both neutral colors and other colors were plotted against the organic carbon content to determine if there is any relationship.

All color determinations were made under similar lighting conditions. The chroma was estimated to the nearest 0.25, and the value was estimated to the nearest 0.1. The color value did not change more than 0.1 when a comparison was made between the whole-rock colors of a shale sample before laboratory preparation and after. The color value for a moist whole-rock sample was consistently about 2.0 lower than that for the dry whole-rock sample. Any human error in determining the color value could be eliminated by using a colorimeter.

Organic carbon refers to the disseminated carbonaceous material derived from both plant and animal organisms. Organic carbon was determined by one of two methods. In the first method, organic carbon is the difference between total carbon, measured by high-temperature combustion, and carbonate carbon, measured by titration (Leventhal, 1979). In the second method, organic carbon is measured directly by a wet oxidation technique (G. E. Claypool and C. N. Threkeld, written commun., 1979). The results of both methods are reported in weight percent (Claypool and others, 1980; Claypool and Stone, 1979).

We compared color value to organic carbon in approximately 880 samples from 50 drill holes throughout New York, Pennsylvania, Ohio, West Virginia, Virginia, Kentucky, and Tennessee. In samples from all but two drill holes, where data are incomplete, an excellent relationship represented by a power-curve regression exists between color value and organic carbon content. A color value of 3.0 to 3.5 or less does indicate that organic carbon is present in concentrations of greater than 7 percent, but it is meaningless in determining organic carbon content accurately because a large increase in the amount of organic carbon results in only a small change in the color value. The correlation coefficients (r) for 48 drill holes ranged from 0.81 to 1.00. However, the spread of color value between drill holes was greater than the excellent individual correlations had led us to expect. This large spread in the color value indicated that there is probably another control in addition to organic carbon content.

The mineralogy of all 880 samples was carefully studied, and we determined that calcite was the only mineral that had any effect on the color value. Calcite

is present in trace amounts throughout most of the Appalachian basin, except in New York and Pennsylvania, where it occurs in amounts of up to 40 percent. The color value at 1.0 percent organic carbon (Schmoker, 1980) ranges from 4.0 to 5.5 for the shales deposited in a high-calcium environment and from 4.8 to 6.1 for the shales deposited in a low- or no-calcium environment. Figure 3 shows the best power-curve fit for 757 samples that contain calcite and for 123 samples that contain only a trace of calcite. The two curves indicate that the average black shales, without calcite, contain more than 1.0 percent organic carbon when the color value is 5.4 or less. The average calcareous black shale, with more than 5 percent calcite, contains more than 1.0 percent organic carbon when the color value is 4.7 or less.

We assume that the influence of calcium on clay minerals during deposition causes the difference in the color values of shale containing calcite and shale that does not contain calcite. All clay minerals are capable of sorbing and retaining anions and cations in an exchangeable state. In a calcium-rich environment, clay minerals adsorb the calcium ions easily and also flocculate readily (Grim, 1968, p. 358). Because calcium ions have strong bonds, more than a stoichiometric amount of organic carbon is needed if the calcium ions are to be replaced by organic carbon. Flocculation of clay minerals, which causes rapid deposition, also prevents interaction with the organic carbon. These two factors leave the organic material free to settle as discrete grains. Conversely, in a calcium-free environment, clay minerals adsorb the organic material instead of calcium ions (McAtee, 1959), and there is no tendency for the clay minerals to flocculate. If the organic matter in shales containing equal amounts of organic carbon is adsorbed by the clay minerals, the color is light because of dilution; if the organic material is free, the color is dark.

MINERALOGY OF THE DEVONIAN SHALES

We determined the clay mineralogy and whole-rock mineralogy of about 2,100 samples from more than 84 drill holes throughout the Appalachian basin. The following shale units were analyzed and will be discussed together in groups because they can be correlated (fig. 4, as modified from Oliver and others (1969)):

- Cleveland Member of Ohio Shale
- Upper unit of Gassaway Member of Chattanooga Shale
- Chagrin Shale
- Three Lick Bed of Ohio Shale
- Middle unit of Gassaway Member of Chattanooga Shale

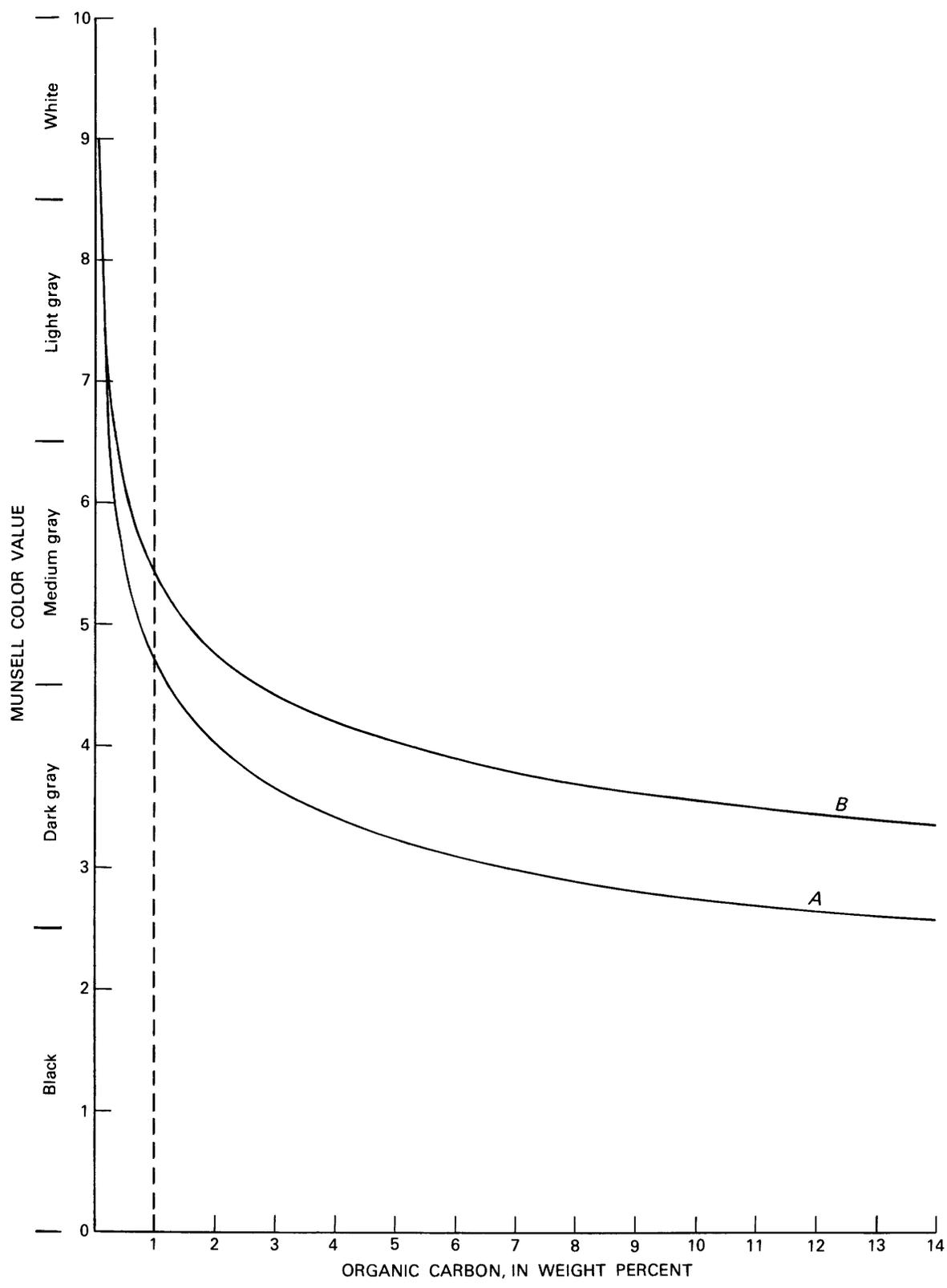


FIGURE 3.—Munsell color value and organic carbon in Devonian-age shale of the Appalachian basin. Curve A is the average of 757 samples of shale containing more than 5 percent calcite. Curve B is the average of 123 samples of shale containing no more than a trace of calcite.

Age	Central and eastern Tennessee and south-central Kentucky	Eastern Ohio northeastern Kentucky and western West Virginia	Western New York and northwestern Pennsylvania	Central Pennsylvania, central West Virginia, and western Virginia			
UPPER DEVONIAN	Chattanooga Shale Gasaway Member Upper unit Middle unit Lower unit	Cleveland Member Three Lick Bed Huron Member Upper unit Middle unit Lower unit Chagrin Shale	Upper Devonian siltstone, sandstone, and shale: several units Dunkirk Shale Member of Perrysburg Formation Hanover Shale Member Pipe Creek Shale Member ? Angola Shale Member Rhinestreet Shale Member Cashaqua Shale Member Middlesex Shale Member West River Shale Member Penn Yan Shale Member Genesee Shale Member Tully Limestone	Brallier Formation gray shale Harrell Shale Burkett Shale Member Mahantango Formation Marcellus Shale Huntersville Chert Oriskany Sandstone			
					Upper unit Lower unit	Java Formation West Falls Formation Sonyea Formation Genesee Formation	Harrell Shale Mahantango Formation Marcellus Shale Huntersville Chert Oriskany Sandstone
					Ohio Shale Olentangy Shale	Dunkirk Shale Member of Perrysburg Formation Hanover Shale Member Pipe Creek Shale Member ? Angola Shale Member Rhinestreet Shale Member Cashaqua Shale Member Middlesex Shale Member West River Shale Member Penn Yan Shale Member Genesee Shale Member Tully Limestone	Harrell Shale Burkett Shale Member Mahantango Formation Marcellus Shale Huntersville Chert Oriskany Sandstone
	MIDDLE DEVONIAN	Diagonal lines (Erosional) Diagonal lines (Hiatus)	Olentangy Shale Tioga Ash Bed	Hamilton Group Moscow Formation Ludlowville Formation Skaneateles Formation Marcellus Formation Onondaga Limestone Needmore Shale Oriskany Sandstone	Harrell Shale Burkett Shale Member Mahantango Formation Marcellus Shale Huntersville Chert Oriskany Sandstone		
						Olentangy Shale Tioga Ash Bed	Hamilton Group Moscow Formation Ludlowville Formation Skaneateles Formation Marcellus Formation Onondaga Limestone Needmore Shale Oriskany Sandstone

FIGURE 4.—Generalized correlation of Devonian shale units studied for clay mineralogy (modified from Oliver and others, 1969).

Upper unit of the Huron Member of Ohio Shale

Middle unit of the Huron Member of Ohio Shale

Lower unit of the Huron Member of Ohio Shale
Dunkirk Shale Member of Perrysburg Formation
Lower unit of Gassaway Member of Chattanooga
Shale

Hanover Shale Member of Java Formation
Pipe Creek Shale Member of Java Formation
Upper unit of Dowelltown Member of Chattanooga
Shale

Rhinestreet Shale Member of West Falls Formation
Lower unit of Dowelltown Member of Chattanooga
Shale

Middlesex Shale Member of Sonyea Formation

Penn Yan Shale Member of Genesee Formation
Genesee Shale Member of Genesee Formation
Burket Black Shale Member of Harrell Shale

Mahantango Formation of Hamilton Group
Millboro Shale (excluding "Marcellus Member")

Marcellus Shale of Hamilton Group
"Marcellus Member" of Millboro Shale

The regional subsurface correlations are based on gamma-ray log interpretations by Roen (1980). These units contain the black shale beds that have proven to be the best sources of natural gas in the Appalachian basin (Bagnall and Ryan, 1976; Patchen, 1977).

CLEVELAND MEMBER OF THE OHIO SHALE

The Cleveland Member of the Ohio Shale and the upper unit of the Gassaway Member of the Chattanooga Shale are correlative (Conant and Swanson, 1961, p. 20; Roen, 1980, fig. 6). We analyzed 73 samples from 20 drill holes in Alabama, Tennessee, Kentucky, Virginia, and Ohio (fig. 5). The dark-gray (10 YR 4.1/2) Cleveland Member and its equivalent have an average composition of 30 percent quartz silt, 65 percent clay, and 5 percent pyrite. Illite is the most abundant clay mineral at 60 percent; illite-smectite mixed-layer clay is at 30 percent, and chlorite is at 10 percent (table 1). The illite-chlorite mixed-layer clay mineral averages about a trace and is found in samples from drill holes Nos. 66, 69, 76, 80, and 83. A trace of kaolinite occurs in samples from drill holes Nos. 66, 72, 74, and 75 in the eastern part of the basin.

CHAGRIN SHALE

The Chagrin Shale and its equivalent, the middle unit of the Gassaway Member of the Chattanooga Shale (Roen, 1980), were sampled from 10 drill holes in Tennessee, West Virginia, and Ohio (fig. 6). The average composition from 131 samples of the shale is 25 percent quartz silt, 75 percent clay, and a trace of pyrite. The average color of the shale is medium gray (N 6.1), although a few light brownish-gray (10 YR 6/5) and bluish-gray (5 B 6/5) beds are present. The average proportion of clay minerals is 15 percent chlorite, 55 percent illite, 25 percent illite-smectite mixed-layer clay, 5 percent kaolinite, and a trace of illite-chlorite mixed-layer clay (table 1). Kaolinite was found in samples from the northern drill holes (Nos. 44, 45, 48, 49, 52, and 54 in Ohio and No. 61 in West Virginia). The illite-chlorite mixed-layer clay is limited to samples from drill holes Nos. 80 and 81 in Tennessee and No. 61 in West Virginia.

HURON MEMBER OF THE OHIO SHALE

UPPER UNIT

Sixty-six samples from the upper unit of the Huron Member of the Ohio Shale from 12 drill holes in Tennessee, Kentucky, Virginia, and Ohio (fig. 7) were analyzed. The medium-gray (10 YR 5.2/5) shale in the upper unit of the Huron Member has an average composition of 25 percent quartz silt, 70 percent clay, and 5 percent pyrite. The clay minerals average 10 percent chlorite, 55 percent illite, 30 percent illite-smectite mixed-layer clay, 5 percent kaolinite, and a trace of illite-chlorite mixed-layer clay (table 1). Kaolinite is widespread throughout the upper unit of the Huron Member and was identified in samples from all drill holes except Nos. 69, 70, and 71 (fig. 7). A trace of illite-chlorite mixed-layer clay was identified in samples from drill hole Nos. 46, 50, 66, and 69.

MIDDLE UNIT

We analyzed 178 samples from the middle unit of the Huron Member of the Ohio Shale from 18 drill holes in Tennessee, Kentucky, Virginia, West Virginia, and Ohio (fig. 8). The shale in the middle unit of the Huron Member has an average composition of 25 percent quartz silt, 75 percent clay, and a trace of pyrite. Its medium-gray (N 5.5) color distinguishes it from the slightly darker upper and lower units. The clay minerals average 10 percent chlorite, 60 percent illite, 5 percent kaolinite, 25 percent illite-smectite mixed-layer clay, and a trace of illite-chlorite mixed-layer clay (table 1). Kaolinite is found in samples from 10 holes (Nos. 53, 54, 57, 58, 60, 61, 62, 72, 73, and 74) in

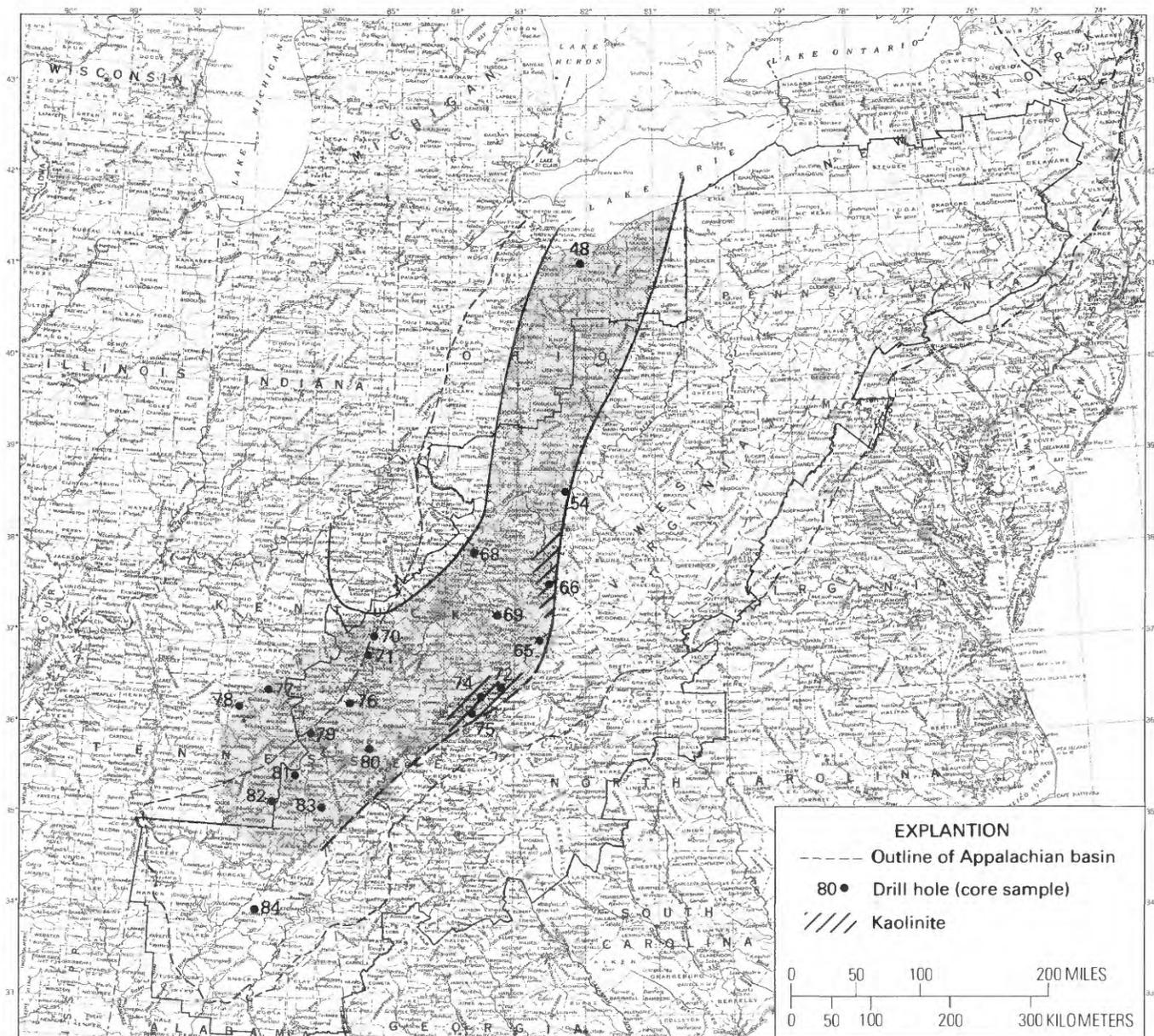


FIGURE 5.—Areal extent (shaded area) of the Cleveland Member of the Ohio Shale and the upper unit of the Gassaway Member of the Chattanooga Shale.

the eastern and southeastern parts of the area. The illite-chlorite mixed-layer clay is concentrated in samples from seven drill holes (Nos. 53, 57, 58, 60, 61, 66, and 69) that are located in the central part of the area.

LOWER UNIT

The lower unit of the Huron Member of the Ohio Shale is correlated with the Dunkirk Shale Member of the Perrysburg Formation and the lower unit of the Gassaway Member of the Chattanooga Shale (Roen, 1980, fig. 5; Conant and Swanson, 1961, p. 20). The

lower unit of the Huron Member and its equivalents consist of medium-gray (10 YR 4.9/5) shale beds having the darkest color of the Huron Member. About 358 samples from 38 drill holes in New York, Ohio, West Virginia, Virginia, Kentucky, and Tennessee (fig. 9) have an average composition of 25 percent quartz silt, 70 percent clay, and 5 percent pyrite. Clay minerals occur in the following proportions: 15 percent chlorite, 60 percent illite, 20 percent illite-smectite mixed-layer clay, 5 percent kaolinite, and a trace of illite-chlorite mixed-layer clay (table 1). The illite-chlorite mixed-layer clay is found in samples from 12 drill holes (Nos. 53, 57, 58, 59, 60, 61, 66, 69, 76, 80, 81, and 83) located

TABLE 1.—Average color and mineralogy of 11 Middle and Upper Devonian shale units in the Appalachian basin
 [—, not present; tr, present in trace amounts]

Unit	No. of drill holes	No. of samples	Total footage sampled	Average Munsell color	Average lithology	Average mineral content (in percent)						Clay mineral content (in percent)				
						Quartz silt	Clay	Pyrite	Calcite	Chlorite	Illite	Mixed-layer clay				
												Illite-smectite	Illite-chlorite	Kaolinite		
Cleveland Member of Ohio Shale and equivalent units.	20	73	574	10 YR 4.1/2	Silty shale	30	65	5	—	10	60	30	tr	tr	tr	tr
Chagrin Shale and equivalent units.	10	131	2,984	N 6.1	Shale	25	75	tr	tr	15	55	25	tr	tr	tr	5
Upper unit of Huron Member of Ohio Shale.	12	66	764	10 YR 5.2/5	-----do.	25	70	5	—	10	55	30	tr	tr	tr	5
Middle unit of Huron Member of Ohio Shale.	18	178	4,602	N 5.5	-----do.	25	75	tr	—	10	60	25	tr	tr	tr	5
Lower unit of Huron Member of Ohio Shale and equivalent units.	38	358	5,254	10 YR 4.9/5	-----do.	25	70	5	—	15	60	20	tr	tr	tr	5
Java Formation and equivalent units.	26	77	1,264	N 6.0	-----do.	25	70	5	tr	20	55	25	tr	tr	tr	tr
Rhinestreet Shale Member of West Falls Formation and equivalent units.	37	189	6,292	10 YR 5.3/5	-----do.	25	75	tr	tr	20	60	20	tr	tr	tr	tr
Middlesex Shale Member of Sonyea Formation.	17	26	1,180	10 YR 4.4/5	-----do.	25	65	5	5	25	55	20	tr	tr	tr	—
Genesee Formation and equivalent units.	29	64	2,290	10 YR 4.5/5	Slightly limy shale	20	60	5	15	25	60	15	tr	tr	tr	—
Mahantango Formation of Hamilton Group and equivalent units.	50	444	14,527	N 5.2	Limy shale	20	60	tr	20	25	60	15	tr	tr	tr	—
Marcellus Shale of Hamilton Group and equivalent units.	48	189	4,952	N 3.4	-----do.	20	50	5	25	15	70	15	tr	tr	tr	—

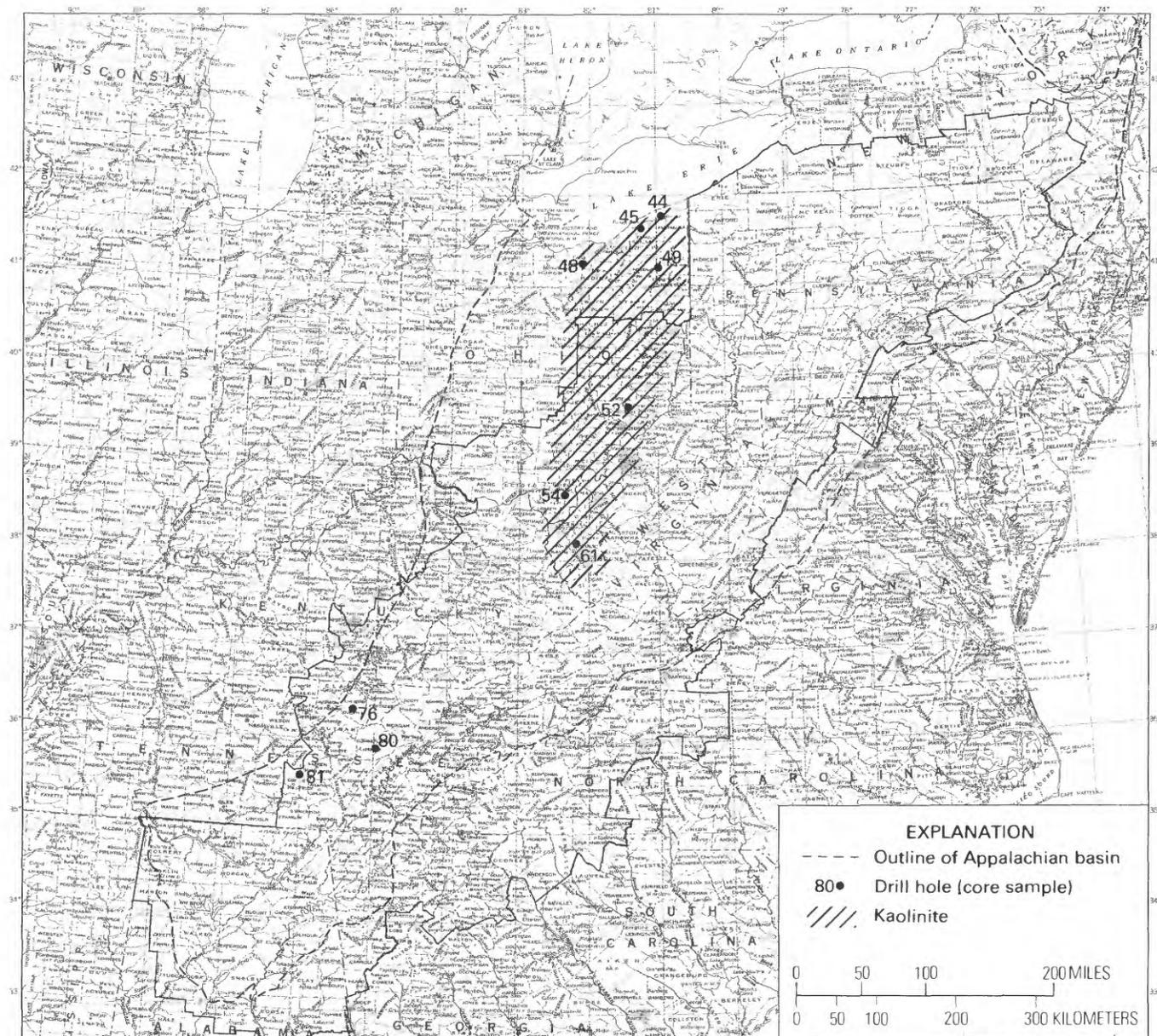


FIGURE 6.—Drill holes from which samples of the Chagrin Shale and the middle unit of the Gassaway Member of the Chattanooga Shale were taken.

near the central portion of the basin near the southern end. Kaolinite was identified in samples from 17 drill holes located on the east and northeast of the area (fig. 9).

JAVA FORMATION

The shale units in the Java Formation—the Hanover Shale Member and the Pipe Creek Shale Member—are correlated with the upper unit of the Dowelltown Member of the Chattanooga Shale (Roen, 1980, fig. 5). Seventy-seven samples of the Java Formation or its

equivalent in 26 drill holes from New York, Ohio, West Virginia, Kentucky, and Tennessee (fig. 10) were analyzed. These medium-gray (N 6.0) shale units have an average composition of 25 percent quartz silt, 70 percent clay, and 5 percent pyrite. There is a trace of calcite in the Java Formation of New York and northern Ohio and a trace of dolomite in the upper unit of the Dowelltown Member of Tennessee. Clay minerals have the following proportions: 20 percent chlorite, 55 percent illite, 25 percent illite-smectite mixed-layer clay, a trace of illite-chlorite mixed-layer clay, and a trace of kaolinite (table 1). The illite-chlorite mixed-

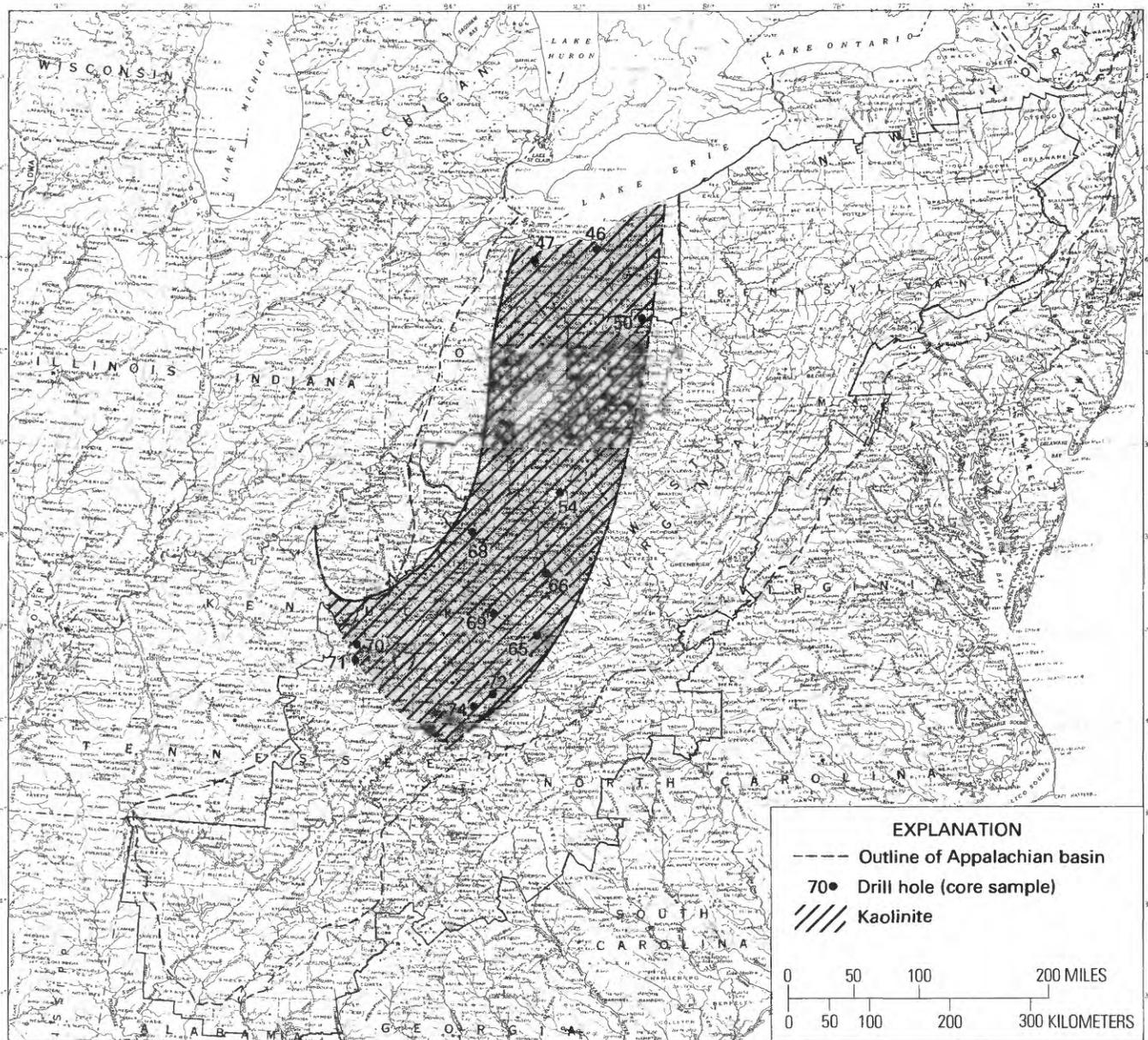


FIGURE 7.—Areal extent (shaded area) of the upper unit of the Huron Member of the Ohio Shale.

layer clay was found in samples from five drill holes (Nos. 58, 59, 61, 66, and 76) near the central part of the southern portion of the basin. Kaolinite was identified in samples from 10 drill holes (Nos. 15, 18, 19, 49, 52, 59, 62, 64, 72, and 74) in the eastern edge of the area.

At the base of the Java Formation is the Pipe Creek Shale Member. This dark-gray (10 YR 3/5) unit is darker in color than most beds in the Java Formation. The Pipe Creek Shale Member is generally less than 20 ft thick and is an excellent marker between the Java Formation and the underlying West Falls Formation.

RHINESTREET SHALE MEMBER OF THE WEST FALLS FORMATION

We analyzed 189 samples from the Rhinestreet Shale Member of the West Falls Formation and its stratigraphic equivalent, the lower unit of the Dowelltown Member of the Chattanooga Shale (Roen, 1980, fig. 5) from 37 drill holes in New York, Pennsylvania, Ohio, West Virginia, Kentucky, and Tennessee (fig. 11). The Rhinestreet Shale Member is a medium-gray (10 YR 5.3/5) shale. It has an average composition of 25 percent quartz silt, 75 percent clay, and a trace of pyrite.

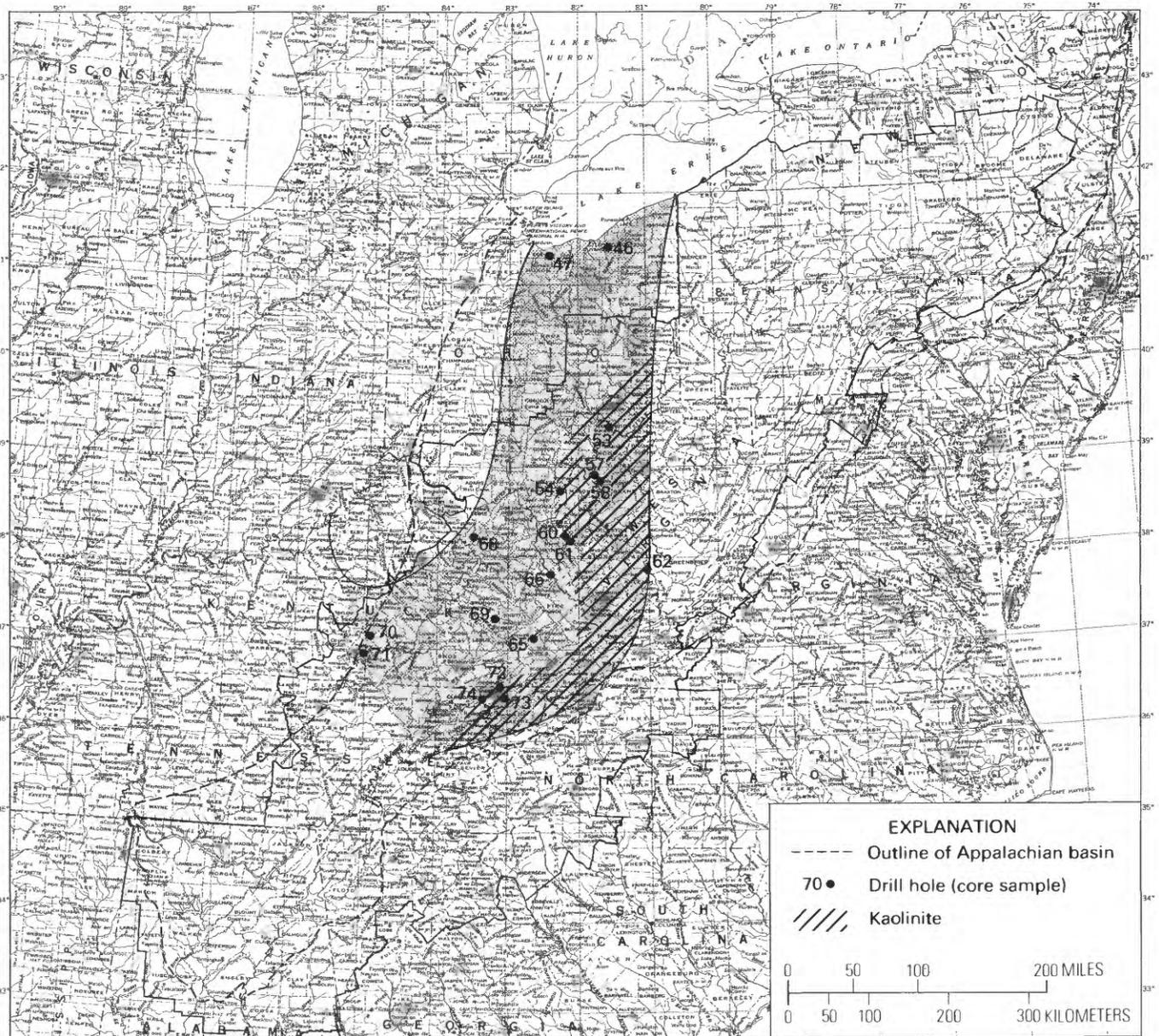


FIGURE 8.—Areal extent of the middle unit of the Huron Member of the Ohio Shale.

The lower unit of the Dowelltown Member contains 5 percent dolomite in central Tennessee. The Rhine-street Shale Member has a trace of calcite in Kentucky, West Virginia, Ohio, Pennsylvania, and New York (table 1). The clay minerals have average proportions of 20 percent chlorite, 60 percent illite, 20 percent illite-smectite mixed-layer clay, a trace of illite-chlorite mixed-layer clay, and a trace of kaolinite (table 1). Illite-chlorite mixed-layer clay was found in samples from 10 drill holes (Nos. 13, 50, 59, 60, 61, 66, 69, 72, 76, and 81) located throughout the central part of the basin. Kaolinite has been identified in samples from

four drill holes (Nos. 12, 15, 18, and 59) located on the eastern edge of the area (fig. 11).

MIDDLESEX SHALE MEMBER OF SONYEA FORMATION

The Middlesex Shale Member of the Sonyea Formation was analyzed in 26 samples from 17 drill holes in New York, Pennsylvania, and West Virginia (fig. 12). The Middlesex Shale Member is a dark-gray (10 YR 4.4/5) shale having an average composition of 25 percent quartz silt, 65 percent clay, 5 percent pyrite, and 5 percent calcite. The clay minerals have average proportions of 25 percent chlorite, 55 percent illite, 20 per-

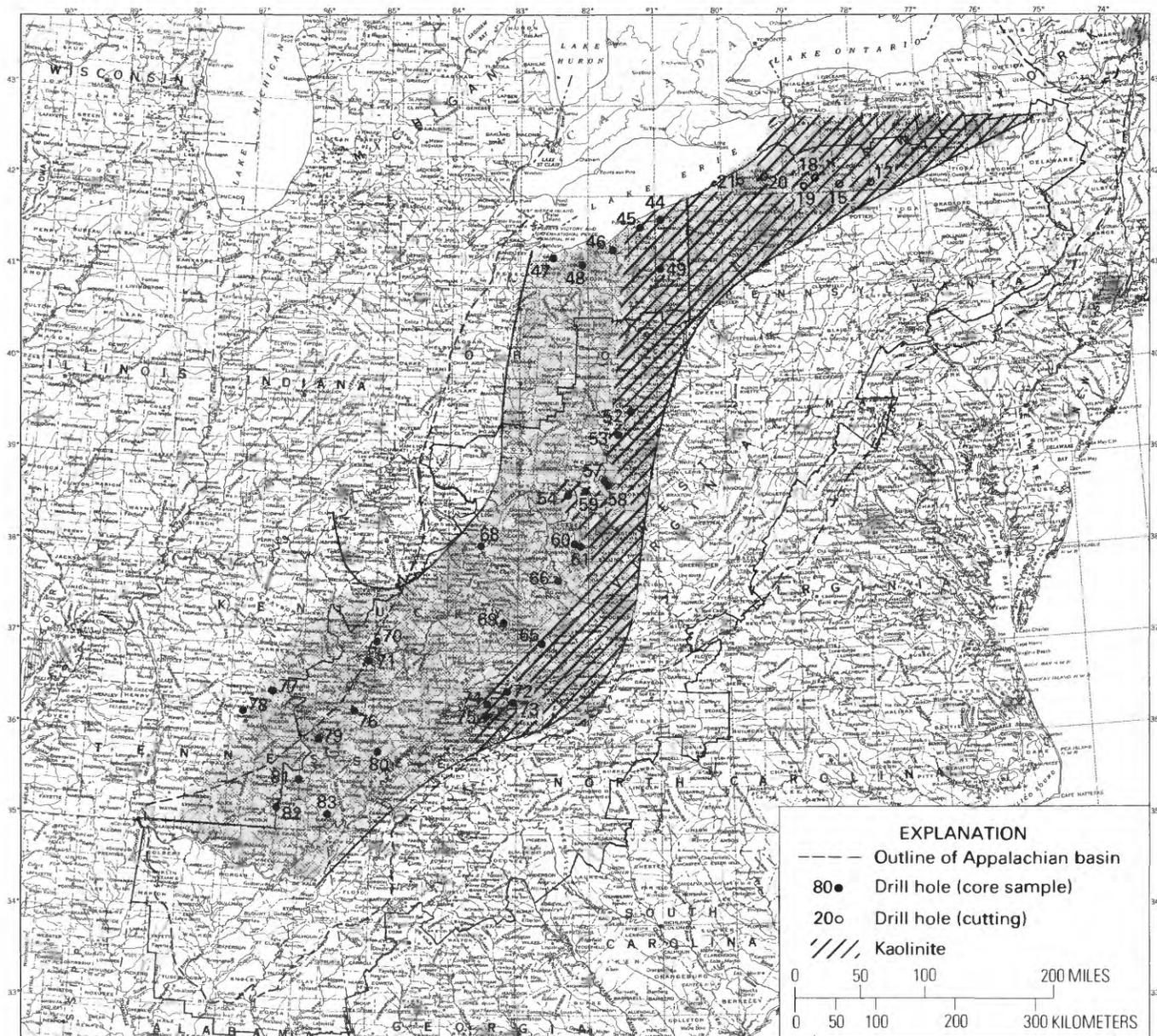


FIGURE 9.—Areal extent (shaded area) of the lower unit of the Huron Member of the Ohio Shale, the Dunkirk Shale Member of the Perrysburg Formation, and the lower unit of the Gassaway Member of the Chattanooga Shale.

cent illite-smectite mixed-layer clay, and a trace of illite-chlorite mixed-layer clay (table 1). Illite-chlorite mixed-layer clay occurs in samples from three drill holes (Nos. 11, 31, and 37) in the north-central part of the basin. Kaolinite was not identified in any samples from the Middlesex Shale Member. Calcite was found in samples from eight drill holes (Nos. 11, 15, 18, 19, 23, 31, 37, and 40) in the center of the basin.

GENESEO SHALE MEMBER OF THE GENESEEE FORMATION

Included with the Geneseo Shale Member of the Genesee Formation are the Penn Yan Shale Member of

the Genesee Formation and the Burket Black Shale Member of the Harrell Shale (Oliver and others, 1969). These units are dark gray (10 YR 4.5/.5) and are composed of slightly limy shale that averages 20 percent quartz silt, 60 percent clay, 5 percent pyrite, and 15 percent calcite. Sixty-four samples from 29 drill holes in New York, Pennsylvania, and West Virginia (fig. 13) show that the clay minerals in the Genesee Shale Member and its equivalent have average proportions of 25 percent chlorite, 60 percent illite, 15 percent illite-smectite mixed-layer clay, and a trace of illite-chlorite mixed-layer clay (table 1). The illite-smectite

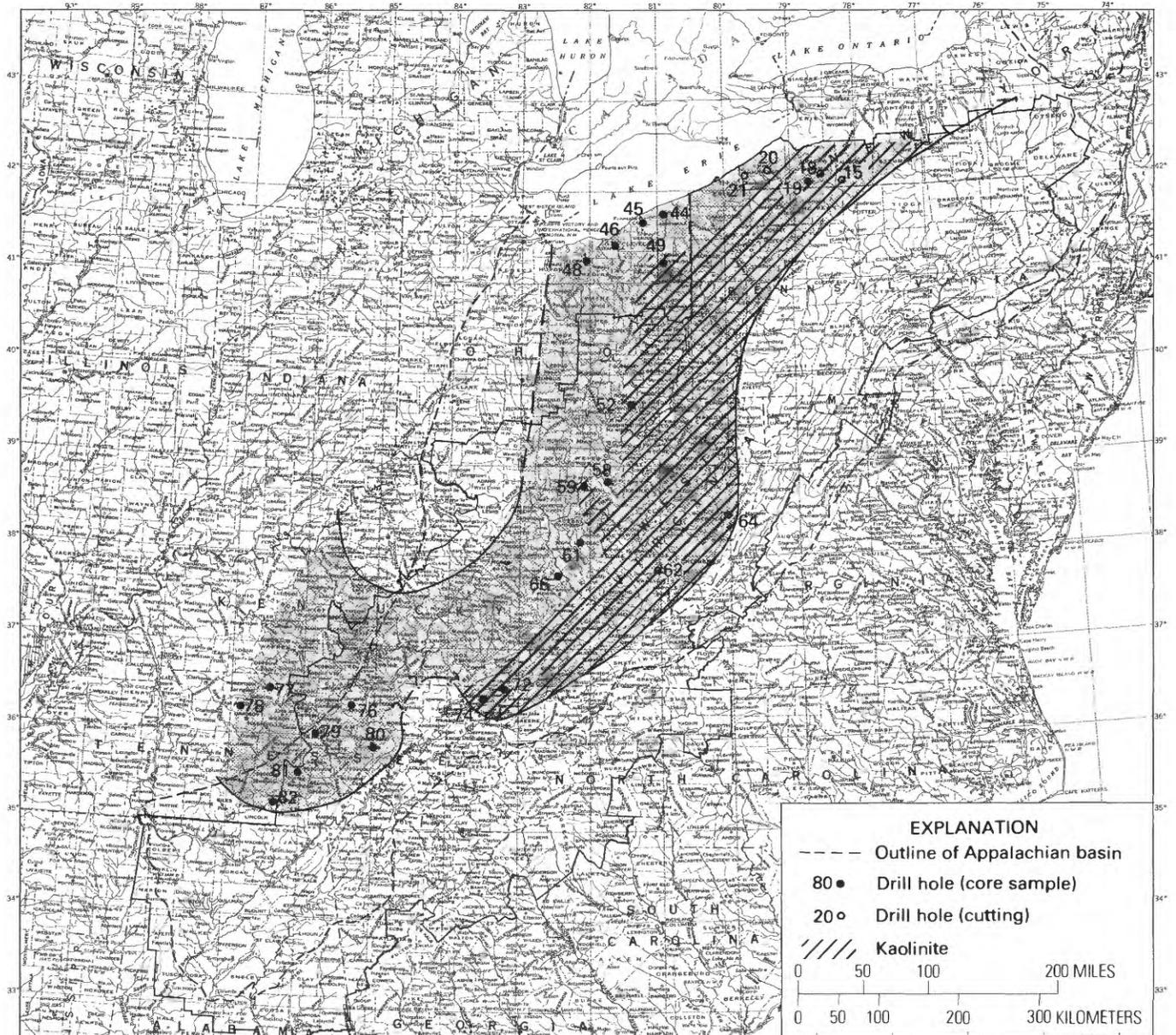


FIGURE 10.—Areal extent (shaded area) of the Hanover Shale and Pipe Creek Shale Members of the Java Formation and the upper unit of the Dowelltown Member of the Chattanooga Shale.

mixed-layer clay was found in samples from four drill holes (Nos. 12, 16, 18, and 36).

MAHANTANGO FORMATION OF THE HAMILTON GROUP

The Mahantango Formation correlates with all formations in the Hamilton Group exclusive of the Marcellus Formation. It also includes the Millboro Shale exclusive of the "Marcellus Member." The Mahantango is a medium-gray (N 5.2) limy shale. The average composition determined from 444 samples of the Mahantango Formation from 50 drill holes in New York, Pennsylvania, Ohio, West Virginia, and Virginia

(fig. 14) is 20 percent quartz silt, 60 percent illite, a trace of pyrite, and 20 percent calcite. Clay minerals occur in proportions of 25 percent chlorite, 60 percent illite, 15 percent illite-smectite mixed-layer clay, and a trace of illite-chlorite mixed-layer clay (table 1). Illite-chlorite mixed-layer clay is found in samples from seven drill holes (Nos. 16, 18, 22, 24, 31, 37, and 39) distributed randomly in New York and Pennsylvania. Calcite is absent in eastern Pennsylvania and eastern New York but increases to 40 percent in western New York, northwestern Pennsylvania, and in the panhandle of West Virginia (fig. 14). Calcite data for most of Ohio are not available.

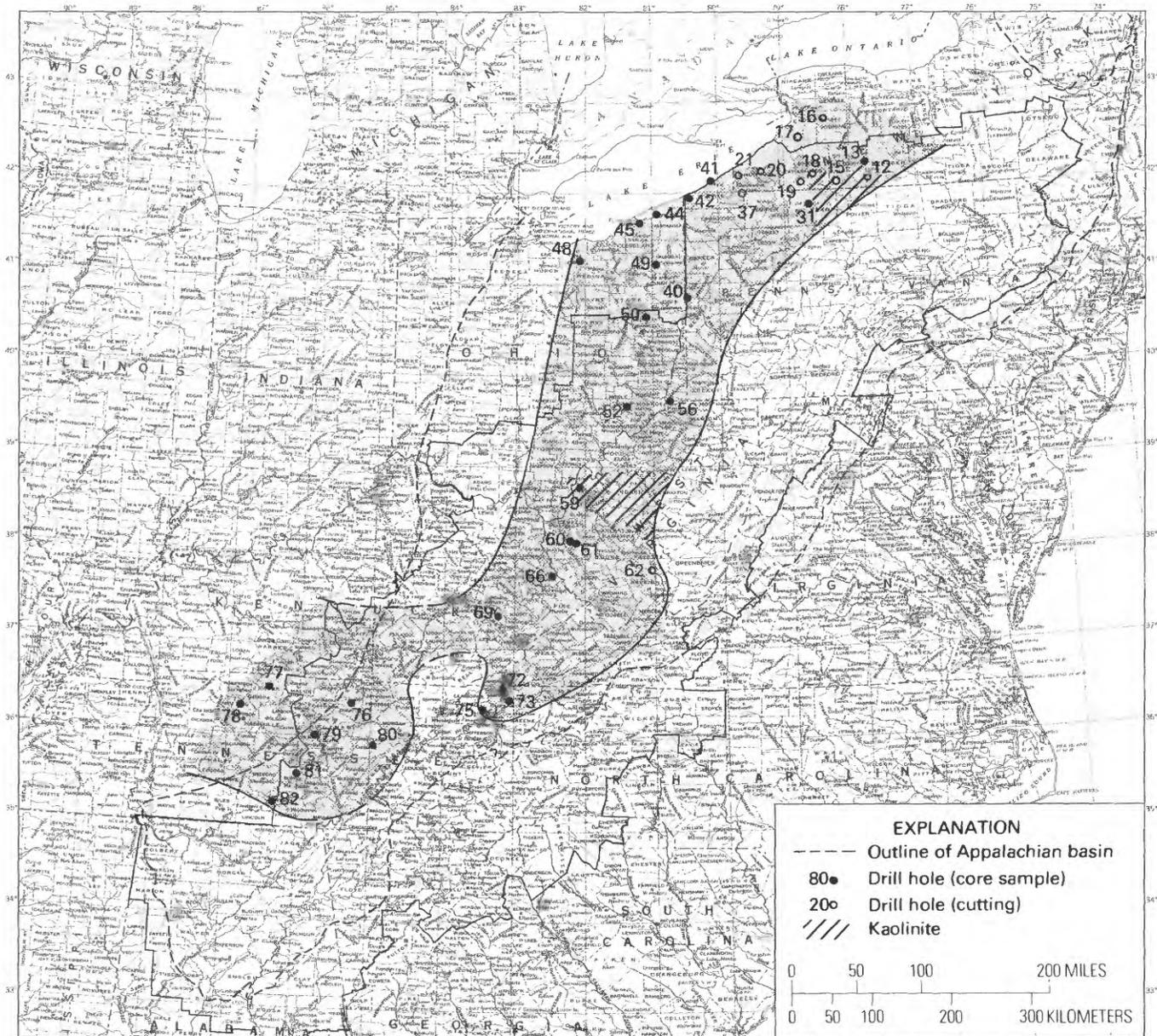


FIGURE 11.—Areal extent (shaded area) of the Rhinestreet Shale Member of the West Falls Formation and the lower unit of the Dowelltown Member of the Chattanooga Shale.

MARCELLUS SHALE OF THE HAMILTON GROUP

The Marcellus Shale of the Hamilton Group and its equivalent beds in the Millboro Shale are a dark-gray (N 3.4) limy shale. The average composition is 20 percent quartz silt, 50 percent clay, 5 percent pyrite, and 25 percent calcite, determined on the basis of 189 samples of the Marcellus Shale from 48 drill holes in New York, Pennsylvania, Ohio, West Virginia, and Virginia (fig. 15). Clay mineral proportions are 15 percent chlorite, 70 percent illite, 15 percent illite-smectite mixed-layer clay, and a trace of illite-chlorite mixed-layer clay. All samples of Marcellus Shale con-

tain some calcite, but the highest amounts occur in western New York, northeastern Ohio, and southwestern Pennsylvania (fig. 15).

ASH BEDS

Three ash beds are definitely recognized in the Middle and Upper Devonian rocks (fig. 4) of the Appalachian basin. In ascending order, they are the Tioga "Bentonite" Bed named by C. R. Fettke (Ebright and others, 1949), the Belpre "Bentonite" Bed of Collins (1979), and an ash bed discovered by Hass (1948) and later designated the Center Hill "Bentonite" Bed by Conant

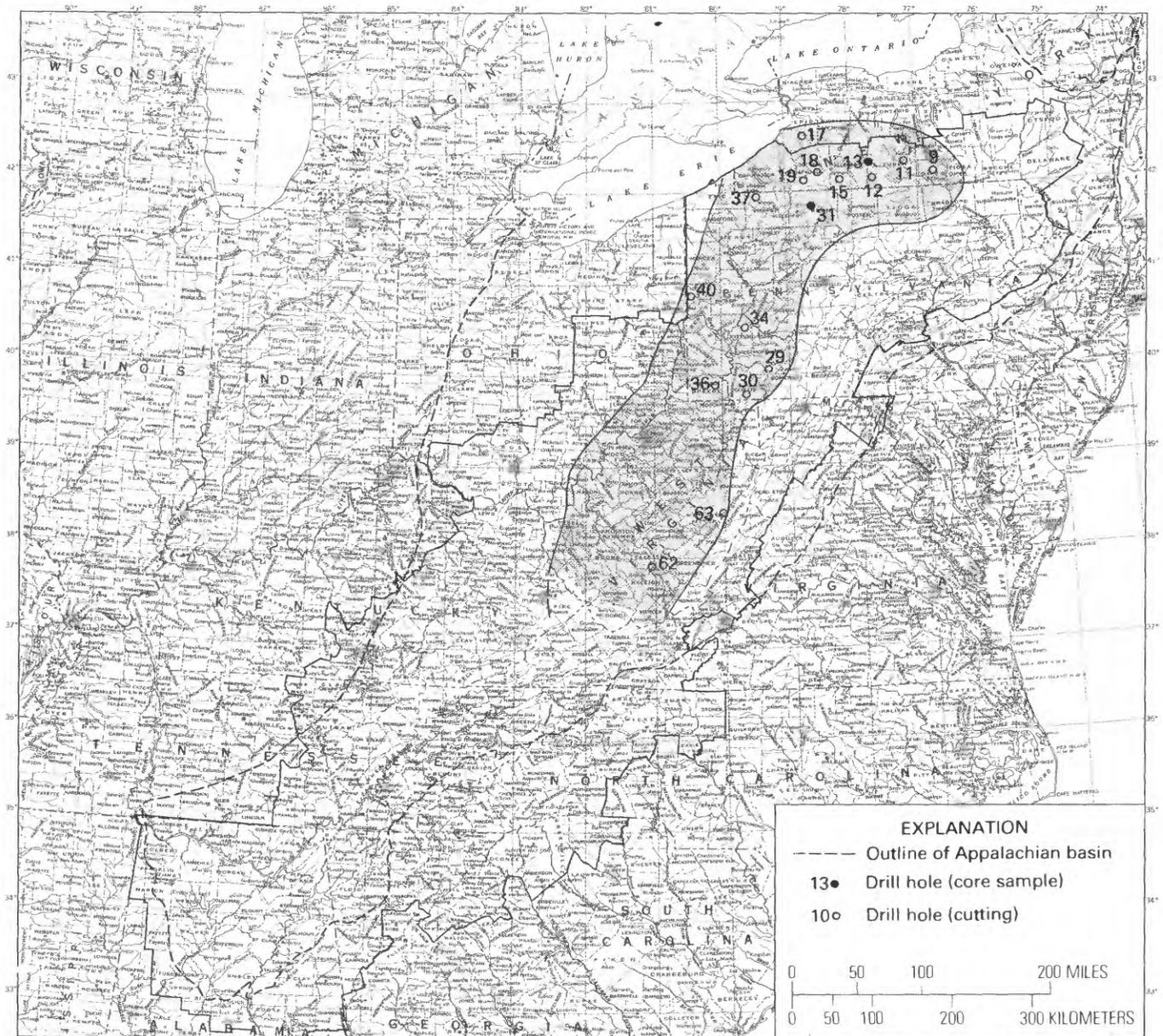


FIGURE 12.—Areal extent (shaded area) of the Middlesex Shale Member of the Sonyea Formation.

and Swanson (1961). Roen and Hosterman (1982) have suggested that the terms "bentonite," "metabentonite," and "K-bentonite" be replaced by the term "ash" for these beds in the Paleozoic rocks of the Appalachian basin. This recommendation is based on the fact that these beds do not conform to the accepted definition of bentonite (Grim and Guven, 1978) with respect to its physical, chemical, and mineralogical properties.

The Center Hill Ash Bed occurs predominantly in the western portion of the Appalachian basin from northwestern Pennsylvania to Tennessee. The bed is in the Pipe Creek Shale Member of the Java Formation and

near the top of the Dowelltown Member of the Chattanooga Shale. The Belpre Ash Bed is near the base of the Rhinestreet Shale Member of the West Falls Formation. Its areal distribution is very similar to that of the Center Hill Ash Bed. The Tioga Ash Bed is probably more widely distributed than the other ash beds. It occurs in the eastern portion of the Appalachian basin from northern New York to southern West Virginia and from eastern Pennsylvania to central Ohio. The Tioga Ash Bed is near the contact between the Onondaga Limestone and the Marcellus Shale of the Hamilton Group. In a few places, it occurs in the Marcellus, but, generally, it is found in the Onondaga.

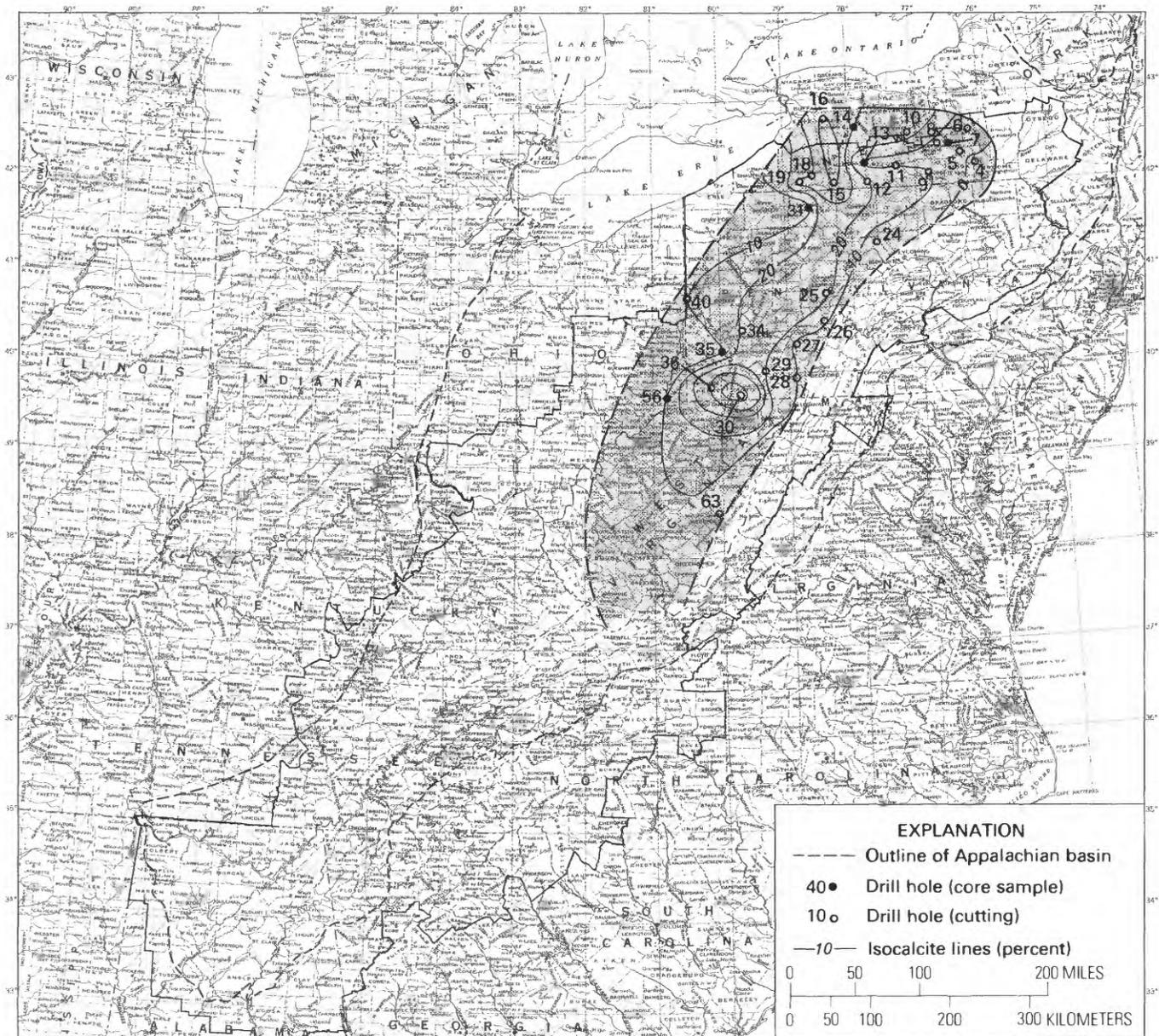


FIGURE 13.—Areal extent (shaded area) of the Genesee Shale and the Penn Yan Shale Members of the Genesee Formation and the Burket Black Shale Member of the Harrell Shale.

The ash beds are difficult to recognize, even though their lithology is different from that of the enclosing rocks, because they are usually very thin and are readily altered by weathering. The beds range in thickness from 1 to 75 mm. In a fresh, unweathered or drill core sample, conspicuous dark-brown to black biotite makes the ash beds recognizable. The biotite occurs in flakes 1 to 2 mm in diameter and ranges in abundance from several percent up to as much as 45 percent. The biotite is also found as scattered flakes in the adjacent enclosing rocks. In a weathered outcrop, the biotite may be recognized by its light-bronze color.

The mineralogy of the ash bed is somewhat different than that of the enclosing rocks but may be contami-

nated by the enclosing rocks. The *Md* illite, like biotite, is another mineral that is unique in the ash beds. However, it may be difficult to recognize if there is any contamination by *2M* illite from the enclosing shales, especially where the ash bed is thin. Both the Center Hill Ash Bed (fig. 16A) and the Belpre Ash Bed (fig. 16B) do occur in shale beds. There is no contamination of *Md* illite by *2M* illite in the Tioga Ash Bed where it occurs in limestone (fig. 16C). Normally, the ash beds do not contain chlorite, but it may be present as a contaminant from the adjacent shale beds. Quartz and kaolinite are present in the Center Hill and Belpre Ash Beds, but neither is present in the Tioga Ash Bed (table 2 and fig. 16). Since the enclosing shales of the Center

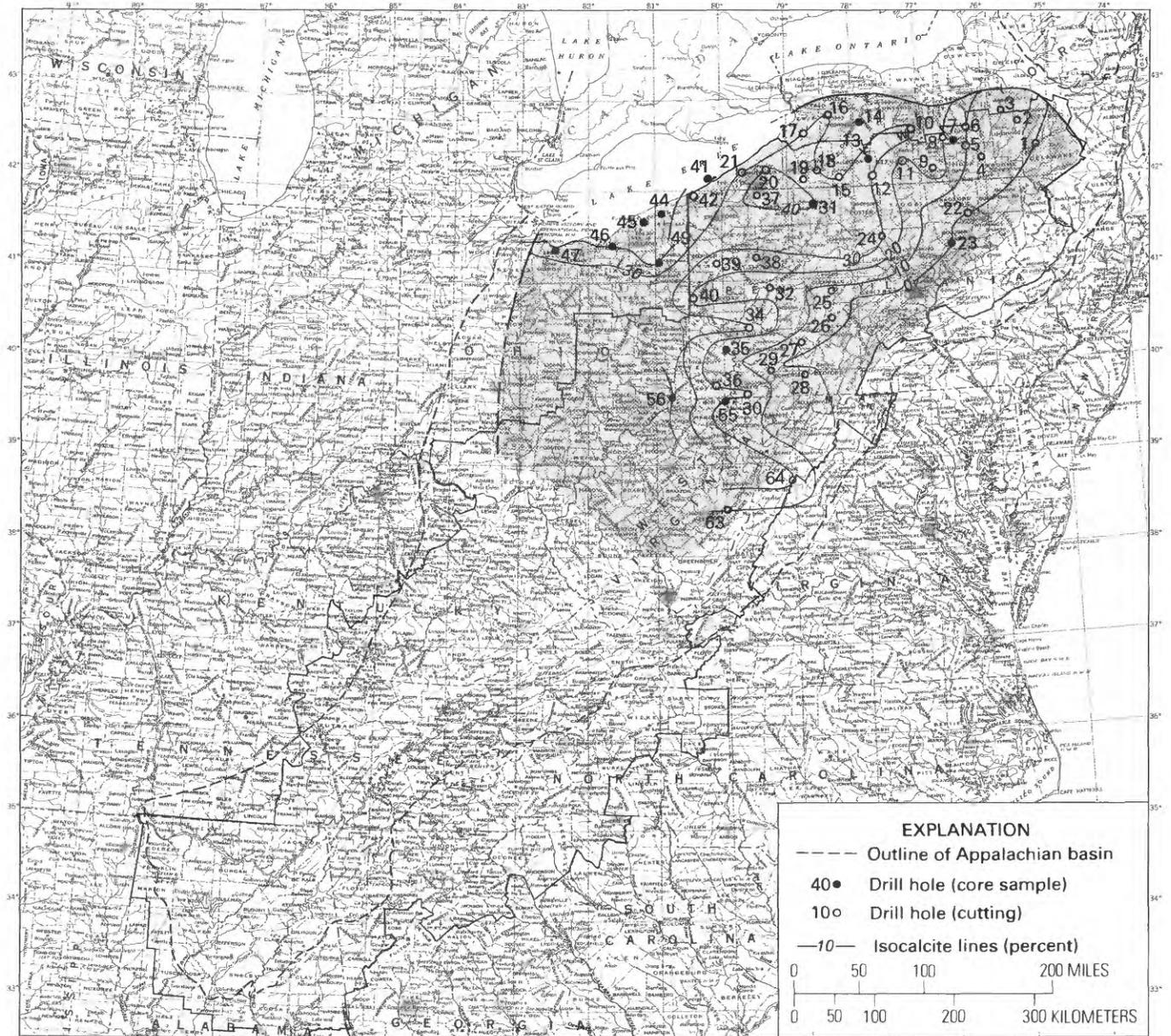


FIGURE 14.—Areal extent (shaded area) of the Mahantango Formation of the Hamilton Group and the Millboro Shale, exclusive of the "Marcellus Member."

Hill and the Belpre do not contain kaolinite, it must be an alteration product of the volcanic ash and not a contaminant. The lack of kaolinite in the Tioga Ash Bed is due to the calcic environment that prevented the formation of kaolinite.

DEPOSITIONAL PATTERN

Shale is a rather loosely used term applied to a fine-grained, indurated, detrital sedimentary rock. It is

formed by the consolidation of clay or mud and is characterized, more or less, by laminated stratification. Shale, as defined in this report, is composed predominantly of clay minerals (hydrous aluminous layered silicates). Quartz and calcite may be present in amounts of as much as 25 percent each, and pyrite is usually, but not always, present in amounts that rarely are as much as 15 percent. It is impossible to tell accurately what the original mineral suite of most shale was because all have been subjected to diagenesis and low-grade metamorphism. Probably the only unaltered original major detrital minerals are quartz and kaolinite. Quartz, which occurs in the silt- and clay-

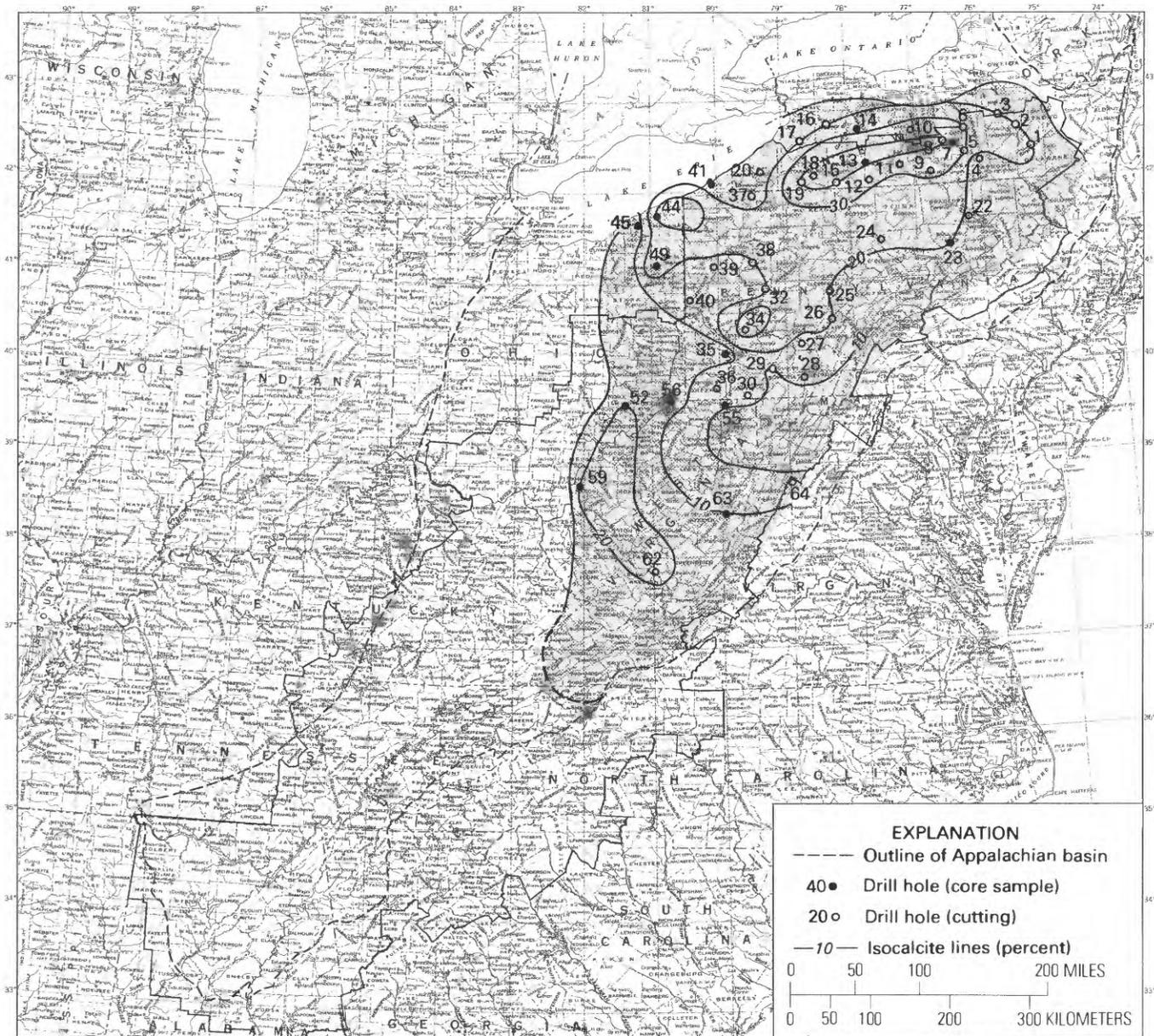


FIGURE 15.—Areal extent (shaded area) of the Marcellus Shale of the Hamilton Group and equivalent beds in the Millboro Shale.

size fraction, is ubiquitous and does not reveal any depositional pattern.

Calcite, a mineral precipitated from seawater, was found only in the oldest four units (table 1), which also do not contain any kaolinite. Calcite increases from about 5 percent in the Middlesex Shale Member of the Sonyea Formation to 25 percent in the Marcellus Shale of the Hamilton Group. The carbonate indicates that these older units were deposited in the relatively shallow water of a shelf area and that the rate of deposition of clastic material was slow enough to allow the concentration of calcium carbonate.

The occurrence of kaolinite in minor amounts, however, does indicate a probable depositional pattern for 7 of the 11 formations discussed in this report. Kaolinite is coarser grained than other clay minerals; therefore, when it is transported by water, it does not remain in suspension long, and it is deposited closer to the source area. Kaolinite has been found to be most abundant near the shoreline in both modern sediments and ancient sedimentary rocks (Parham, 1966). Kaolinite was not observed in the four older shale units (figs. 12-15)—the Marcellus Shale of the Hamilton Group, the Mahantango Formation of the Hamilton Group,

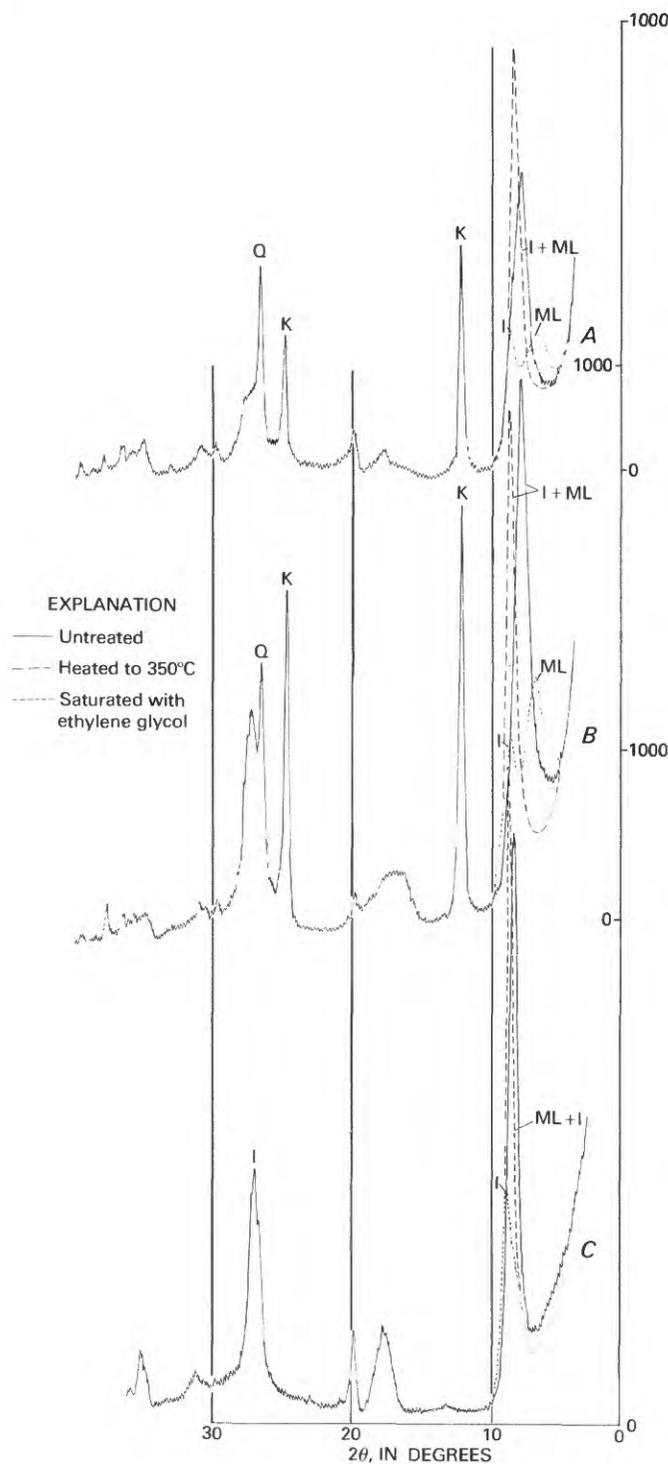


FIGURE 16.—X-ray diffraction traces of the Center Hill (A), Belpre (B), and Tioga (C) Ash Beds. ML is mixed-layer clay, I is *Md* illite, K is kaolinite, and Q is quartz.

the Genesee Shale Member of the Genesee Formation, and the Middlesex Shale Member of the Sonyea Formation. The Rhinestreet Shale Member of the West Falls Formation contains two small areas of kaolinite in northern Pennsylvania and adjacent New York and in West Virginia (fig. 11). Kaolinite is much more widespread in the younger units (figs. 6–10)—the Chagrin Shale, all three units of the Huron Member of the Ohio Shale, and the Java Formation. The kaolinite occurrence in the Cleveland Member of the Ohio Shale is limited to small areas in eastern Kentucky and eastern Tennessee (fig. 5).

The distribution of kaolinite in the seven youngest shale units studied indicates that the source area for kaolinite and other detrital material was to the east or northeast. Because no kaolinite is present in the four oldest units, the location of the source area is speculative at best. However, the kaolinite distribution in the younger units and the calcite distribution in the older units suggest that the source area was probably also east or northeast of the basin. The distance from the source area to the Appalachian basin is problematic. However, it seems that the distance between the source area and the basin of deposition was probably greatest during Marcellus time and least during deposition of the Java, the lower unit of the Huron, and the Dunkirk, as the presence of kaolinite in the Huron and the Dunkirk and the absence of kaolinite in the Marcellus Shale suggest. In all probability, the same source supplied sediment to the basin throughout Devonian time. The size of the accumulation basin, the distance from the center of accumulation to the shoreline, and the depositional energy are all factors that probably brought more kaolinite into the younger black shales.

Possibly, some of the material deposited during Devonian time was derived from volcanic ash. The widespread Tioga, Belpre, and Center Hill Ash Beds (table 2) (Roen and Hosterman, 1982) and the occurrence of scattered biotite flakes indicate the possibility of partial volcanic ash origin. Also the present clay-mineral suite was probably derived from smectite, a clay mineral very common in volcanic ash.

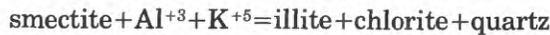
DIAGENESIS AND METAMORPHISM

The major shale components of *2M* illite, chlorite, and mixed-layer clay minerals are the result of diagenesis and greenschist (low-grade) metamorphism. The *2M* illite was derived from degraded and disordered (*Md*) illite and smectite; chlorite was also derived from smectite. Illite-smectite mixed-layer clay was formed from a mixture of *Md* illite and smectite; illite-chlorite mixed-layer clay was formed from *Md* illite and smectite. Nondetrital quartz resulted from the formation of the above minerals in the reaction

TABLE 2.—*Mineralogy of the Center Hill, Belpre, and Tioga Ash Beds*

[—, not present; tr, present in trace amounts]

Ash bed and location	Drill hole no.	Depth (in ft)	Color	Mineral composition (in percent)						Clay mineral content (in percent)			Enclosing rock	
				Quartz	Clay	Biotite	Pyrite	Plagio-clase	Calcite	Chlorite	<i>Md</i> illite	Mixed layer illite-smectite		Kaolinite
Center Hill:														
Erie Co., Pa.—	41	1,027.9	10 YR 4.8/5	15	80	5	—	tr	—	—	25	55	20	Shale
Mason Co., W. Va.—	59	3,140.0	N 4.5	20	80	tr	—	—	—	5	30	40	25	Do.
Hancock Co., Tenn.—	72	675.8	N 6.5	15	40	45	—	—	—	tr	20	10	70	Do.
Belpre:														
Ashtabula Co., Ohio—	43	1,192.3	N 5.3	5	80	tr	15	tr	—	—	15	55	30	Do.
Trumbull Co., Ohio—	49	2,551.9	N 5.1	10	75	tr	10	5	—	—	25	60	15	Do.
Noble Co., Ohio—	52	4,080.4	10 YR 4/5	10	85	tr	5	—	—	—	50	25	25	Do.
Mason Co., W. Va.—	59	3,363.	N 5.5	15	70	tr	5	—	10	—	20	65	15	Do.
Tioga:														
Tompkins Co., N.Y.—	7	1,452.0	N 5.8	—	90	tr	—	10	—	—	55	45	—	Limestone
Allegheny Co., Pa.—	35	7,485.4	N 5.5	—	90	10	—	—	—	—	70	30	—	Do.



(Hower and others, 1976). Potassium was made available from the feldspars and (or) from free ions in the water.

The distribution patterns of the clay minerals due to the low-grade metamorphism have become quite evident in the Devonian black shales studied. In all units except the Marcellus Shale of the Hamilton Group, chlorite content increases from 10 percent in the youngest units to 25 percent in the oldest units (table 1). Conversely, the illite-smectite mixed-layer clay mineral content generally decreases from 30 percent in the youngest units to 15 percent in the oldest units. The amount of illite remains more or less constant in all shale units.

The symmetry of the 001 X-ray diffraction peak for illite shows a slight variation. This symmetry of peak area to peak height was used as a measure of crystallinity and the following formula was derived:

$$x = h/A$$

where A is the area of the 001 illite peak on the X-ray diffraction trace, h is the height of the same illite peak, and x is the crystallinity factor. For the 2*M* illite, the relative crystallinity factor ranged from about 0.10 for the lowest symmetry to 0.14 for the highest symmetry. There is considerable variation in the crystallinity of the 2*M* illite, but, in general, the crystallinity increases with depth in almost every core sampled; it also increases regionally in the east to southeast direction (fig. 17). This regional change in crystallinity corresponds very closely to the regional increase in the thickness of the Devonian rocks and to the conodont color alteration index (CAI) (Epstein and others, 1977). A crystallinity factor of 0.11 closely matches the conodont CAI of 2.5 to 3, which has a temperature range of

110° to 200°C, and a crystallinity factor of 0.10 closely matches a CAI of 1.5 to 2, which has a temperature range of 50° to 140°C.

As we mentioned above, the Marcellus Shale does not fit the pattern of increasing abundance of chlorite in older units (table 1). One explanation may be that the Marcellus contains more calcite than any of the other units studied. Such a concentration of calcite may prevent the temperature and pressure increases required for the formation of chlorite. Calcite, however, does not prevent the formation of 2*M* illite during diagenesis.

SUMMARY

Detailed mineralogical study of Devonian black shale in the Appalachian basin has produced some new data on the shale that are summarized here. Although the shale contains occasional traces of sulfides (galena and chalcopyrite) and sulfates (barite and gypsum), there is no evidence for the existence of a large disseminated mineral deposit. The organic content of the shale can be estimated from the Munsell color value if its calcite content is known. For example, a shale having a Munsell color value of 3.5 contains about 12 percent organic carbon if it also contains more than 5 percent calcite, but, if it contains less than 5 percent calcite, the same color shale contains only about 4 percent carbon.

The mineralogy of the shales provides information about the possible location of the source area and about metamorphic intensity. The presence of kaolinite, the only unaltered detrital clay mineral in the shales, indicates that the source area during Devonian time was east and northeast of the basin of deposition. The crystallinity factor of 2*M* illite supports the conodont color alteration index and indicates that the intensity of low-grade metamorphism increases to the northeast in the Appalachian basin.

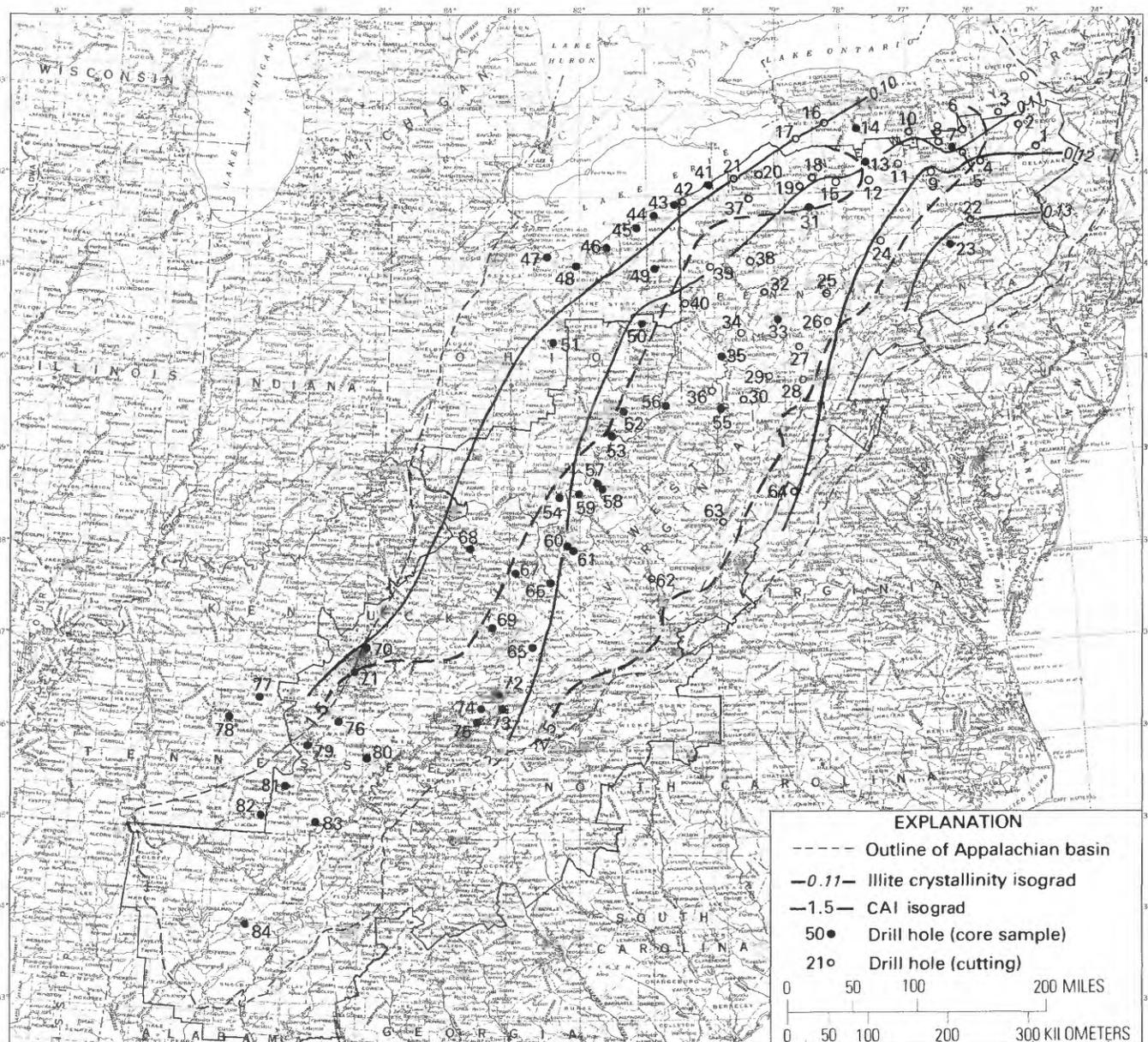


FIGURE 17.—Illite crystallinity isograds of Devonian black shale in the Appalachian basin.

APPENDIX

[GL, ground level, in feet about mean sea level; TD, total depth, in feet above mean sea level; DF, derrick floor, in feet above mean sea level; KB, Kelley bushing, in feet above mean sea level]

1. Gulf Oil Corp.
C. E. Leslie No. 1
1.9 mi S. of 42°25' N.
2.3 mi W. of 75°00' W.
Oneonta 7½-minute quadrangle
Franklin Township
Delaware Co., N.Y.
Elev. 1486 GL, TD 7952
API No. 31-025-04455

2. Bradley Producing Co.
C. C. Lobdell No. 1
9,700 ft N. of 42°40' N.
3,150 ft W. of 75°20' W.
New Berlin 7½-minute quadrangle
Columbus Township
Chenango Co., N.Y.
Elev. 1373 DF, TD 5637
API No. 31-017-01160
3. New York State Natural Gas Corp.
D. L. Branagan No. 1
2 mi S. of 42°50' N.
3.4 mi W. of 75°35' W.

- West Eaton 7½-minute quadrangle
Lebanon Township
Madison Co., N.Y.
Elev. 1544 GL, TD 5703
API No. 31-053-03970
4. Fenix and Scissen
L and N Richards No. 1
3,600 ft S. of 42°20' N.
8,430 ft W. of 75°55' W.
Whitney Point 7½-minute quadrangle
Triangle Township
Broome Co., N.Y.
Elev. 996 GL, TD 9640
API No. 31-007-05087
5. C. Frulich and Suburban Propane
Phillip Overbaugh No. 1
Harford 7½-minute quadrangle
Harford Township
Cortland Co., N.Y.
API No. 31-023-02308
6. New York State Natural Gas Corp.
R. A. Butler No. 1
Homer 7½-minute quadrangle
Homer Township
Cortland Co., N.Y.
API No. 31-023-00644
7. Cargill Salt Company
Core Test No. 17
1.29 mi S. of 42°32'30" N.
0.27 mi W. of 76°30' W.
Ithaca East 7½-minute quadrangle
Lansing Township
Tompkins Co., N.Y.
Elev. 835 DF, TD 2784
API No. 31-109-13173
8. Great Lakes Gas Corp.
J. W. Agard No. 1
Ludlowville 7½-minute quadrangle
Ulysses Township
Tompkins Co., N.Y.
API No. 31-109-05017
9. Belmont Quad Drilling Corp.
E. A. Treat No. 118
Erin 7½-minute quadrangle
Erin Township
Chemung Co., N.Y.
API No. 31-015-00509
10. CGS Management Co.
Greger Borglum No. 1
42°41'01" N.
77°01'20" W.
Penn Yan 7½-minute quadrangle
Benton Township
Yates Co., N.Y.
API No. 31-123-04796
11. Anchor Petroleum Co.
Blair Storage Well No. 1
9,400 ft S. of 42°20' N.
1,800 ft W. of 77°15' W.
Savona 7½-minute quadrangle
Bath Township
Steuben Co., N.Y.
Elev. 1073 GL, TD 3347
API No. 31-101-02679
12. Empire Gas and Fuel Co.
Amos Rogers No. 1
Greenwood 7½-minute quadrangle
Greenwood Township
Steuben Co., N.Y.
API No. 31-101-00053
13. National Fuel Gas Supply Co.
(EGSP NY No. 1)
No. 6213 (JO)
9,430 ft S. of 42°22'30" N.
7,620 ft W. of 77°47'30" W.
Alfred 7½-minute quadrangle
Almond Township
Allegany Co., N.Y.
Elev. 1852.7 KB, 1839.7 GL, TD 2975
API No. 31-003-13549
14. International Salt Company
H. Stewart No. 6701
42°44'43" N.
77°50'24" W.
Sonyea 7½-minute quadrangle
Livingston Co., N.Y.
Elev. 603.45 KB, 578.45 GL, TD 1439
API No. 31-051-14100
15. Bradley Prod. Corp.
H. Ames No. 1
Friendship 7½-minute quadrangle
Wirt Township
Allegany Co., N.Y.
API No. 31-003-04654
16. Great Lakes Gas Corp.
R. Hall et al No. 1
Cowlesville 7½-minute quadrangle
Bennington Township
Wyoming Co., N.Y.
API No. 31-121-04542
17. Iroquois Gas Corp.
Well No. 796
42°35'30" N.
78°45'10" W.
Langford 7½-minute quadrangle
Concord Township
Erie Co., N.Y.
API No. 31-029-03269
18. Comaco Oil Inc.
Humphrey 7½-minute quadrangle
Carrollton Township
Cattaraugus Co., N.Y.
API No. 31-009-05106
19. Devonian Gas and Oil Co.
Seneca Nations No. 3
Allegany Indian Reservation

- Salamanca 7½-minute quadrangle
South Valley Township
Cattaraugus Co., N.Y.
Elev. 1300.6 GL, TD 4680
API No. 31-009-04088
20. C. E. Bournique et al
Robert Bates No. 1
Ellery Center 7½-minute quadrangle
Ellery Township
Chautauqua Co., N.Y.
API No. 31-013-01457
21. Apache Corp.
Carnahan No. 1
1,000 ft S. of 42°10' N.
19,000 ft W. of 79°40' W.
South Ripley 7½-minute quadrangle
Mina Township
Chautauqua Co., N.Y.
Elev. 1485.5 GL, TD 3578
API No. 31-013-04152
22. Pure Oil Co.
C. Blemle No. 1
740 ft S. of 41°35' N.
7,700 ft W. of 76°20' W.
Colley 7½-minute quadrangle
Wilmot Township
Bradford Co., Pa.
Elev. 1560.8 GL, TD 12817
API No. 37-015-00001
23. California Company
A. W. Bennett No. 1
6,700 ft N. of 41°20' N.
4,350 ft W. of 76°30' W.
Sonestown 7½-minute quadrangle
Davidson Township
Sullivan Co., Pa.
Elev. 1482 DF, TD 12343
API No. 37-113-00005
24. New York State Natural Gas Corp.
Pennsylvania Tract 101 No. 1
Slate Run 7½-minute quadrangle
Lycoming Co., Pa.
API No. 37-081-20004
25. Texaco
General Refractories No. 1
40°56'47" N.
78°16'40" W.
Wallaceton 7½-minute quadrangle
Clearfield Co., Pa.
API No. 37-033-20537
26. Peoples Natural Gas Corp.
Weldon No. 1
3.0 mi S. of 40°40' N.
1.5 mi W. of 78°20' W.
Altoona 7½-minute quadrangle
Antis Township
Blair Co., Pa.
Elev. 1473 GL, TD 5820
API No. 37-013-20006
27. Pennzoil
Heidingsfelder No. 1
6,950 ft S. of 40°20' N.
4,475 ft W. of 78°50' W.
Geistown 7½-minute quadrangle
Richland Township
Cambria Co., Pa.
Elev. 2218 GL, TD 9590
API No. 37-021-20013
28. Peoples Natural Gas Co.
N. R. Mowry No. 1
New Baltimore 7½-minute quadrangle
Allegheny Township
Somerset Co., Pa.
Elev. 1952 GL, TD 9253
API No. 37-111-20029
29. Peoples Natural Gas Co.
H. K. Dupre No. 1
Seven Springs 7½-minute quadrangle
Middle Creek Township
Somerset Co., Pa.
Elev. N/A, TD 8189
API No. 37-111-20034
30. Zenith Oil Co.
Ryan No. 2
Brandonville 7½-minute quadrangle
Fayette Co., Pa.
API No. 37-051-20094
31. Minard Run Oil Company
(EGSP-PA No. 1)
Minard Run Exploration No. 1
1,100 ft S. of 41°52'30" N.
2,900 ft E. of 78°37'30" W.
Cyclone 7½-minute quadrangle
Lafayette Township
McKean Co., Pa.
Elev. 2260 GL, TD 5230
API No. 37-083-36382
32. Peoples Natural Gas Co.
L. M. Martin No. 4
2 mi S. of 40°55' N.
1 mi W. of 79°20' W.
Distant 7½-minute quadrangle
Wayne Township
Armstrong Co., Pa.
Elev. 1585 GL, TD 6891
API No. 37-005-00005
33. Gruy Federal, Inc.
(EGSP-PA No. 4)
Glenn McCall No. 5
Indiana 7½-minute quadrangle
White Township
Indiana Co., Pa.
Elev. 1535 KB, 1523 GL, TD 7868
API No. 37-063-25073
34. Fox and Sloan
F. M. Sloan No. 1
Murraysville 7½-minute quadrangle
Franklin Township

- Westmoreland Co., Pa.
Elev. N/A, TD 7415
API No. 37-129-00080
35. Combustion Engineering
(EGSP-PA No. 2)
Consolidated Edison Power System No. 1
40°11'30" N.
79°53'30" W.
Monongahela 7½-minute quadrangle
Allegheny Co., Pa.
Elev. 759, TD 7505
API No. 37-003-20980
36. Fox and Coen
Gordon No. 4
Waynesburg 7½-minute quadrangle
Greene Co., Pa.
API No. 37-059-20038
37. Columbia Gas Transmission Corp.
H. Christensen No. 1
41°55'14" N.
78°33'12" W.
Corry 7½-minute quadrangle
Warren Co., Pa.
Elev. 1525 GL, TD 4664
API No. 37-123-24704
38. Fairman et al
J. May No. 1
1.7 mi N. of 41°10' N.
2 mi W. of 79°20' W.
Clarion 7½-minute quadrangle
Clarion Township
Clarion Co., Pa.
Elev. 1451 KB, TD 7906
API No. 37-031-20168
39. United Natural Gas Corp.
Minnis No. 1
Grove City 7½-minute quadrangle
Mercer Co., Pa.
API No. 37-085-00018
40. Quaker State Oil Refining Co.
Metropolitan Industries No. 1
40°45'01" N.
80°27'38" W.
New Galilee 7½-minute quadrangle
East Palestine Township
Beaver Co., Pa.
Elev. 948 GL, TD 6654
API No. 37-007-20054
41. Monsanto Research Corp.
(EGSP-PA No. 3)
Presque Isle State Park No. 1
4,100 ft S. of 42°10'00" N.
440 ft W. of 80°07'30" W.
Erie North 7½-minute quadrangle
Erie Co., Pa.
Elev. 580, TD 1276
API No. 37-049-20846
42. Ohio Oil Co.
N. Blickensdefer No. 22
1.74 mi S. of 42°00' N.
4.09 mi W. of 80°30' W.
Conneaut 7½-minute quadrangle
Springfield Township
Erie Co., Pa.
Elev. 642 GL, TD 4457
API No. 37-049-00412
43. Thurlow Weed and Associates
(EGSP-OH No. 4)
Bessemer and Lake Erie RR No. 1
6,500 ft S. of 41°57'30" N.
2,900 ft W. of 80°32'30" W.
Conneaut 7½-minute quadrangle
Conneaut Township
Ashtabula Co., Ohio
Elev. 583 GL
API No. 34-007-21087
44. International Salt company
Fred C. Gerald No. 1
41°50'32" N.
80°52'21" W.
Ashtabula South 7½-minute quadrangle
Saybrook Township
Ashtabula Co., Ohio
Elev. 691 GL, TD 2400
API No. 34-007-06002
45. Diamond Alkali Company
Diamond Alkali Company No. 201
728,530 N., 2,338,560 E.
Mentor 7½-minute quadrangle
Lot 18, Concord Township
Lake Co., Ohio
Elev. 882 GL, TD 3104
API No. 34-085-06002
46. International Salt Company
Whiskey Island Core
City of Cleveland No. 1
666,160 N., 2,214,770 E.
Cleveland South 7½-minute quadrangle
Cuyahoga Co., Ohio
Elev. 582.9 GL, TD 2400
API No. 34-035-01001
47. Ohio Edison Company
Erie Nuclear Power Plant No. B-19
611,971 N., 2,006,989 E.
Huron 7½-minute quadrangle
Berlin Township
Erie Co., Ohio
Elev. 656.5 GL, TD 346
API No. 34-043-20057
48. Columbia Gas Transmission Corp.
(EGSP-OH No. 5)
B & R McGuire No. 20149T
568,600 N., 2,130,500 E.
Lagrange 7½-minute quadrangle
Grafton Township
Lorain Co., Ohio
Elev. 878 GL, 888 KB, TD 1340
API No. 34-093-21100

49. Columbia Gas Transmission Corp.
(EGSP-OH No. 7)
Anna A Meleski
Newton Falls 7½-minute quadrangle
Newton Township
Trumbull Co., Ohio
Elev. 962 KB, 951 GL, TD 2710
API No. 34-155-21238
50. Belden and Blake, Inc.
(EGSP-OH No. 1)
Glen-Gary No. S-745
40°37'34" N.
81°17'54" W.
Mineral City 7½-minute quadrangle
Rose Township
Carroll Co., Ohio
Elev. 1045 KB, 1039 GL, TD 5187
API No. 34-019-20835
51. Thurlow Weed and Associates
(EGSP-OH No. 3)
Louise Beckholt No. 1
40°23'53" N.
82°30'10" W.
Fredericktown 7½-minute quadrangle
Clinton Township
Knox Co., Ohio
Elev. 990 GL, TD 1260
API No. 34-083-22599
52. Donhue Anstey and Morrill
(EGSP-OH No. 8)
Schockling No. 1
625,730 N., 2,291,950 E.
Macksburg 7½-minute quadrangle
Enoch Township
Noble Co., Ohio
Elev. 860 GL
API No. 34-121-22255
53. River Gas Company
(EGSP-OH No. 2)
Florence L. House No. R109
39°23'36" N.
81°33'48" W.
Fleming 7½-minute quadrangle
Washington Co., Ohio
Elev. 828 KB, 816 GL, TD 6262
API No. 34-167-23521
54. Mitchell Energy Corp.
(EGSP-OH No. 6-4)
Straight-Wisemandle Unit 1-B
Mercerville 7½-minute quadrangle
Harrison Township
Gallia Co., Ohio
Elev. 921 KB, 910 GL, TD 3072
API No. 34-053-20477
55. U.S. Department of Energy
(EGSP-WV No. 6)
MERC No. 1
0.13 mi N. of 39°40' N.
3.15 mi W. of 79°55' W.
Morgantown North 7½-minute quadrangle
Morgan District
Monongalia Co., W. Va.
Elev. 973 KB, 959 GL, TD 7520
API No. 47-061-20370
56. Mobay Chemical Corp.
(EGSP-WV No. 7)
H. Emch and A. Pyles Unit No. 1
39°40'37" N.
80°49'26" W.
New Martinsville 7½-minute quadrangle
Proctor District
Wetzel Co., W. Va.
Elev. 1344 GL, 1355 KB, TD 7007
API No. 47-103-20645
57. Consolidated Gas Company
(EGSP-WV No. 1)
E. L. Bailer No. 11940
0.32 mi S. of 38°50'00" N.
2.18 mi W. of 81°50'00" W.
Cottageville 7½-minute quadrangle
Jackson Co., W. Va.
Elev. 846 KB, 835 GL, TD 3935
API No. 47-035-21369
58. Consolidated Gas Company
(EGSP-WV No. 2)
W. L. Pinnell 12041
38°57'35" N.
81°49'08" W.
Cottageville 7½-minute quadrangle
Jackson Co., W. Va.
Elev. 673 KB, 662 GL, TD 3744
API No. 47-035-21371
59. Reel Energy, Inc.
(EGSP-WV No. 5)
D/K Farm No. 3
38°55'30" N.
82°03'45" W.
Cheshire 7½-minute quadrangle
Robinson District
Mason Co., W. Va.
Elev. 675 KB, 665 GL, TD 3420
API No. 47-053-20146
60. Columbia Gas Transmission Corp.
(EGSP-WV No. 4)
No. 20402
4.83 mi S. of 38°10'00" N.
3.94 mi W. of 82°10'10" W.
Hager 7½-minute quadrangle
Lincoln Co., W. Va.
Elev. 1163 KB, 1153 GL, TD 3983
API No. 47-043-21636
61. Columbia Gas Transmission Corp.
(EGSP-WV No. 3)
No. 20403
4.5 mi S. of 38°10'00" N.
3.1 mi W. of 82°10'00" W.
Hager 7½-minute quadrangle
Lincoln Co., W. Va.
Elev. 1202 KB, 1190 GL, TD 4065
API No. 47-043-21637

62. Godfrey L. Cabot
C. E. Quinn No. 1
3.27 mi S. of 37°50' N.
4.62 mi W. of 80°50' W.
Meadow Creek 7½-minute quadrangle
Richmond District
Raleigh Co., W. Va.
Elev. 1294 GL, TD 6397
API No. 47-081-00036
63. Columbian Carbon Co.
U.S. I-3 No. 1297
Durbin 7½-minute quadrangle
Greenbank District
Pocahontas Co., W. Va.
Elev. N/A, TD 6055
API No. 47-075-00015
64. Shell Oil Co.
R. J. Whetzel No. 1
4.7 mi N. of 38°50' N.
2.1 mi W. of 78°55' W.
Orkney Springs 7½-minute quadrangle
Rockingham Co., Va.
Elev. 1464.8 GL, TD 14,176
API No. 45-165-20007
65. Columbia Gas Transmission Corp.
(EGSP-VA No. 1)
No. 20338
37°00'37" N.
82°41'14" W.
Flat Gap 7½-minute quadrangle
Wise Co., Va.
Elev. 2405.5 KB, 2395.5 GL, TD 5741
API No. 45-195-20253
66. Columbia Gas Transmission Corp.
(EGSP-KY No. 3)
No. 20336
2750 FNL X 1650 FWL Sec. 16-P-85
Kermit 7½-minute quadrangle
Martin Co., Ky.
Elev. 994 KB, 934 GL, TD 3457
API No. 16-159-31020
67. Ashland Oil Company
(EGSP-KY No. 4)
Skaggs-Kelly Unit No. 3-RS
36°57'40" N.
82°56'20" W.
1780 FNL X 1230 FEL Sec. 12-R-79
Redbush 7½-minute quadrangle
Johnson Co., Ky.
Elev. 961 GL, 972 KB, TD 1510
API No. 16-115-33985
68. Nuclear Engineering Company
NECO No. 5E (Maxey Flats)
2600 FSL X 600 FEL Sec. 25-V-72
Plummers Landing 7½-minute quadrangle
Fleming Co., Ky.
Elev. 1022, TD 317
API No. 16-069-06001
69. Kentucky West Virginia Gas
(EGSP-KY No. 1)
Nicholas Combs No. 7239
1960 FNL X 325 SWL Sec. 19-K-76
Hazard North 7½-minute quadrangle
Perry Co., Ky.
Elev. 1090 KB, 1080 GL, TD 3734
API No. 16-193-28982
70. W. Blankenship
(KGS No. C-182)
Redman No. 1
1500 FNL X 200 FWL Sec. 9-G-53
Russell Springs 7½-minute quadrangle
Russell Co., Ky.
Elev. 960, TD 235
API No. 16-207-90003
71. Murray Drilling Co.
Jeff Story (Bell) No. 1
800 FNL X 900 FWL Sec. 1-E-53
Jamestown 7½-minute quadrangle
Russell Co., Ky.
Elev. 995
API No. 16-207-32515
72. Tennessee Geological Survey
(EGSP-TN No. 3)
803,150 N., 2,836,050 E.
Sneedville 7½-minute quadrangle
Hancock Co., Tenn.
Elev. 1230 GL, TD 755.6
API No. 41-067-01001
73. Tennessee Geological Survey
(EGSP-TN No. 4)
761,500 N., 2,855,050 E.
Camelot 7½-minute quadrangle
Hawkins Co., Tenn.
Elev. 1245 GL, TD 1525.1
API No. 41-073-01002
74. Tennessee Geological Survey
(EGSP-TN No. 1)
767,150 N., 2,756,500 E.
Howard Quarter 7½-minute quadrangle
Claiborne Co., Tenn.
Elev. 1100 GL, TD 254
API No. 41-025-06001
- Tennessee Geological Survey
(EGSP-TN No. 2)
765,900 N., 2,755,300 E.
Howard Quarter 7½-minute quadrangle
Claiborne Co., Tenn.
Elev. 1120 GL, TD 115.6
API No. 41-025-06002
75. Grainger County Commission
(EGSP-TN No. 9)
Grainger Co. Industrial Park
36°18'56" N.
83°24'23" W.
Avondale 7½-minute quadrangle
Grainger Co., Tenn.
API No. 41-057-01003

76. Dresser Industries
OCI-8 Diamond Drill Hole
100 FSL X 1650 FWL Sec. 4-38-52 E
Crawford 7½-minute quadrangle
Overton Co., Tenn.
Elev. 900+ GL, TD 409+
API No. 41-133-90001
77. U.S. Bureau of Mines
NV-56, Watkins Gran
36°23'55" N.
86°35'45" W.
Cottontown 7½-minute quadrangle
Summer Co., Tenn.
Elev. N/A, TD 44.9
API No. 41-165-06001
78. U.S. Bureau of Mines
NV-54, G. F. Stenberg
36°15'05" N.
86°52'15" W.
Forest Grove 7½-minute quadrangle
Davidson Co., Tenn.
Elev. N/A, TD 41.7
API No. 41-037-01001
79. U.S. Bureau of Mines
YB-39, Everett Pedigo
35°58'30" N.
85°45'45" W.
Smithville 7½-minute quadrangle
DeKalb Co., Tenn.
Elev. N/A, TD 179.1
API No. 41-041-01001
80. U.S. Bureau of Mines
WR-50, J. C. Kemmer and Son
35°52'10" N.
84°53'30" W.
Dorton 7½-minute quadrangle
Cumberland Co., Tenn.
Elev. N/A, TD 177.2
API No. 41-035-06001
81. U.S. Bureau of Mines
YB-43, Hockett
35°38' N.
86°05' W.
Fredonia 7½-minute quadrangle
Coffee Co., Tenn.
Elev. N/A, TD 119.3
API No. 41-031-01001
82. U.S. Bureau of Mines
YB-45, Cumberland Springs Land
35°19'30" N.
86°15'40" W.
Lynchburg East 7½-minute quadrangle
Moore Co., Tenn.
Elev. N/A, TD 21.4
API No. 41-127-01001
83. U.S. Bureau of Mines
WR-47, Mattie Barber
35°11'15" N.
85°26' W.
Ketner Gap 7½-minute quadrangle
Marion Co., Tenn.
Elev. N/A, TD 311.8
API No. 41-115-01001
84. U.S. Bureau of Mines
AL-65, Paul Freeman
34°04'05" N.
86°29'20" W.
Clarence 7½-minute quadrangle
Blount Co., Ala.
Elev. N/A, TD 52.4
API No. 01-009-01001

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