

Oil Yield and Uranium Content of Black Shales

GEOLOGICAL SURVEY PROFESSIONAL PAPER 356-A

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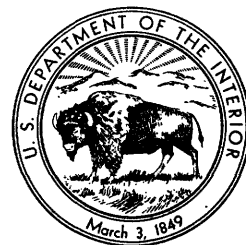
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By VERNON E. SWANSON

URANIUM IN CARBONACEOUS ROCKS

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CONTENTS

	Page		Page
Abstract.....	1	Black shales of Pennsylvanian age in eastern Kansas and northeastern Oklahoma.....	16
Introduction.....	1	Black shales of Pennsylvanian age in Illinois.....	17
General economic significance.....	3	Black shales in the Phosphoria formation.....	18
Uranium.....	4	Black shale in the Sharon Springs member, Pierre shale.....	19
Organic matter and oil yield.....	6	Oil shales in the Green River formation in Colorado, Utah, and Wyoming.....	19
Sampling methods.....	6	Shales in foreign countries.....	21
Analytical methods.....	7	Theoretical role of organic matter in oil yield and uranium concentration.....	22
Chattanooga shale and correlatives in the eastern and central United States.....	7	Summary.....	26
Chattanooga shale in the southeastern States.....	8	Literature cited.....	28
Antrim shale in Michigan.....	14	Index.....	43
Chattanooga and Woodford shales in the midcontinent area.....	15		

ILLUSTRATIONS

FIGURE	1. Map of United States showing localities of samples and of black shales.....	2
	2. Possible associations and time of emplacement of uranium with shale constituents.....	5
	3. Relation of oil yield to uranium content of the Chattanooga shale.....	9
	4. Localities represented by sample data in figures 3, 5, 6, 7, and 8.....	10
	5. Relation of oil yield to uranium content, upper unit of Gassaway member of Chattanooga shale.....	10
	6. Uranium content and oil yield, Gassaway member of Chattanooga shale.....	10
	7. Uranium and carbon, Gassaway member of Chattanooga shale.....	11
	8. Relation of specific gravity of oil to uranium content, Chattanooga shale.....	12
	9. Relation of specific gravity of oil to percent of organic matter converted to oil, in oil shales from Brazil, Australia, Manchuria, and South Africa.....	13
	10. Diagrams giving data on oil shales from Brazil and South Africa.....	13
	11. Relation of uranium content to oil yield, Antrim shale.....	14
	12. Relation of uranium and carbon contents, Antrim shale and two other Paleozoic shales.....	15
	13. Relation of uranium content to (A) oil yield and (B) specific gravity of oil, Woodford shale.....	15
	14. Diagrams indicating uranium content is related to phosphate content rather than oil yield in uppermost black shale unit of Cherokee shale.....	17
	15. Relation of uranium contents to oil yields of two black shales of Pennsylvanian age.....	18
	16. Relation of uranium content to (A) oil yield, (B) P ₂ O ₅ , and (C) P ₂ O ₅ and oil in Retort phosphatic shale member of Phosphoria formation.....	19
	17. Relation between oil yield and uranium content in black shale of Late Cambrian age in Sweden.....	21
	18. Relation between uranium and carbon content in kolm from Upper Cambrian shale in Sweden.....	22
	19. Possible relations of uranium content to oil yield of marine black shale as controlled by total organic matter and proportions of humic and sapropelic material.....	26
	20. Humic and sapropelic materials in a shallow sea and uranium content and oil yield of resulting black shale.....	27
	21. Relation of uranium content to oil yield in theoretical black shale unit.....	28

TABLE

TABLE 1. Sampled localities and uranium content, oil yield, and other analyses of black shales.....	31
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URANIUM IN CARBONACEOUS ROCKS

OIL YIELD AND URANIUM CONTENT OF BLACK SHALES

By VERNON E. SWANSON

ABSTRACT

Some black shales contain as much as one hundred times more uranium than other common sedimentary rocks and they also contain organic matter that will yield oil when subjected to destructive distillation. Such shales may be referred to as uraniferous oil shales and have been considered as a potential source of both oil and uranium; oil yield and uranium determinations on more than five hundred samples of these shales are recorded in this report.

Slightly more than half of these samples are from the Late Devonian Chattanooga shale and its partial correlatives in the eastern and midcontinent areas of the United States. In central Tennessee, the upper member of the Chattanooga shale is about 15 feet thick, contains 0.006 percent uranium, and will yield about 10 gallons of oil per ton of shale. Limited data indicate that the Chattanooga shale in Alabama and southern Kentucky, the Antrim shale of Michigan, the New Albany shale of Indiana and northwestern Kentucky and its stratigraphic equivalent in southern Illinois, and the Chattanooga and Woodford shales of the midcontinent area have slightly lesser quantities of both oil and uranium. A channel sample of 5 feet of the Doublehorn shale member of the Houy formation in central Texas indicates that this unit has a uranium content of 0.009 percent and an oil yield of 21.8 gallons of oil per ton of shale.

Some of the marine black shales in the cyclothem of Pennsylvanian age in Illinois, Kansas, and Oklahoma contain between 0.004 and 0.010 percent uranium and yield 8 to 15 gallons of oil per ton of shale, but generally these shales are less than 3 feet thick. Some shale units in the Phosphoria formation of Permian age in southwestern Montana, which are about 10 feet thick, will yield 10 to 15 gallons of oil per ton of shale, but their uranium content of 0.001 to 0.004 percent is relatively low.

The few data available indicate the Sharon Springs member of the Pierre shale of Late Cretaceous age in the Great Plains area has an oil yield of less than 8 gallons per ton of shale and a uranium content of about 0.002 percent. The Green River formation of Eocene age in Colorado and Utah has beds of oil shale tens of feet thick that will yield more than 25 gallons of oil per ton of shale, but the uranium content of these beds is low, generally between 0.0003 and 0.0010 percent.

Both oil and uranium have been recovered in large quantities from the Upper Cambrian black shales of Sweden, which yield about 14 gallons of oil per ton of shale and about 0.023 percent uranium. Some other oil shales from foreign sources that yield 50 or more gallons per ton generally contain about 0.0005 percent or less uranium.

A fair positive relation between oil yield and uranium content exists for some of these shales, particularly for parts of the Chattanooga shale locally and the Antrim shale, but in other shales little or no relation is apparent. In some of the Pennsylvanian shales and in those in the Phosphoria formation the uranium is more closely related to the phosphate content.

Whereas the oil from these shales is inherent to and derived directly from the organic matter, most of the uranium is attached to or precipitated in the presence of organic matter just before or during the time of deposition of the organic-rich sediment. It is suggested that two types of organic matter should be distinguished, the sapropelic type derived principally from algae, pollen and spores, resins, and the fatty tissues of animals, and the humic type which is derived principally from cellulose and lignin or the woody parts of plants. The sapropelic type of organic matter generally yields four or five times more oil than the humic type, but, because of its general resistance to decay, is probably insignificant in the process of concentrating uranium. The humic type of organic matter, either in its solid form or as soluble humic acid extracts, or, indirectly, as it creates a reducing and acidic environment during its decay, is believed responsible for the precipitation or sorption of the uranium in black shales. Only where the proportion of sapropelic to humic type of organic matter remains the same in an otherwise homogeneous black shale will the oil yield and uranium content have a high positive correlation.

INTRODUCTION

During the 1944-54 period of intensive search for sources of uranium in the United States, a part of the effort of the U.S. Geological Survey was devoted to the finding and study of uraniferous marine black shales. Several of the more than one hundred black shale units checked contain more than average amounts of uranium; these were subjected to detailed stratigraphic and geochemical study. Laboratory analyses of several kinds were made on more than five thousand samples of these shales, and it is the purpose of this paper to present some of the analytical data and some of the possible geologic interpretations and economic implications derived therefrom.

In the general geologic sense, many marine black shales may be classed as oil shales. Because of their

URANIUM IN CARBONACEOUS ROCKS

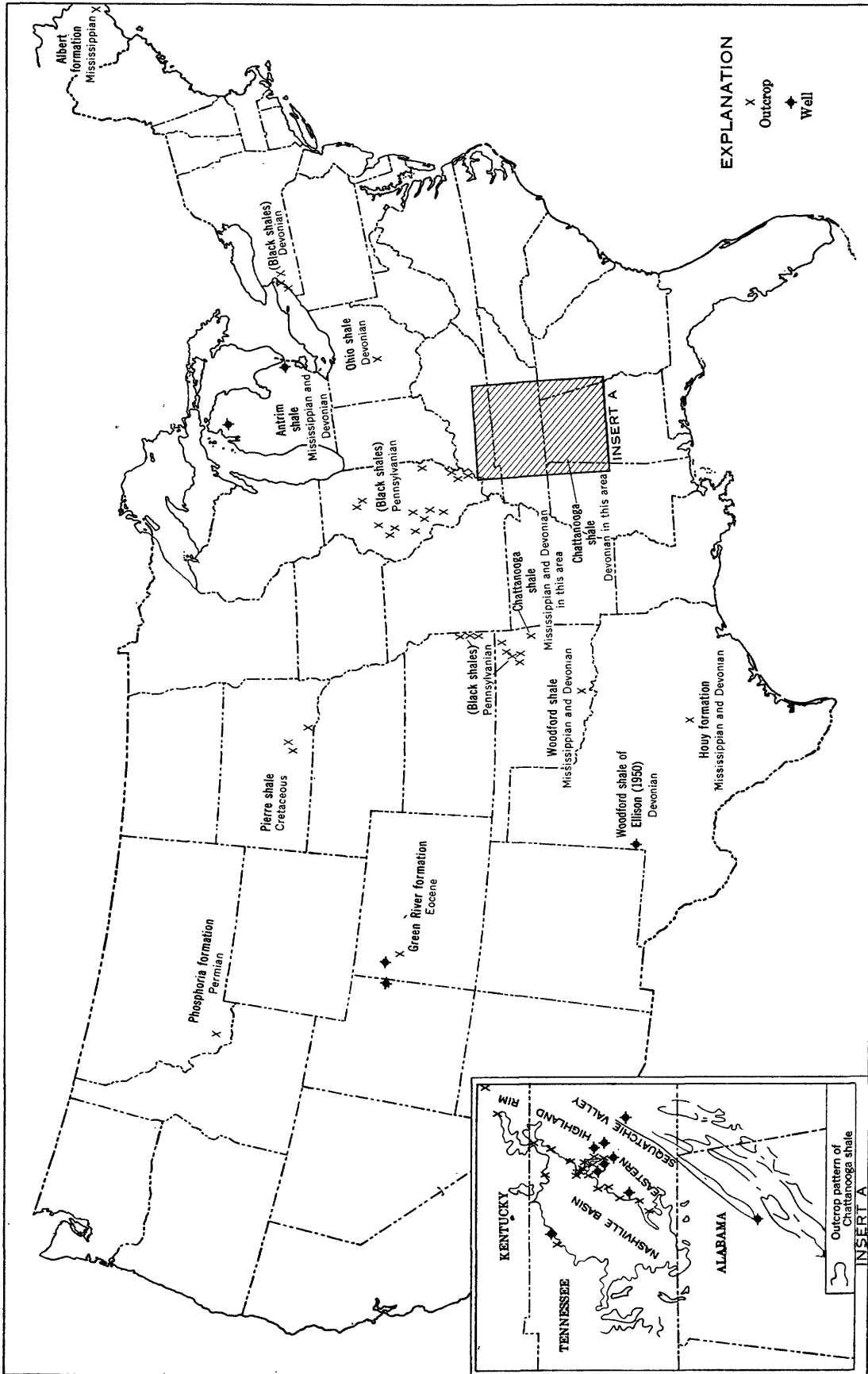


FIGURE 1.—Map of United States showing localities of samples and of black shales for which oil yield and uranium content have been determined.

large amount of carbonaceous organic matter, fluid and gaseous hydrocarbons can be produced from these shales by destructive distillation (pyrolysis). The oil obtainable from shales having a relatively high uranium content logically is considered as a possibly important byproduct if and when the uranium is extracted. Figure 1 indicates those black shales in the United States whose oil yield and uranium content have been determined and shows the localities where these shales were sampled.

The most distinctive feature common to rocks called "black shales," "oil shales," and "carbonaceous shales" is their relatively high content of organic matter. It is not the purpose of this paper to classify and define carbonaceous rocks; thus, only general meanings are ascribed to these lithologic terms. As used here, the three names are used interchangeably; all three rock types are fine grained (with clay- and silt-size particles), are thinly laminated, and generally contain more than 2 percent organic carbon. A marine origin for most of these shales is inferred on the basis of the contained fossils and the lithologic uniformity of the rock over tens or hundreds of thousands of square miles. An arbitrary minimum amount of oil distillable from a carbonaceous shale is not used here in determining when the shale is or is not an oil shale; the fact is implied that little or none of the contained organic matter is soluble in ordinary petroleum solvents, but a large proportion is convertible to artificial petroleum on heating. A shale is here considered uraniumiferous only if it contains 0.002 percent or more uranium through most of its vertical and lateral extent.

In a compilation and summary paper such as this, the work of many persons is represented. Most of the collecting of samples, field study, and laboratory analyses were accomplished by members of the Geological Survey. Hence, this paper should be recognized as a result of a joint effort within the Geological Survey, though the author assumes responsibility for the interpretations made. This report was prepared on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission.

Several samples of Pennsylvanian black shales in Illinois were made available to the author by the Illinois States Geological Survey, for analytical work. For this cooperation, the author thanks particularly J. C. Frye, M. E. Ostrom, and J. E. Lamar. S. P. Ellison, Jr., and V. E. Barnes were helpful in obtaining samples of the Woodford shale equivalent in Texas. The use of unpublished data provided by the U.S. Bureau of Mines and T. B. Dahlman of the Geological Survey of Sweden is also gratefully acknowledged.

GENERAL ECONOMIC SIGNIFICANCE

Tonnages of uraniumiferous black shales in the United States may be calculated in the trillions, and, similarly, the oil that can be recovered from them may be estimated in trillions of barrels. Most of these shales, however, contain recoverable oil in such small quantities, less than 15 gallons per ton, that it is doubtful they will be considered as a source of oil for many decades.

The amount of uranium in these shales is extremely large, reckoned in billions of tons of metallic uranium. In view of the present large high-grade sources of uranium and the probable future demand for the metal, it is also unlikely that these shales will be mined and processed for uranium in the near future.

As most of the shales discussed in this report generally contain less than 15 gallons of oil per ton and less than 0.01 percent uranium, they are far from being competitive with the existing sources of crude oil or uranium. Possibly certain other constituents, such as sulfur and nitrogen compounds, aluminum, and titanium, could be extracted during the processing of these shales and the combined production of several of these, including the oil and uranium, may some day be the critical basis for a profitable venture.

The Gassaway member of the Chattanooga shale in a part of the central Eastern Highland Rim of Tennessee can be cited as an example of a possible low-grade and common source of oil and uranium. This unit averages 15 feet in thickness and contains an average of 0.0060 percent uranium; an average of 10 gallons of oil per ton can be recovered from it. Computed on a square mile basis, this unit comprises an "ore body" of about 30 million tons of shale. The shale in this square mile contains about 1,800 tons of metallic uranium; or, for sake of comparison, this "ore body" contains uranium nearly equal to that in a million-ton ore deposit, of which less than 10 were known in the United States at the beginning of 1957 (U.S. Atomic Energy Commission, 1957, p. 7).

In the course of processing the shale for its uranium, the shale probably would be retorted, and the extracted oil would be a significant byproduct. Over 7 million barrels of oil could be produced from the shale in the square mile mentioned above, an amount of oil equivalent to the total estimated production of a fair-sized oilfield. Large amounts of sulfur and nitrogen compounds, and possibly other materials also, might be economically recovered to add to the total value of the shale.

This example of the potential products in a specific shale is not purported to be representative. Rather,

it cites a shale in the United States that is known to have a uniformly high uranium content over hundreds of square miles and for which much detailed geologic and chemical information is available. The cost of mining and extraction is economically prohibitive today, but in light of the history and exploitation of large deposits of low-grade ores in the iron and copper industries, the importance of shales as possible sources of petroleum and uranium will increase in the decades ahead.

URANIUM

The average uranium content of all shales is estimated to be between 0.0003 and 0.0004 percent (3 to 4 parts per million), which is about the same as for granites (Holland and Kulp, 1954, p. 203). Carbonaceous shales, here arbitrarily defined as those that contain 2 percent or more organic carbon, have a uranium content that generally ranges from 0.000X to 0.0X percent. However, very few contain more than 0.005 percent; the author estimates that the average for all carbonaceous shales is probably about 0.0008 percent.

The highest uranium content known in a marine black shale in the United States is from a correlative of the Chattanooga shale in northern Arkansas; a small selected sample of a layer less than 1 inch thick, made up largely of compacted opaque coaly attritus, contained 0.7 percent uranium. In southern Sweden, the black organic-rich kolm lenses which are sparingly distributed through parts of the Cambrian and Ordovician alum shales contain about 0.4 percent uranium, but the "richest" shale unit, which in the Billingen area is about 10 feet thick and contains the kolm, has an average content of about 0.03 percent uranium (T. B. Dahlman, oral communication, 1957).

In the United States, parts of a few black shale units of Pennsylvanian age in the midcontinent area locally contain between 0.010 and 0.017 percent uranium, but these more uraniferous beds are generally only 1 to 2 feet thick. In central Tennessee, the Gassaway member of the Chattanooga shale contains 0.0060 percent uranium over hundreds of square miles (Kehn, 1955); this unit is about 15 feet thick and is of Late Devonian age.

The lateral distribution of the uranium in these black shales is generally uniform, varying less than a few thousandths of one percent over hundreds, and in some areas thousands, of square miles. Generally, the greater the ratio of organic to mineral material, the greater is the uranium content of these widespread marine shales; the less the amount of calcium carbonate, the greater is the uranium content; and the

slower the interpreted rate of deposition, the greater is the uranium content (also see McKelvey and Nelson, 1950, p. 38-39). These generalizations can be applied successfully in the study of some shales, but, as is the case with most generalizations in geology, they must always be tempered and adjusted by other geologic factors when a particular unit in a particular area is studied in detail.

The uranium in marine black shales may have been localized and incorporated in several ways, 12 of which are shown on figure 2. Five types of material are involved, namely, the resistates, clay, organic material, phosphatic material, and hydrogen sulfide as represented indirectly by iron sulfide minerals. The emplacement of the uranium in and with these shale components began before erosion of the original source rock and probably ended some time after sediment deposition during an early stage of diagenesis. Because most of the uranium accumulated with the sediments, it is regarded as syngenetic.

Of the 5 types of material indicated as being genetically associated with uranium in marine black shales, 2 types, the vegetal and the phosphatic materials, probably account for more than 90 percent of the total amount of uranium. The proportion of uranium associated with these two types differs greatly from one shale to the other; the Chattanooga shale of Tennessee might be considered as one extreme, where the organic matter holds or is associated with probably in excess of 90 percent of the uranium, and the phosphate only a few percent. At the other extreme are the phosphate-rich units of the Phosphoria formation of Idaho where the reverse proportion holds.

Phosphate, in the form of scattered nodules, pellets, oolites, thin layers, and discrete microscopic grains of carbonate-fluorapatite, is a common and distinctive component of most marine black shales. The uranium in phosphate is tetravalent and is believed to have been substituted isomorphously for calcium (Altschuler, Clarke, and Young, 1954). Some of this phosphatic material may contain as much as 0.1 percent uranium, but the general range is 0.00X to 0.01X.

Some of the uranium in the organic matter, which constitutes as much as 25 percent by weight of some shales, may have been absorbed during plant growth, but, as will be discussed later, most of it is believed to have been directly precipitated or adsorbed in a stable form as disseminated uranium dioxide or as a metal-organic compound on products of plant decomposition or disintegration.

The chemical conditions that control the preferential attachment of uranium to the phosphate or the organic material in a common depositional environment have not been clearly determined. It is the

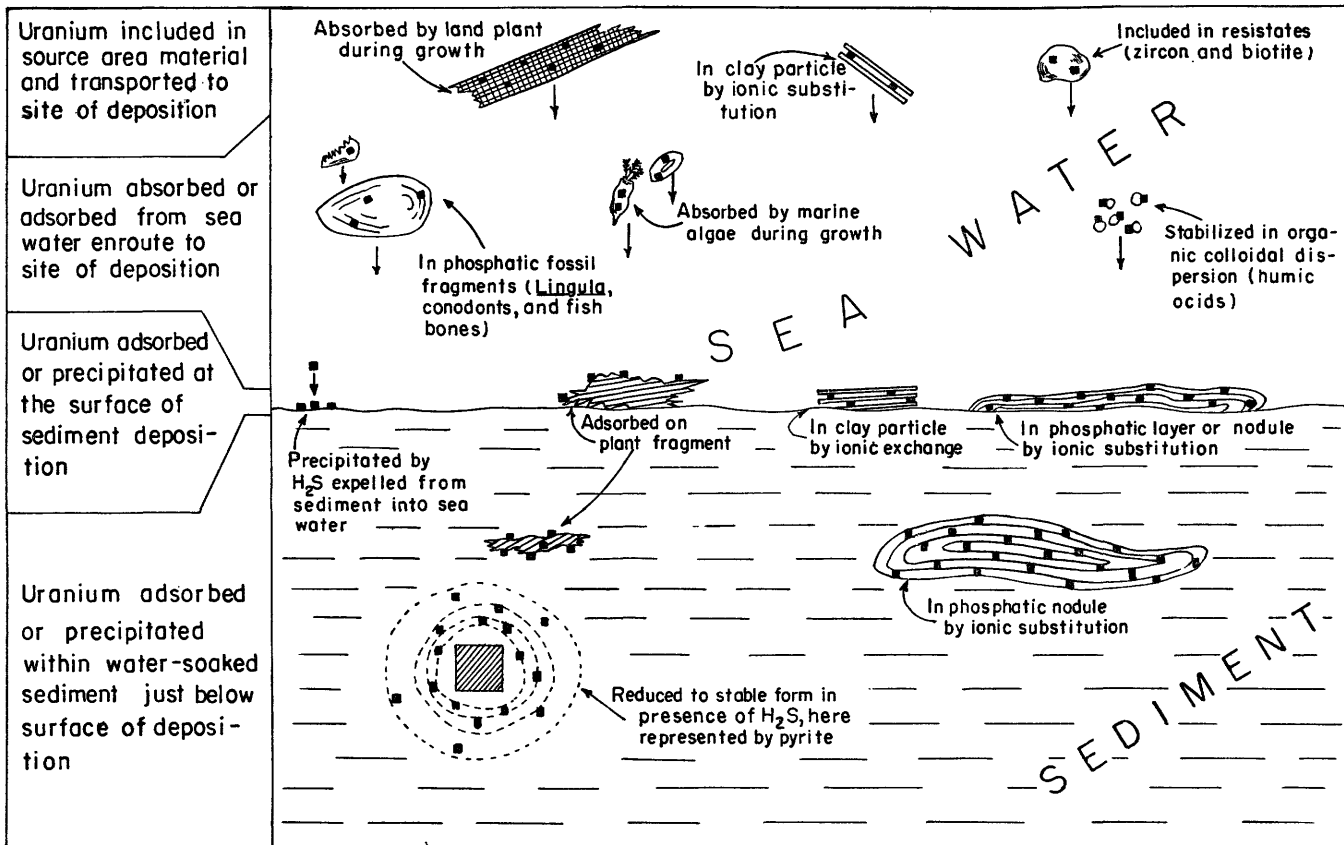


FIGURE 2.—Diagrammatic sketch showing possible associations and time of emplacement of uranium with common constituents of marine black shales. Uranium represented by black squares.

writer's opinion that if the phosphate forms at or very near the surface of deposition, the phosphate captures the available uranium more readily than does the organic matter; the organic matter either incorporates most of its uranium in stable form prior to reaching this sphere of competition with phosphate or captures most of the uranium where phosphate precipitation is minimal. That phosphate that is precipitated and forms concretions a few inches to several feet below the surface of deposition commonly contains less uranium than the surrounding organic material; the interstitial water from which this phosphate is precipitated probably was earlier depleted in its soluble uranium.

The resistates and the clays are believed to be of minor importance in accounting for the total uranium in marine black shales. Zircon, sphene, and monazite, the most important uraniferous resistates, make up less than 1 percent of most shales, and, though they may contain from a few hundredths to a few tenths percent uranium, they probably contribute, at most, only 1 or 2 parts per million (0.000X percent) to the total uranium in most marine black shales. The clays, which comprise more than 50 percent of some shales, are believed to contribute a similarly minute part of the total uranium content.

The generation of hydrogen sulfide, represented in many shales by pyrite, is a part of the process of decay of organic matter which produces a reducing acidic chemical environment conducive to uranium precipitation. The hydrogen sulfide is released either from sulfur-bearing organic matter or from sulfate ions in sea water by anaerobic or sulfur-reducing bacteria. Pyrite itself, though abundant in most uraniferous shales, is not chemically associated with the uranium but is simply precipitated simultaneously with uranium oxide in the presence of decomposing organic matter.

Most of the uranium in marine black shales was derived from ancient sea water, and therefore the amount of uranium available in sea water was an obviously important factor in controlling the amount of uranium deposited with these sediments. Both organic matter and phosphate are uranium acceptors, but if these substances accumulated in water depleted in uranium, they will contain no uranium; or, if the influx of uranium to these waters was erratic, a positive relation between the amounts of uranium and one or both of these substances could not be expected. The supply and availability of uranium generally

can be considered as more or less constant, however, because the volumes of sea water in which black shales were deposited probably were very large, because uranium was and is highly soluble in normal sea water and thereby widely distributed, and because the net contribution of soluble uranium from the many and varied sources would not change appreciably during the period of black shale deposition.

ORGANIC MATTER AND OIL YIELD

The amount of uranium in a black shale may be directly related to the amount of organic matter present. Because the organic matter yields oil on pyrolysis, an indirect but positive relation may exist between the uranium content and oil yield of a shale. The recoverable uranium and oil are of potential economic interest; hence, the general tenor of this paper will be to relate these two constituents. This approach, however, is not intended to result in the establishment of widely applicable principles on the common geologic and geochemical history and occurrence of the two constituents in shales. The history of accumulation, the type and amount of organic matter, the chemical makeup, and the amounts of other constituents present involve numerous and complex variations, only a few of which are completely understood at this time.

The carbonaceous matter in black shales ranges from material that may have remained almost unchanged in form and composition since it was deposited, to material that may have been radically changed in composition and whose source and parent material is unknown. Regardless of its origin and subsequent history, most of this carbonaceous material will yield oil on destructive distillation, and if this carbonaceous matter is incorporated in shale, the rock can be loosely termed an oil shale.

Without invading the complex subject of classifications of this organic material, several factors that are pertinent to the understanding of the type and oil yield of the organic matter in the shales are discussed below. With the exception of the oil shales in the Green River formation of Eocene age in Colorado, Wyoming, and Utah, all the shales discussed are of marine origin. Most of the organic matter in all the shales is believed to be of plant origin, and most of the organic matter in these shales is believed to have been but little altered, with the exception of physical comminution and compaction, since it was deposited.

The catch-all term "kerogen" has been used to refer to that organic matter in oil shales that will yield volatile hydrocarbons when subjected to destructive

distillation. For the purpose of this discussion, however, the writer prefers to divide the organic matter that includes kerogen into two major types, sapropelic (predominantly algal remains) and humic (mainly degraded vascular or woody plant tissues). Most oil shales contain both types of organic material, but the general proportions of each in a shale are believed to be important controlling factors in determining the oil yield. The subjectiveness of this point is clearly recognized, in that the amount of structureless unidentifiable organic matter in oil shales greatly exceeds the amount that can be determined to be of either algal or vascular-plant origin.

Dulhunty (1944, p. 32) stated that fossil algal material (torbanite) has an oil yield on pyrolysis of 60 to 90 percent by weight; the coals, which are predominantly made up of vascular plant debris, yield only 15 to 40 percent. Some samples of torbanite oil shales of New South Wales have yielded as much as 200 gallons of oil per ton of shale, whereas coals rarely yield more than a few tens of gallons per ton except when artificially hydrogenated. It may be deduced then that an oil shale having a large proportion of algal matter will have a greater oil yield than one having a large proportion of coaly or humic matter. This and other significant characteristics of organic matter bearing on the oil yield and uranium content are discussed in more detail on p. 22-26.

SAMPLING METHODS

This report is based primarily on the analyses for oil yield and uranium content of 526 samples, a total of over 1000 chemical determinations (table 1, p. 31-41). Determinations for oil yield and equivalent uranium were available for an additional 260 samples, and analyses of some shales solely for uranium are noted in the text. Thus, over 800 samples, collected and analyzed individually, are represented in this report.

Most of the shale samples represented by analytical data were collected at the outcrop and are channel samples of 1 foot or more of shale. The samples were taken in most cases to represent specific lithologically homogeneous units; where more than one sample was collected within a stratigraphic unit, the analytical data were weighted according to thickness of sampled interval in calculating an average uranium content and oil yield for that unit. In a few cases, the samples were made up from either vertical splits of well cores or chip samples from well cuttings; a few special samples represent a unique lithologic type and are considered "selected" samples. With the exception of core, chip, and selected samples, the average weight of samples collected was about 5 pounds.

Because most of the samples were collected at outcrops, changes in oil yield and uranium content of the rock due to weathering should be considered. Weathering breaks down the organic matter by oxidation; thus, other factors being equal, the more weathered the shale, the less the oil yield. For example, a sample of surficial weathered shale from the Mahogany ledge of the Green River formation assayed 12.8 gallons of oil per ton, whereas a sample of unweathered shale taken 2 feet behind the surface assayed 45.5 gallons per ton (Guthrie, 1938, p. 99; similar data, Stanfield and others, 1951, p. 20-22). Similarly, samples of weathered Chattanooga shale taken from an old road outcrop in eastern DeKalb County, Tenn., yielded an average of 2.2 gallons of oil per ton of shale; samples of shale representing the same stratigraphic interval, taken from a core drilled a few hundred feet away, yielded an average of 11.8 gallons of oil per ton.

The changes in the uranium content of a shale due to weathering are more complex. The oxidation and addition of water involved in the weathering process readily cause the decomposition of the abundant iron sulfides in carbonaceous shales. These decomposing sulfides produce oxidizing sulfuric-acid waters that readily take much of the disseminated uranium into solution. If these acid waters leach out and transport the uranium away from the outcrop, the weathered shale contains less uranium. But commonly the uranium is retained and even concentrated in the hydrous ferric and ferrous sulfate minerals precipitated on the surface of the outcrop. Thus, deeply weathered outcrop samples of Chattanooga shale may contain from 0.0020 to 0.0040 percent more or less uranium than a "fresh" sample from the same unit.

In compiling the data used in this report it was impossible to establish quantitatively the magnitude of the weathering factor for each sample. In general, the samples are considered to be unweathered shale, and any "weathering factor" is ignored.

ANALYTICAL METHODS

Most of the chemical determinations used in the preparation of this report are for uranium content and oil yield (table 1). Where available, analyses for other constituents, for example percent organic carbon and P_2O_5 , are also included in the table.

Each sample submitted to the laboratory was crushed to a coarse-mesh size, and the sample was split into two parts; one split was then further crushed to -8 mesh for the determination of oil yield, and the other split was crushed to -80 mesh for the uranium determination. For the oil determination, ap-

proximately 125 grams are needed; for the uranium determination, 1 gram is sufficient. Two "raw shale" splits of each sample, about $\frac{1}{2}$ pint of -20 mesh and a similar quantity of -80 mesh, were retained and stored, for use in additional analysis, either in the Survey's laboratory in Washington, D. C. or in the one in Denver, Colo.

Most of the determinations of oil yield were made by the modified Fischer retort assay method (Stanfield and Frost, 1949); the oil-yield determinations on the Antrim shale and on the core samples of the Green River formation were made by the photometric method devised by Cuttitta (1953a). The reproducibility of these determinations of oil yield is considered to fall within ± 0.5 gallons of oil per ton of shale; all determinations of less than 5 gallons of oil per ton are estimated figures.

All the uranium analyses were made using the fluorometric method described by Grimaldi and Levine (1954). Most of the determinations for uranium listed in this paper were reported in percent by weight to the fourth decimal place (for example, 0.0053 percent), but the probable error is estimated as ± 0.0005 percent. The percent equivalent uranium was determined for most samples, but, because of the low total radioactivity in the sampled shales and the variable abundance in most shales of the radioactive isotope of potassium (K^{40}) and because of the fact that radioactive equilibrium is upset by changes due to weathering, these data are not considered reliable for any statistical treatment.

CHATTANOOGA SHALE AND CORRELATIVES IN THE EASTERN AND CENTRAL UNITED STATES

The Chattanooga shale is a part of an extensive unit of marine black shale of Late Devonian and Early Mississippian age that extends with remarkably uniform lithology and thickness over hundreds of thousands of square miles of the North American continent. The New Albany, Ohio, Antrim, Dunkirk, Mountain Glen, Woodford, and Lodgepole are some of the names that refer to stratigraphic equivalents or partial equivalents of the Chattanooga shale.

In the eastern and central United States the Chattanooga shale and its stratigraphic equivalents are estimated to have an average uranium content of 0.003 percent and an average oil yield of about 5 gallons per ton of shale. Its thickness generally ranges from 0 to 100 feet and averages about 40 feet. The amount of uranium and oil that can be extracted from the Chattanooga shale in a small area of east-central DeKalb County, Tenn., is discussed in more detail on p. 3.

CHATTANOOGA SHALE IN THE SOUTHEASTERN STATES

Though the Chattanooga shale is less uraniferous than, for example, the alum shales of Sweden, it contains more uranium per unit of thickness over a wider area than other known shales in the United States. The area where the uranium content is uniformly the highest and mining conditions most favorable is in the central part of the Eastern Highland Rim of the Nashville Basin, Tenn. (fig. 1); this shale of high uranium content extends eastward for 75 miles beneath the Eastern Highland Rim to the Sequatchie Valley. The distribution of uranium and the mineralogy of the shale were described by Brown (1956) and Bates and Strahl (1957). The geology of the Chattanooga shale in this area and parts of adjacent states was described in detail by Hass (1956) and by Conant and Swanson (written communication, 1959).

In general, the Chattanooga shale has 5 lithologic units, the lower 2 composing the Dowlstown member and the upper 3 the Gassaway member (fig. 3). These 5 units, from oldest to youngest, are: (1) a black shale unit, commonly 5 to 8 feet thick, with a basal sandstone 1 or 2 inches thick; (2) a unit, about 8 feet thick, of gray shale with some interbedded black shale; (3) a black shale unit about 7 feet thick; (4) a unit characterized by gray quartz siltstone interbedded with black shale, generally 1 or 2 feet thick; and (5) a black shale unit at the top, about 5 feet thick. Where the Chattanooga shale decreases in thickness, the decrease generally is by loss of successive units from the bottom, so that where the shale is only a few feet thick, only the top black shale unit of the Gassaway member is represented. Lateral changes in thickness are gradual, commonly only a few inches per mile, and areas of hundreds of square miles exist where changes in thickness and lithology are small.

Correlation of the uranium determinations of some 3,000 samples with the stratigraphic features of the Chattanooga shale has established field criteria for locating those parts of the shale that contain the most uranium. Those units that have the most uranium characteristically are the "blackest" and have the most organic matter, contain the least calcium carbonate, and can logically be interpreted as having been deposited at the slowest rate; abundance of pyrite, excellent fissility, and paucity of thin quartz siltstone layers are secondary criteria. Beds an inch or less in thickness contain 0.010 percent uranium for distances of a mile or more; the upper unit of the Gassaway member of the Chattanooga shale, about 5 feet thick, contains about 0.008 percent uranium over an

area of several tens of square miles; and, similarly, the entire Gassaway member, about 15 feet thick, contains about 0.006 percent uranium over hundreds of square miles.

The fact that the Chattanooga shale yields oil when subjected to pyrolysis has long been known; it was the stratigraphic correlative of this shale in the Ohio River Valley that was first commercially used to produce oil in 1857. Guthrie (1938) summarized the potential recovery and chemistry of the oil from the Upper Devonian and Lower Mississippian shales in the eastern United States; some of the shales will yield between 18 and 26 gallons of oil per ton.

When the exploitation of the uranium in the Chattanooga shale in central Tennessee was considered, the recoverable oil was anticipated to be an important byproduct; consequently, about 325 of the thousands of samples analyzed for uranium also were analyzed for oil yield. By reason of the emphasis in studies on the areas where the Chattanooga contains the most uranium, most of these oil assays were made on samples from the Eastern Highland Rim in Tennessee.

From the oil determinations reported previously in the literature (Ashley, 1917; Crouse, 1925; Guthrie, 1938; Lamar, Armon, and Simon, 1956) and from those of this report, the broad regional and vertical variations in oil yield of the Chattanooga shale and its stratigraphic equivalents are difficult to interpret. In general, parts of the shale probably would yield 10 or more gallons of oil per ton of shale over tens of thousands of square miles in Tennessee, Kentucky, Ohio, southern Illinois, and Indiana. Along most of the Eastern Highland Rim in Tennessee, where more numerous data are available, the 15-foot thick Gassaway member will yield between 5 and 12 gallons of oil per ton, with some channel samples of parts of this member yielding 15 to 17 gallons of oil per ton.

There is no question that, in general, as the oil yield of the Chattanooga shale increases, the uranium content also increases; the simple contrasting of pertinent data on a light-gray shale with that on a dense black shale best illustrates this generalization. However, if all the oil and uranium determinations on individual samples (table 1) of the entire formation from Tennessee and Kentucky are plotted, a scatter diagram with randomly distributed points is the result, and no relation between uranium and oil is indicated. Only when the data are organized and plotted for individual stratigraphic units within small geographic areas do they show the positive relationship between oil yield and uranium content.

The relation that exists between uranium content and oil yield in the Chattanooga shale and the general

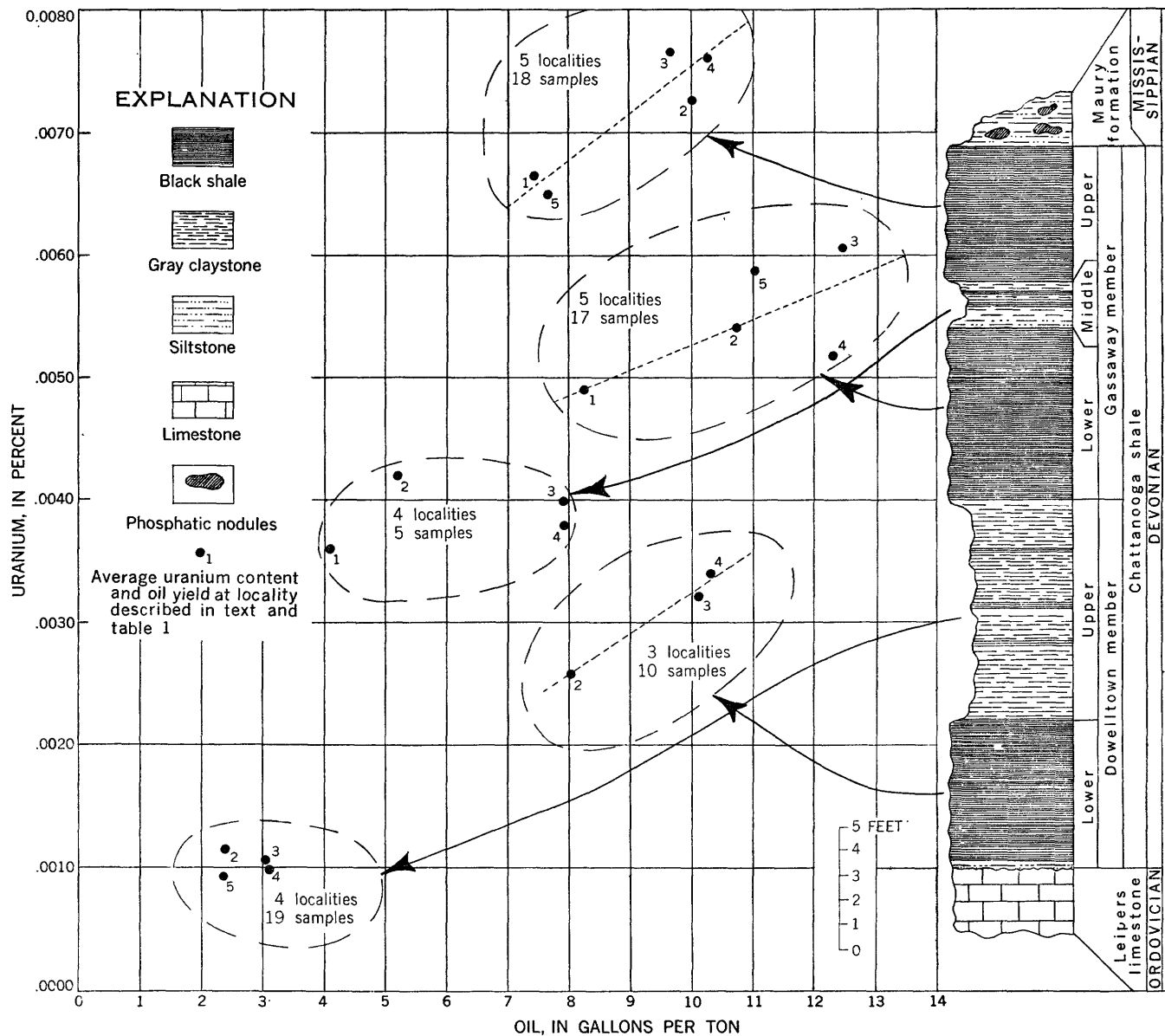


FIGURE 3.—Relation of oil yield to uranium content of the 5 stratigraphic units of the Chattanooga shale at 5 localities in DeKalb County area, central Tennessee. (See fig. 4.)

lithologic and stratigraphic factors that control them are indicated in figure 3. As shown in this figure, each of the five stratigraphic units in the Chattanooga shale is distinguished by a different relation between uranium content and oil yield; the figure further shows that the relation for each stratigraphic unit is fairly consistent from one locality to another. The area of the 5 localities of figure 3 (fig. 4), in and near DeKalb County in east-central Tennessee, was selected because it had several closely spaced localities for which reliable stratigraphic and analytical data were available for each of the five stratigraphic units. Figure 5 indicates the relation of oil yield to uranium content for all the 18 samples from the upper unit

of the Gassaway member in this area and best illustrates the close relation between the two components of the shale in a thin unit within a small area. Figure 6 shows the relation of oil yield to uranium content for all the samples (41) of the entire Gassaway member in this same area, but lumping of the data of several stratigraphic units results in less well defined relation.

In the field, the most obvious characteristic that can be related to the amount of uranium and oil in the Chattanooga shale, as indicated by analytical data, is that of color, or "blackness," which is a crude measure of the amount of organic matter in the shale. Thus, the upper unit of the Dowelltown member, which is

URANIUM IN CARBONACEOUS ROCKS

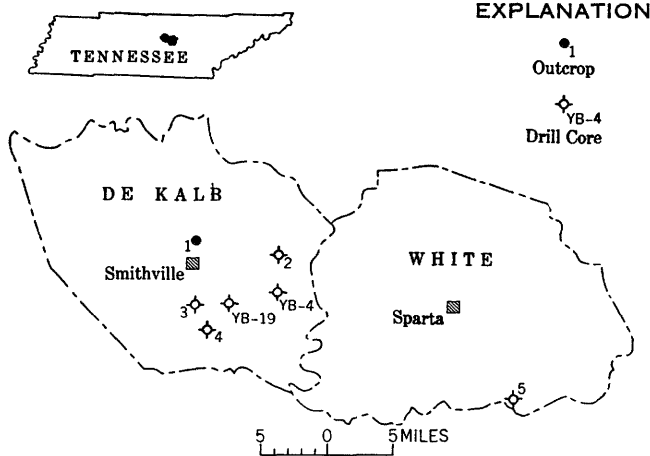


FIGURE 4.—Map showing localities in DeKalb County area, Tennessee, that are represented by sample data in figures 3, 5, 6, 7, and 8.

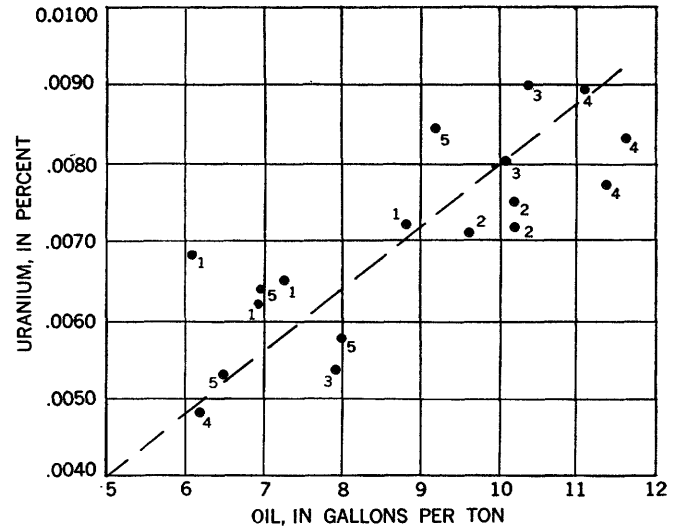


FIGURE 5.—Relation of oil yield to uranium content of 18 samples representing upper unit of Gassaway member of Chattanooga shale at 5 localities in DeKalb and White Counties, Tenn. Numbers indicate localities from which samples were obtained. (See fig. 4.)

light gray, has the lowest uranium content and oil yield. On closer observation of the rock, it is also obvious that some parts of the formation have a greater proportion of clastic minerals (for example, thin layers of quartz siltstone) and consequently have less organic matter. Thus, the middle unit of the Gassaway member has a relatively low oil yield and uranium content.

Physical differences among the three units of massive black shale (the lower unit of the Dowelltown and the lower and upper units of the Gassaway) are

not readily observed in the field. All 3 contain abundant organic matter, generally about 20 percent. Only on detailed study of cores and of thin sections are small differences observed in proportion of organic matter to clastic minerals, in degree of sorting, and possibly in type of organic matter. If these lithologic parameters were recorded for each sample, differences in uranium content and recoverable oil between sam-

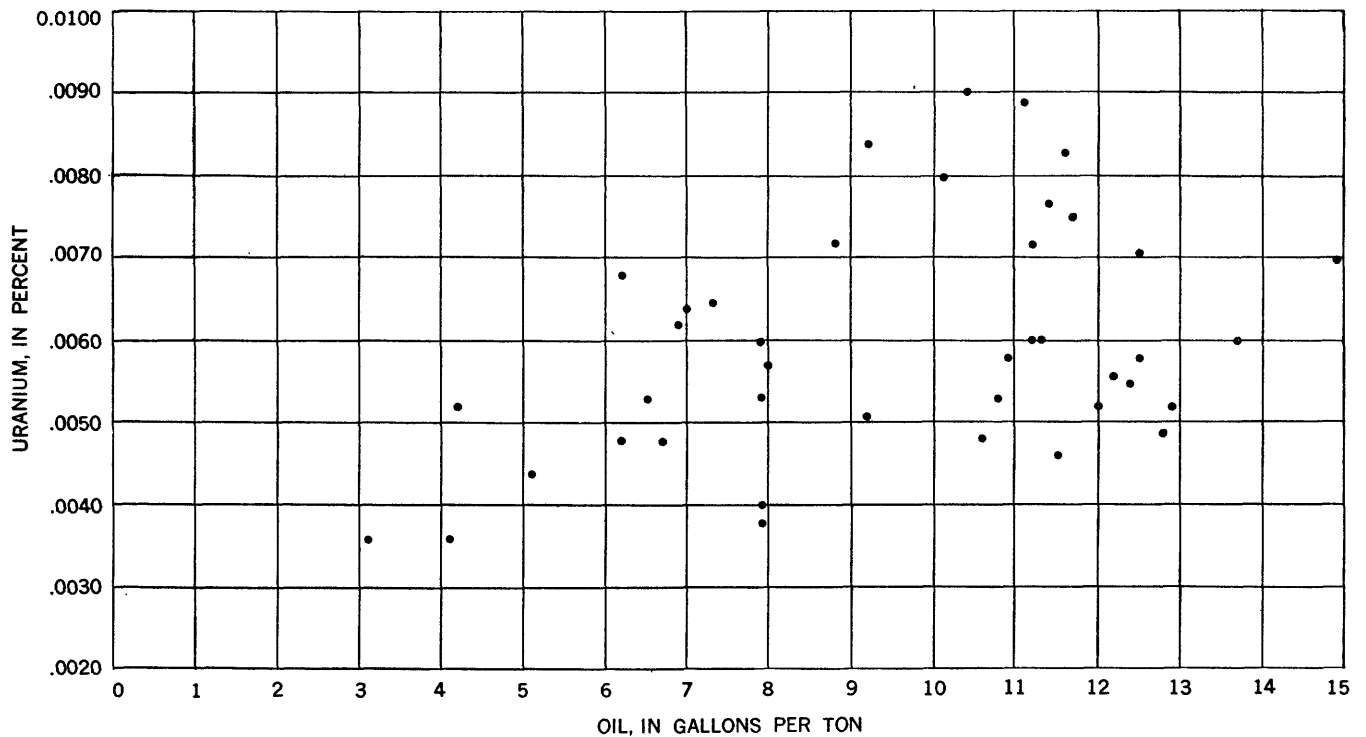


FIGURE 6.—Relation of uranium content to oil yield in 41 outcrop samples of Gassaway member of Chattanooga shale at 5 localities, DeKalb County area, Tennessee. (See fig. 4.)

ples presumably could be explained more clearly.

Bates and Strahl (1956, p. 1669) showed that the uranium content of the Gassaway member can be directly correlated with the amount of carbon, but that the correlation coefficient (0.69) is not exceptionally high. Using their data (Bates and others, 1956, p. 38-39), the relation between uranium and carbon in the shale from 2 drill cores (YB-4 and YB-19) taken in DeKalb County, Tenn. is shown in figure 7. Again, a direct relation is suggested as it is when uranium content and oil yield are compared (figs. 6, 7). Neither carbon nor oil is the exact key, however, to the amount of uranium in the shale.

The proportions of the two main types of organic matter, the humic and the sapropelic, may be more indicative of the oil yield and uranium content than are total carbon and oil yield. The only data available that can be presented to support this concept are from a hand-picked sample composed of *Foerstia* sp., a planktonic marine alga, which was separated from the Huron member of the Ohio shale, a partial correlative of the Chattanooga in Ohio; and from a sample of a fragment of coalified driftwood of the fossil land plant *Callixylon* from the Chattanooga shale in Tennessee (J. M. Schopf, written communication, 1953). Both are common identifiable con-

stituents in the Chattanooga shale and may be considered representative of the sapropelic and humic types of organic matter, respectively.

According to Schopf (written communication, 1953) the *Foerstia* sample contained 0.0016 percent uranium and yielded 26.5 gallons of oil per ton, the sample having an ash content of 55.8 percent.

The *Callixylon* sample contained as much as 0.033 percent uranium (Breger and Schopf, 1955) and yielded 18.3 gallons of oil per ton, but this material had an ash content of only a few percent.

For the purpose of comparison, the oil yield of these two end-member types of organic matter may be computed on an ash-free basis; thus, the *Foerstia* sample, a sapropelic type, would have an oil yield of 59.9 gallons per ton, and the *Callixylon* sample, a humic type, about 18.5 gallons per ton. These figures are in general agreement with the oil yield of the different types of organic matter (Francis, 1954, p. 400) that would be here considered sapropelic and humic. Assuming that the uranium content is related to the organic matter, and that both types of hypothetically pure organic matter have 1 percent ash, the *Foerstia* sample would have 0.0036 percent uranium, and the *Callixylon* sample 0.033 percent.

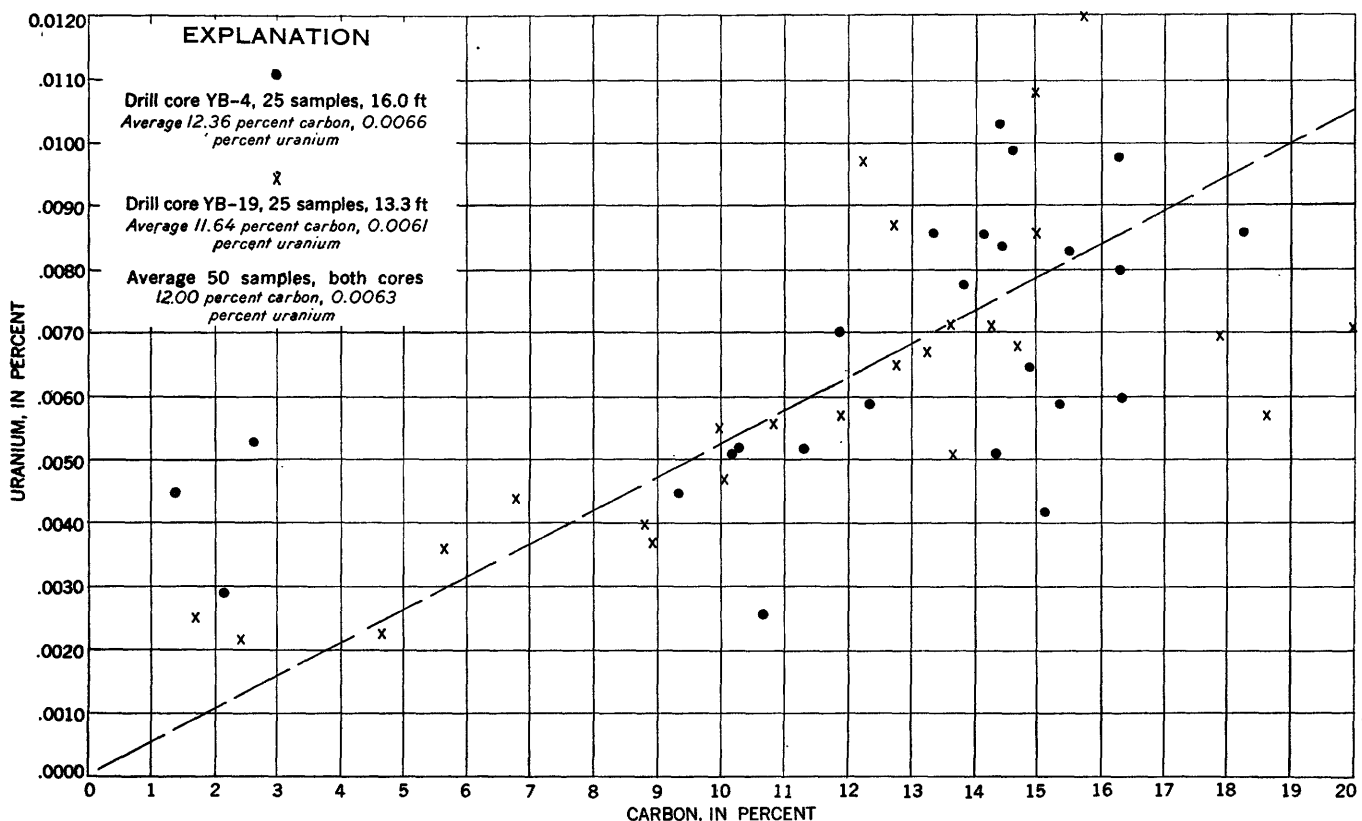


FIGURE 7.—Relation of uranium to carbon in 50 samples from 2 drill cores of Gassaway member of Chattanooga shale, DeKalb County, Tenn. (See fig. 4.) Analytical data on Geological Survey cores by Pennsylvania State University (Bates and others, 1956, p. 38-39).

Extrapolating from these postulations, one could in turn attempt to estimate the general ratio of sapropelic to humic material in the Chattanooga shale. For example, general averages for the uranium content and oil yield of the Chattanooga shale in Tennessee may be considered 0.004 percent and 7 gallons per ton, respectively. Assuming that the average content of organic matter in the shale is 20 percent, then the organic matter would be composed of about 50 percent sapropelic matter and 50 percent humic matter.

Another example, though even more tenuous, of how such data might be used is seen in attempting to relate the uranium content (0.0060 percent) to the oil yield (9.5 gallons per ton) of the Gassaway member of the Chattanooga shale in the central part of the Eastern Highland Rim of central Tennessee (fig. 6). Organic matter constitutes 20 percent of this rock, and, hence, hypothetically the pure organic matter would contain 0.030 percent uranium and yield 47.5 gallons of oil per ton. By analogy to the data on the *Foerstia* sample, about 60 percent of the organic matter should be sapropelic to accord with the oil yield of 47.5 gallons per ton; however, the uranium content could not be explained even if all the organic matter is humic, as indicated by the data on the *Callixylon* sample. The discrepancy could be explained by assigning a 0.07 percent uranium content to the humic fraction; more likely, both the oil yield of the sapropelic material and the uranium content of the humic fraction have higher values than indicated by the meager data on the samples of *Foerstia* and *Callixylon* material. Worthy of special note with regard to the high oil yield of the *Foerstia* sample, however, is that White and Stadnichenko (1923) long ago recognized this alga in Devonian black shales as one of the main "mother plants" of the oil that can be derived from these shales; the abundant spore cases, with their similar "waxy-resinous" protective coatings were also noted as source substances for the extractable oil.

The specific gravity of the oil extracted from the Chattanooga shale seems to increase as the uranium content of the shale increases (fig. 8). The reasons for this relation are not known, and in view of the information presently available, any possible explanation that might be put forward must be viewed as very tentative.

If the uranium content of the Chattanooga shale were controlled largely by the type of organic matter in the shale and if the specific gravity of the oil distilled from this shale were similarly controlled, a positive relation between the uranium content of the shale and specific gravity of the oil from the shale would be expected.

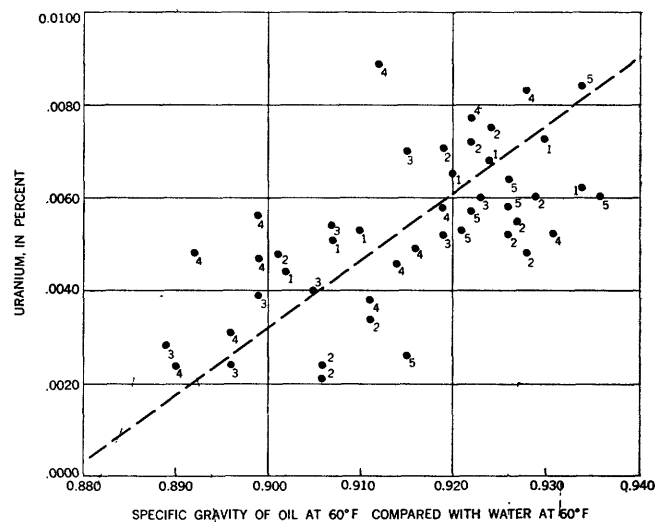


FIGURE 8.—Relation of specific gravity of extracted oil to uranium content, as determined on 46 samples of Chattanooga shale from 5 localities, DeKalb County area, Tennessee. (See fig. 4.)

Determination of specific gravity of the oil extracted from a shale is part of the routine modified Fischer assay method (Stanfield and Frost, 1949). In this assay method, a 100-gram sample of ground shale is heated from room temperature to 500° C in 40 minutes and maintained at this temperature for an additional 20 minutes. If the shale is heated to higher or lower temperatures, or for much longer or shorter periods, the same shale will yield oils having different specific gravities; but the fact that different shale samples produce oils of different specific gravities under standard time and temperature conditions may indicate fundamental differences in the type or combination of types of organic matter among the shale samples. These differences in the organic matter might be substantiated by microscopic observation, solvent properties, ultimate coal analyses, infrared spectrographic analyses, and many other ways, but these observations and analyses are not available for the described Chattanooga shale samples. Information on other shales can be presented, however, to illustrate the probable control that the type of organic matter contained has on the specific gravity of the oil produced from a shale.

W. C. Kommes and J. W. Smith (U.S. Bureau of Mines, written communication, 1952) made oil and organic-matter determinations on several suites of samples of oil shales of foreign countries. From their data, the approximate percentage of organic matter converted to oil can be estimated. A graph of the estimated data plotted against the specific gravities of the respective oils (fig. 9) indicates that within a suite of samples the greater the percentage of organic matter converted to oil, the lighter the oil. In terms

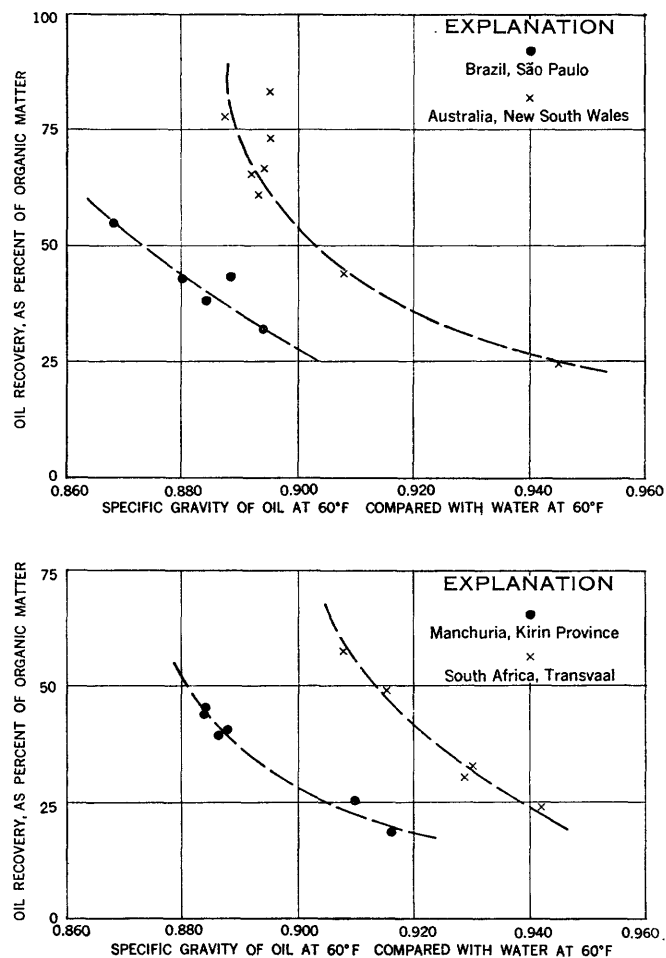


FIGURE 9.—Relation of specific gravity of extracted oil to oil recovery, as percent of organic matter converted to oil; based on Fischer assays of samples of oil shale from Brazil, Australia, Manchuria, and South Africa. (Data from W. C. Kommes and J. W. Smith, U.S. Bureau of Mines, written communication, 1952.)

of the types of organic matter previously discussed, where the sapropelic type of organic matter has a much greater oil yield than the humic type, in general 4 or 5 times as much, the logical conclusion would be that the greater the percentage of sapropelic substance in the total organic matter, the lower the specific gravity of the derived oil. Conversely, the greater the percentage of humic substance in a shale, the higher the specific gravity of the derived oil will be.

Support for these conclusions is found by observing the relation of the specific gravity of the oils extracted from the shales to the hydrogen content of the organic matter. Plotted data of 2 of the suites of samples of figure 9, the shales from Brazil and South Africa, show that as the hydrogen content of the organic matter increases, the oil becomes lighter (fig. 10). Figure 10 also shows a positive relation between hydrogen content of the organic matter and the amount of that organic matter converted to oil.

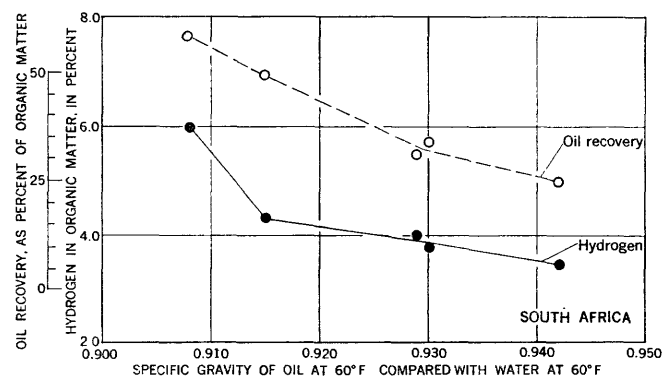
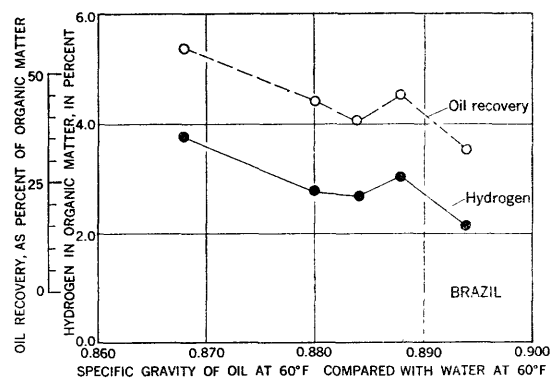


FIGURE 10.—Diagrams indicating that the specific gravity of oil extracted from shale is related both to the hydrogen content of the organic matter and to the amount of organic matter converted to oil; based on Fischer assays on samples of oil shales from Brazil and South Africa. (Data from W. C. Kommes and J. W. Smith, U.S. Bureau of Mines, written communication, 1952.)

The data on shales from other countries are reviewed here to show that changes in the specific gravity of oils derived from a shale by the Fischer method are probably a function of the variations in the proportions of sapropelic to humic types of organic matter. The suggested conclusion is that, for a group of samples from an oil shale, low specific gravity of oil, high percentage of organic matter converted to oil, and organic matter of high hydrogen content are indicative of a preponderance of the sapropelic type of organic matter in an oil shale; conversely, high specific gravity of oil, low percentage of organic matter converted to oil, and organic matter of low hydrogen content are indicative of a preponderance of the humic type of organic matter. If this conclusion can be proved, the observed relation between the uranium content of the Chattanooga shale and the specific gravity of the derived oil (fig. 8) can be used as additional proof of the theory that, other factors being equal, the amount of uranium deposited in a shale has a positive relation to the amount of humic organic matter being deposited at the same time.

The author does not wish to invade the complex subject of the relation that exists between uranium

and liquid petroleum; but it is of interest that, in a study of uranium in oils and asphalts in the United States, K. G. Bell (written communication, 1958) found that the heavier asphalt-base crude oils in general contain several times as much uranium as do the lighter paraffin-base oils, and they show a slight positive correlation between specific gravity and uranium content. The uranium contents of the crude oils generally range from a fraction of one part per billion to a few parts per billion.

No uranium analyses have been made on oils derived from oil shales, to the author's knowledge, but these oils undoubtedly contain only a few parts per billion. Breger, Meyrowitz, and Deul (1954) subjected samples of Chattanooga shale, *Callixylon* from the Chattanooga, subbituminous coal, and Swedish kolm to destructive distillation tests; they showed that most, if not all, of the uranium in these rocks does not volatilize with the resulting oil but remains with the char residue.

In summary, a positive relation between uranium content and oil yield in the Chattanooga shale would suggest a constant proportion of humic to sapropelic material in the shale. The positive relation between uranium content and oil yield exists for thin units in a small geographic area but becomes less distinct where thicker units or larger areas are considered. The apparent positive relation of uranium content to the specific gravity of the oil derived from the shale further supports the suggestion that the proportion of humic to sapropelic matter controls the uranium content of the shale and probably also controls the amount and type of oil that can be distilled from the shale.

ANTRIM SHALE IN MICHIGAN

Determinations of uranium content and oil yield for 38 samples of the Antrim shale from 2 wells in Michigan are given in table 1 and shown in figure 11. The Antrim is a marine Devonian black shale that is in part correlative with and lithologically similar to the Chattanooga shale. The organic content of parts of the Antrim is about 10 percent; its known uranium content rarely exceeds 0.004 percent. As indicated by available analyses, the oil yield ranges from no measurable oil to 16.9 gallons per ton of shale, with the best 10 feet of shale yielding 15.0 and 13.4 gallons of oil per ton of shale in the Pure Oil Co. and the Cook Drilling Co. Bonardi wells, respectively.

The analytical data on samples from several feet of section from 2 localities about 200 miles apart are not intended to be representative of the large body of Antrim shale that generally ranges from 100 to 650 feet in thickness. On the other hand, the simi-

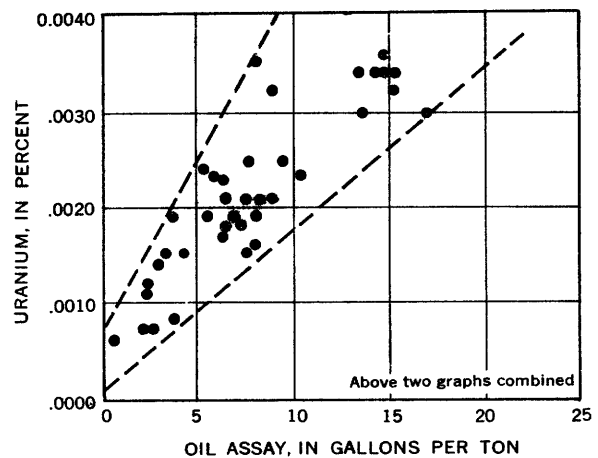
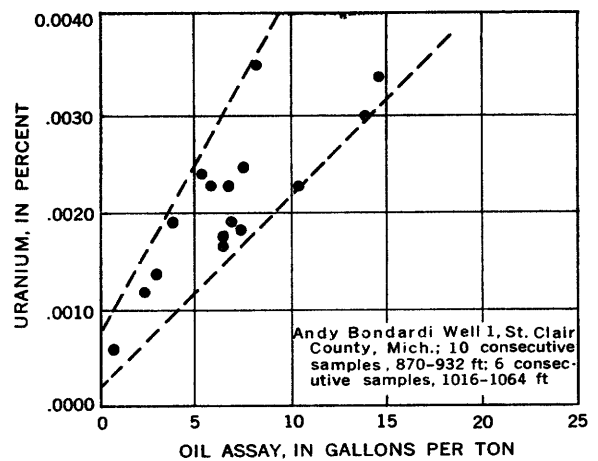
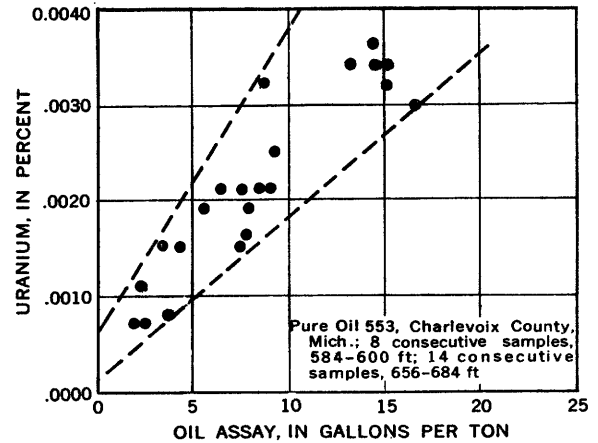


FIGURE 11.—Relation of uranium content to oil yield in 38 samples of Antrim shale in Michigan.

larity in the distribution of points in the scatter diagrams is readily observed. As is the case for some other shales, a general positive relation of uranium contents to oil yields is indicated, and the general increase of uranium content with an increase of recoverable oil is certainly suggested. The oil yield of

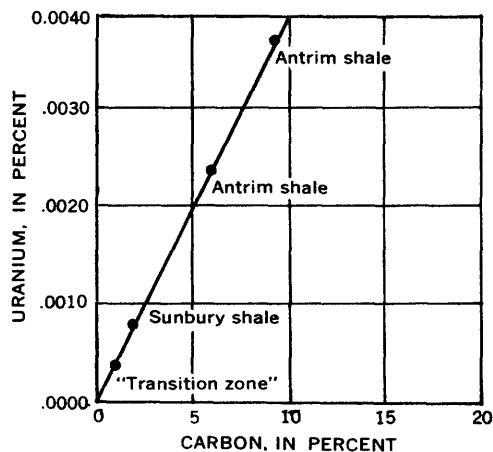


FIGURE 12.—Relation of uranium and carbon contents of Antrim and two other Paleozoic shales in Michigan. (Modified from Beers, 1945, fig. 10.)

the Antrim shale samples was determined by the photometric method of Cuttitta (1953a), which unfortunately does not include specific gravity determinations on the oil; thus, any relation of the uranium content of the shale to the specific gravity of the oil is not known.

Beers (1945, p. 11) presented some carbon and uranium determinations of the Antrim shale and two overlying Paleozoic shales in Michigan, and from these data he concluded that there was high positive correlation between these two components (fig. 12). Because the amount of carbon in the Antrim is a crude measure of the amount of oil that can be produced, some positive correlation between the oil and the uranium would be expected; the limited new data presented here are believed to support this conclusion.

CHATTANOOGA AND WOODFORD SHALES IN THE MIDCONTINENT AREA

Lucas (1953) briefly described the methods of distillation of the Woodford shale of Oklahoma, and, on the basis of a few samples, reported that this shale yields about 9.3 gallons of oil per ton. Landis (1958) summarized the uranium contents of the Woodford and the Chattanooga shales and their stratigraphic correlatives in the central midcontinent area.

Too few analyses of the Chattanooga and Woodford shales (approximate correlatives) of the midcontinent area are available to appraise them as potential sources of oil or to demonstrate conclusively any relationship of their oil yield to uranium content. Seven channel samples, representing 30 feet of the Woodford shale in Murray County, Okla., yielded as much as 15.3 gallons of oil per ton and 0.007 percent uranium; the average was 11.5 gallons per ton and 0.005 percent uranium. Data shown on figure 13 suggest that a

slight positive relation exists between the uranium content and the oil yield of these shale samples and also between the uranium content of the shale and the specific gravity of the oil; however, the data are insufficient to draw any conclusions on their validity. Eleven samples of the lower 11 feet of the Chattanooga shale about 100 miles north in Cherokee County, Okla., all contained less than 2 gallons of oil per ton; the uranium content ranged from 0.002 to 0.007 percent and averaged 0.005 percent. The shale in the two areas appears lithologically similar, but detailed studies might reveal distinct differences in the amount and type of organic material, which would explain the differences in oil yield. In turn, the difference in type of organic material could be related to paleogeographic position of the two areas, with respect to source of the dominating types of plant matter contributed to the Chattanooga sea.

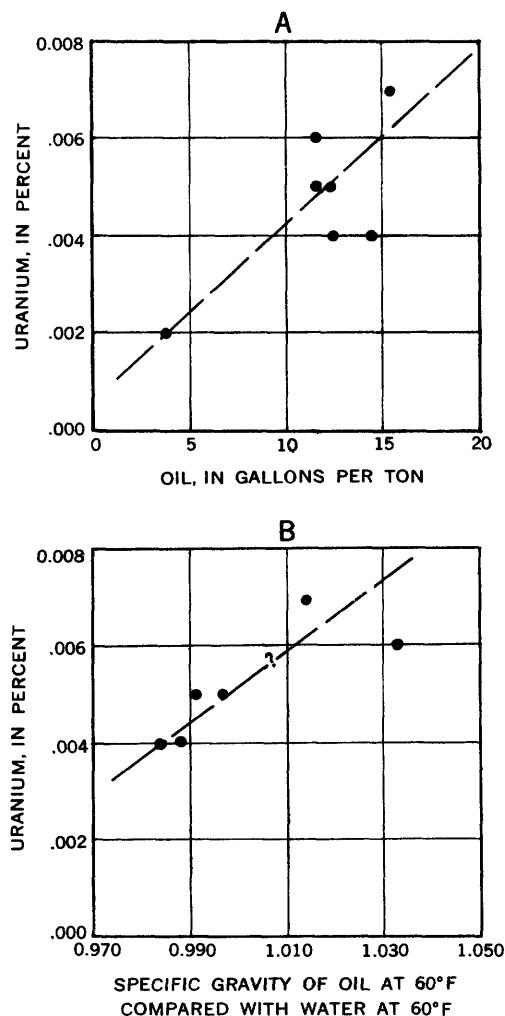


FIGURE 13.—Relation of uranium content to (A) oil yield and (B) specific gravity of oil, Woodford shale, Oklahoma. (Note: Insufficient oil from sample yielding 3.8 gallons of oil per ton for specific gravity determination.)

Samples were obtained from a core of Woodford shale equivalent from Sinclair Prairie Oil University 6 "154," Andrews County, in western Texas, through the courtesy of S. P. Ellison, Jr. (see Ellison, 1950, p. 9). The analyses (table 1) that were made on samples from 10 feet of this core indicate a uranium content of 0.003 percent and an oil yield of about 8.4 gallons of oil per ton of shale. When the data on oil and uranium in the nine samples are compared, no obvious positive or negative relation can be shown to exist. The only analyses that are available for comparison with the Woodford equivalent of western Texas are those on a 5-foot channel sample of the black shale of the Doublehorn shale member of the Houy formation (Cloud, Barnes, and Hass, 1957), a partial correlative of the Woodford that is exposed in the Llano area, Burnet County, Tex. This sample, which represents the upper part of the 8-foot unit, contained 0.009 percent uranium and the Fischer assay was 21.8 gallons of oil per ton. Pertinent to the nearly threefold difference of both the oil yields and uranium contents of these Upper Devonian and Lower Mississippian (?) black shales in Texas are the readily apparent differences between the shales of the two areas as observed in thin sections. The shale from the Llano area, which has the higher oil yield and uranium content, is finely laminated and contains an estimated 40 percent organic matter by volume, with numerous recognizable spore exines. The Woodford shale equivalent of western Texas is poorly sorted, contains more clastic mineral grains, and the organic matter, which constitutes an estimated 25 to 30 percent by volume, is macerated and contains very few recognizable spores.

The stratigraphically equivalent black shales of Late Devonian and Early Mississippian age in southern Illinois generally yield less than 5 gallons of oil per ton (Lamar, Armon, and Simon, 1956, p. 5). The uranium content of these shales is estimated to be about 0.005 percent, based on the radioactivity data presented by Ostrom and others (1955).

BLACK SHALES OF PENNSYLVANIAN AGE IN EASTERN KANSAS AND NORTHEASTERN OKLAHOMA

Within the thick sequence of rocks of Pennsylvanian age in the central midcontinent area are some 40 marine black shale units, most of which are only a few feet thick, contain scattered phosphatic nodules, and commonly overlie coal beds. In the course of the Geological Survey's reconnaissance investigations for uraniumiferous black shales most of these shales were checked for their radioactivity, (reviewed in Swanson, 1956, p. 454-455) and, more recently, the distribution and genesis of uranium in black shales of Des Moines

age have been investigated (Walter Danilchik and H. J. Hyden, written communication, 1957).

Runnels and others (1952) reported the oil yields of 59 samples from 20 of these black shale units in Kansas as ranging from a trace to a maximum of 22.8 gallons per ton. The oil yields and uranium contents of 16 additional samples are reported here. These data suggest that the following units, which are black shales 2 to 5 feet thick, may be expected to yield 5 to 10 gallons of oil per ton of shale over areas of hundreds of square miles: Heebner shale member of the Oread limestone; Eudora shale member of the Stanton limestone; black shale in the Lenapah limestone; black shale at the base of the Pawnee limestone; black shale in the Fort Scott limestone. The average uranium content of each of these units is estimated to be about 0.005 percent.

The scattered phosphatic nodules in these shales, which were described and analyzed by Runnels, Schleicher, and Van Nortwick (1953), generally contain 0.01 to 0.09 percent uranium and undoubtedly are the major uranium-bearing material in many of the shales. In contrast to the uranium of some of the shales cited in this report, most of the uranium of the Pennsylvanian shales apparently is not related to the organic matter, and the uranium content and oil yield are independent of each other. These relations are indicated by the analyses of seven samples (table 1) of the uppermost black shale unit of the Cherokee shale as shown in figure 14; Danilchik and Hyden (written communication, 1957) concluded that most of the uranium is in the carbonate-fluorapatite present in these shales.

Burton and Sullivan (1951, p. 884) pointed out the positive correlation between the radioactivity and organic carbon in eight cores of the Cherokee shale in Oklahoma; Whitehead (1952, p. 196) observed an increase of radioactivity with increase in phosphorus in the same cores. Whitehead further indicated (1952, p. 198) by autoradiographic studies that about three times more radioactive alpha particles originate in the phosphatic material than in the organic matter.

There is no doubt that the three constituents, uranium, phosphate, and organic material, are genetically interrelated in these Pennsylvanian shales. Inasmuch as phosphorus, which is one of the major inherent elements in plants and which is concentrated by many animals, is an essential element in living organisms, the phosphorus in the phosphate in these shales was probably derived in large part from the decaying organic matter, most likely plant matter. The phosphorus thus contributed precipitated out in combination with calcium and fluorine to form phosphate,

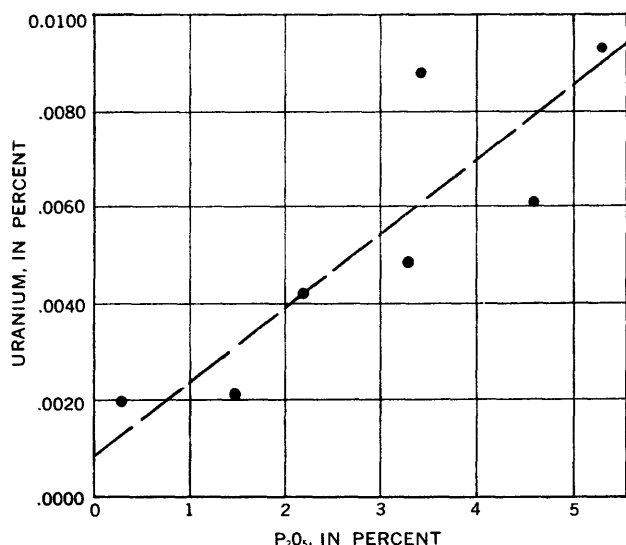
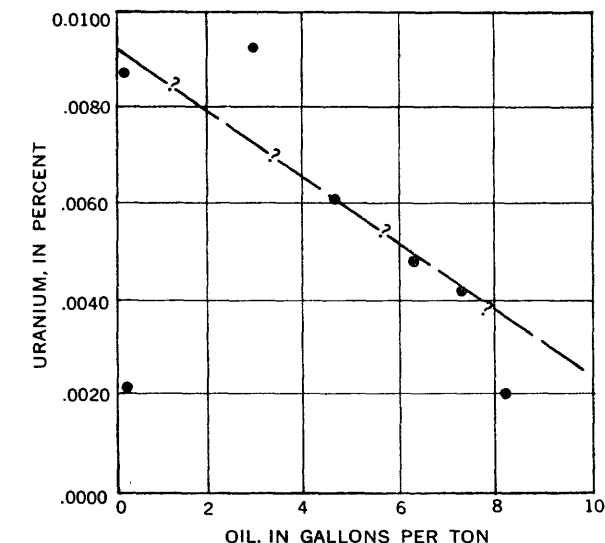


FIGURE 14.—Scatter diagrams that indicate uranium content is related to phosphate content rather than to oil yield in the uppermost black shale unit of the Cherokee shale of Pennsylvanian age in southeastern Kansas. Both diagrams based on same set of samples.

which preferentially attached most of the available uranium.

BLACK SHALES OF PENNSYLVANIAN AGE IN ILLINOIS

Marine black shales in the Pennsylvanian rocks in Illinois are similar in thickness, age, and cyclothem position to the shales in eastern Kansas and northeastern Oklahoma. The oil yield of 114 samples from some 30 of these shale units ranged from 0 to 40 gallons per ton, but 88 percent of them contained less than 15 gallons per ton (Lamar, Armon, and Simon, 1956, p. 1). The radioactivity of most of these same samples is presented by Ostrom and others (1955).

An attempt was made to determine if there is any relation between the oil yield and radioactivity of 92 of the samples for which both oil and uranium determinations are given in the two publications cited above. No significant relation was determined, probably because of the inherent variability of the radioactivity measurements (expressed as equivalent uranium oxide), and the many variable factors involved in the wide geologic and geographic distribution of the outcrop samples.

Splits of 7 samples from the shale above the No. 2 coal, Carbondale group, and of 7 samples from the shale below the Shoal Creek limestone, McLeansboro group, were obtained from the Illinois State Geological Survey for additional chemical study (table 1). The oil yield and uranium determinations are plotted in figure 15. For the shale above the No. 2 coal, which is 1 to 3 feet thick, the graph shows a slight suggestion that oil yield increases with increasing uranium content, but no relation is indicated by the data on the shale below the Shoal Creek limestone, which is also about 1 to 3 feet thick.

Inasmuch as some or all of the uranium may be associated with the phosphate in these shales, as it seems to be in some of the Pennsylvanian shales of Kansas and Oklahoma, the uranium determinations were compared with percent P_2O_5 determinations. The amount of P_2O_5 in the 14 samples of figure 15 ranged from 0.3 to 4.0 percent and averaged 1.4 percent. Again, no relation is apparent, nor is there when the sums or different ratios of the oil and phosphate analyses are compared with uranium content. The author believes, however, that if analyses were available on numerous samples systematically selected from a shale unit in a small area, a clear-cut relation could be shown to exist among the three constituents, uranium, phosphate, and organic matter. This conclusion is almost opposite to that reached by Krumbein and Slack (1956) in their statistical analysis of the distribution of radioactivity in the Pennsylvanian black shale overlying "Coal No. 6" in Illinois. In this study, this black shale was interpreted statistically as a "homogeneous sampling stratum" (p. 745) because the radioactivity of their closely spaced channel samples varies greatly, but nonsystematically, in either vertical or lateral directions. The present author believes that it is within this internal variation that rather precise local and regional differences could be determined. The greater part of the radioactivity is caused by the uranium, which in these Pennsylvanian black shales is related mainly to the phosphate and, to a lesser extent, to the organic matter. It is the changes in the distribution and amount of these two components and the amount of uranium associated

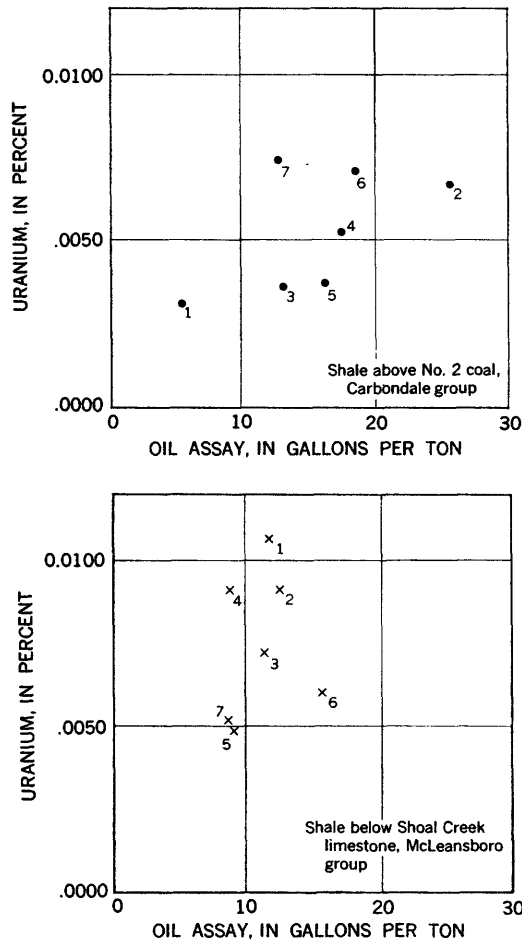


FIGURE 15.—Relation of uranium contents to oil yields of two black shales of Pennsylvanian age in Illinois. (Oil assays from Lamar, Armon and Simon, 1956; uranium determinations by U.S. Geological Survey on sample splits provided by Illinois State Geological Survey.)

with each that would provide the basis for determining patterns of radioactivity differences that were not made apparent in the study made by Krumbein and Slack.

BLACK SHALES IN THE PHOSPHORIA FORMATION

Condit (1919) presented a general review of the shale-oil potential of the Phosphoria formation in western Montana, southeastern Idaho, and adjacent parts of Wyoming and Utah. He reported that shales in the lower part of the Phosphoria in the Dillon-Dell area of southwestern Montana yield the most oil, about 20 gallons per ton of shale, of any part of the Phosphoria throughout these states. The shales, which are also phosphatic, range from a few to 20 feet in thickness and are interbedded with phosphatic units that contain as much as 30.5 percent P_2O_5 .

Extensive studies by the Geological Survey have shown that the uranium in the Phosphoria formation, which ranges from 0.001 to 0.06 percent, is most closely associated with the phosphate (reviewed in McKelvey and Carswell, 1956); any future production of uranium from this formation will be as a byproduct in the well-established phosphate industry. Thompson (1953, p. 62) found, however, that in samples having a low equivalent-uranium content (average of less than 0.010 percent) there is a direct relation between uranium content and organic matter; most of the beds that might be termed oil shales probably fall into this group.

The only available analyses of samples of the black shale in the Phosphoria formation considered applicable to this discussion are on 48 samples from the Retort phosphatic shale member (McKelvey and others, 1956; unit *D* of Cressman, 1955) of the Phosphoria formation in Beaverhead County, southwestern Montana (table 1). Of these 48 samples, which represent a total thickness of 58.2 feet, 21 contiguous samples (Nos. 20-40) of a part of the member 26.7 feet thick near the middle of the unit were chosen for diagrammatic comparison of their uranium content, P_2O_5 , and oil yield (fig. 16). The diagrams suggest that the oil yield and uranium content bear little or no relation to each other, and that the P_2O_5 and uranium contents have a generally positive relation. There seems to be an even closer correlation when the uranium content is compared with the sum of the percentage of oil yield and percentage of P_2O_5 ; this correlation suggests that the phosphate and the organic matter together account for most of the uranium in this shale.

Numerous other multiple analyses of samples of phosphatic units in the Phosphoria formation that

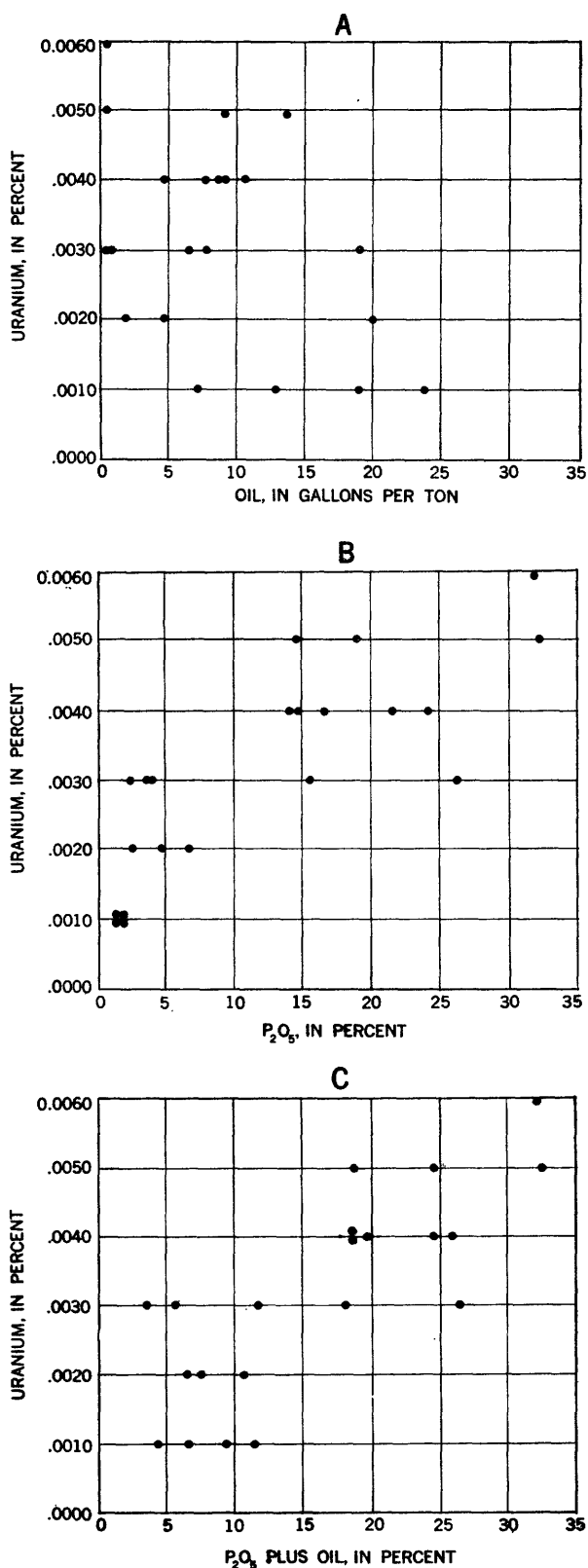


FIGURE 16.—Relation of uranium content to (A) oil yield, (B) P_2O_5 , and (C) P_2O_5 , and oil for 21 vertically contiguous samples (Nos. 20–40) of the Retort phosphatic shale member of the Phosphoria formation, Beaverhead County, southwestern Montana. (All data except uranium determinations from Swanson and others, 1953, p. 16–24.)

include determinations of oil yield (V. E. McKelvey, written communication, 1957) are not reviewed here or included in the table, as the determinations all show less than 4 gallons of oil per ton and most less than 1 gallon per ton.

BLACK SHALE IN THE SHARON SPRINGS MEMBER, PIERRE SHALE

A part of the Sharon Springs member of the Pierre shale in South Dakota, Nebraska, and Kansas is hard black organic-rich shale that contains as much as 0.010 percent uranium, but generally only about 0.003 percent (Tourtelot, 1956). The thickness of the member generally ranges from 20 to 500 feet, but typically only the lowest part of the unit contains more than 0.001 percent uranium.

Too few determinations are available to estimate the oil yield of the Sharon Springs member, but it is doubtful that more than a few beds a few feet thick would yield more than 5 gallons per ton of shale. A sample from a bed about 3 feet thick in Lyman County, S. Dak., yielded 8.1 gallons per ton, the highest of the 3 analyses available, but the sample contained only 0.002 percent uranium (R. C. Kepferle, written communication, 1956; table 1). Runnels and others (1952, p. 179) reported shale about 10 feet thick in the Sharon Springs member of the Pierre shale of Wallace County, Kans., would yield slightly more than 6 gallons of oil per ton, but the uranium content is not known.

OIL SHALES IN THE GREEN RIVER FORMATION IN COLORADO, UTAH, AND WYOMING

The oil shales in the Green River formation extend over a large area in northwestern Colorado, northeastern Utah, and southwestern Wyoming. Of all the oil shales in the United States, those in the Green River have the greatest immediate potential for commercial production of oil, and have thus received intensive geologic and economic study by private companies and government agencies.

The oil shales of the Green River formation are not intended to be compared directly with the other shales discussed in this paper, as they are markedly different in overall composition and origin; but, because they are economically important as a potential source of oil and because their uranium content has been investigated, they are pertinent to this discussion. No attempt is made here to review the voluminous literature on the geology and oil potential of the Green River formation. The reader is referred to general papers on its geology and origin (Bradley, 1931; Donnell, Cashion, and Brown, 1953; Picard,

1955), the physical and chemical properties of its oil shale (Stanfield and others, 1951), its oil resources (Donnell, 1957), and the mining and processing of the shale (U.S. Bureau of Mines, 1954).

In 1944, Russell, (p. 191) observed that of all the sedimentary rocks tested, oil shales had the highest average radioactivity; thus early in the post-World War II search for sources of uranium, the radioactivity of the oil shales in the Green River formation was tested. This early reconnaissance work indicated that the general positive correlation between uranium and organic content observed in other shales did not apply in the case of the oil shales of the Green River, and subsequent investigations and analytical data substantiated this conclusion. The paucity of uranium in these widespread rich oil shales, however, does lend support to and serves to clarify several interpretations and conclusions on the geologic controls involved in the syngenetic concentration of uranium in other shales.

The average uranium content of the oil shales in the Mahogany ledge, Parachute Creek member, based on 46 channel samples, each representing 1 to 5 feet of section, from 3 localities in northwestern Colorado and northeastern Utah (table 1), is about 0.0006 percent, only very slightly higher than the average uranium content for all shales. The range in uranium content in this suite of samples is small, 0.0003 to 0.0013 percent. The oil yield ranged from 1.0 to 42.7 gallons per ton, and the 2 samples that yielded 1.0 and 42.7 gallons per ton both contained 0.0006 percent uranium. Furthermore, the 3 samples that contained 0.0010 percent uranium yielded 5.3, 16.8, and 26.0 gallons per ton; of the 9 samples that contained only 0.0003 percent uranium, the oil yield ranged from 9.7 to 30.5 gallons per ton. Thus, no relation appears to exist between the uranium content and oil yield in this suite of 46 samples; nor is any relationship apparent when the oil yields and uranium contents of samples from individual localities are compared. Comparison of the uranium content of the shale with the specific gravities of the oil derived from the shale also gives a random pattern. Until more detailed studies prove otherwise, it is doubted that the small amount of uranium in the oil shales of the Green River formation is chemically or genetically associated with the abundant organic matter in these shales. More likely, it is contained in the resistates, in the clay fraction, and in the volcanic ash that is distributed through the Green River formation.

As emphasized by Bradley (1931, p. 7) and as a point of definite contrast to most of the shales discussed in this paper, the oil shales in the Green River formation would be better described as marlstones

rich in organic matter. The predominant minerals in both rich and lean oil-shale beds of the formation are calcite and dolomite, which constitute about 25 percent of most of them and over 50 percent of some. Other important differences between the "oil shales" of the Green River and other oil shales described are: (a) The Green River formation was deposited in an increasingly saline lake, as indicated by the biota, detailed paleogeographic studies, and saline constituents such as sodium sulfates, sodium bicarbonates, and magnesium salts; thus, it is nonmarine. (b) The major part of the organic matter in the "oil shales" of the Green River appears to be of algal origin and can thus be compared to the boghead coals, whereas the organic matter in most of the other shales, though not so well known, is probably a combination of vascular-plants and marine plankton. (c) This difference in type of organic material is probably the chief reason for the difference in type and amount of distillable oil—the "oil shales" of the Green River formation have yielded as much as 100 gallons of oil per ton of shale and the oil is a lighter paraffinic type, but the oil yield of the marine oil shales rarely exceeds 20 gallons of oil per ton and the oil is generally a heavy and aromatic type.

A complete evaluation of these differences for the purpose of interpreting the reason why the rich "oil shales" in the Green River formation have only a small fraction of the uranium content of marine oil shales will not be presented here. The most obvious conclusion is either that the lake waters contained little or no uranium or that the conditions conducive to uranium precipitation or adsorption on or within the organic matter never existed. The abundance of carbonate minerals intimately mixed with the organic matter indicates a carbonate environment with neutral to slightly alkaline pH and slightly oxidizing conditions wherein the uranium would be retained in solution, probably as uranyl carbonate complexions. The sapropelic type of organic matter, mainly of algal origin, does not assimilate uranium, nor does it lend itself to the decomposition by anaerobic bacteria that would result in the acid and reducing environment in overlying waters that would be favorable for uranium precipitation. The pyrite in these shales probably formed under the reducing conditions created within the sediment some distance below the sediment-water interface where little or no reducible uranium was present.

It should be mentioned that several thin beds in the Laney shale tongue of the Green River formation near Green River, Wyo. are abnormally radioactive along an outcrop distance of more than 90 miles (Love, 1955, p. 263). The most radioactive bed is a

yellowish-gray silty claystone, one sample of which contained 0.15 percent uranium; another bed, 3 inches thick, is an olive-gray low-grade oil shale, which contains as much as 0.014 percent uranium. J. D. Love and Charles Milton (written communication, 1959) reported that the uranium in these beds is related to their P_2O_5 content, which is as much as 20 percent. Similar occurrences are known in southern Uintah County, Utah. As suggested by the widespread and uniform distribution of these uraniferous beds, the uranium was very likely incorporated by the phosphate at the same time the sediments were deposited.

SHALES IN FOREIGN COUNTRIES

Little detailed information is available on the uranium content of the many well-known oil shales in other countries, such as the *Dictyonema* shales and kukersite of Estonia and the U.S.S.R., the Cambrian and Ordovician alum shales of Sweden, the Lower Carboniferous shales of Scotland, the Permian torbanites of Australia, and many others. For descriptions of many of these oil shales and the oil produced from them the reader is referred to Cadman (1948), Sell (1951), and Guthrie and Klosky (1951).

Splits of 3 samples of oil shale from the Glen Davis mine in New South Wales, Australia, were obtained from the U.S. Bureau of Mines; each contained less than 0.0005 percent uranium but yielded (U.S. Bur. Mines, written communication, 1952) 82.9, 119.7, and 135.9 gallons of oil per ton, respectively. Similarly, 2 samples of oil shale from Breyton, Transvaal, South Africa, which yielded 45.0 and 45.6 gallons per ton each, contained less than 0.0005 percent uranium. A large sample of shale from the Albert formation of Early Mississippian age, collected by K. G. Bell from a mine dump in Albert County, New Brunswick, Canada, contained 0.0012 percent uranium and yielded 48.6 gallons of oil per ton of shale. The *Dictyonema* shale of Early Ordovician age in the U.S.S.R. reportedly contains between about 0.005 and 0.025 percent uranium (Orlov and Kurbatov, 1934-1936; Glebov, 1941), but its oil yield is low, generally less than 10 gallons of oil per ton (Gäbert, 1921). Conversely, the Middle Ordovician beds of kukersite in Estonia, which have been extensively mined for many years for oil production, have an average yield of about 60 gallons per ton (Winkler, 1930, p. 145-148) but probably contain less than 0.0010 percent uranium. The author ventures the guess that most of the other commercially worked oil shales in the world, particularly those yielding in excess of 25 gallons of oil per ton from shale having only 20 to 30 percent organic matter, also contain only a few

parts per million (0.000X percent) of uranium. The Swedish shale, which has a relatively low oil yield, is an exception.

Plants for extracting oil and uranium from the Upper Cambrian alum shales have been in production at Kvarntorp, Närke region, Sweden for some years (Guthrie and Klosky, 1951, p. 33; Magnuson, 1957, p. 6). Dr. T. Bertil Dahlman (oral communication, 1957) of the Geological Survey of Sweden, stated that a lower unit of the *Peltura* zone in the shale of the Närke region has an average yield of between 13 and 14 gallons of oil per ton and that the upper 15 feet of this shale zone, which is mined for uranium, contains about 0.023 percent uranium. In the Billingen area of Västergötland, an extensive layer of this Upper Cambrian shale is about 10 feet thick and has an average uranium content of 0.030 percent; this same shale, however, will yield only a few gallons of oil per ton, much of the oil originally in the shale presumably lost by natural fractionation or low-temperature pyrolyzation during the intrusion of an overlying diabase sill (Dahlman, oral communication, 1957; McKelvey, Everhart, and Garrels, 1955, p. 519-520).

Figure 17 shows a crude relation between the oil yield and uranium content of a part of the oil shale in Närke. Based on data obtained from Bates and others, (1956, p. 89), figure 18 shows a more positive relation of the uranium content to the carbon content of the scattered lenses of kolm in the shale from Billingen, Västergötland, Sweden. Oil yield data on

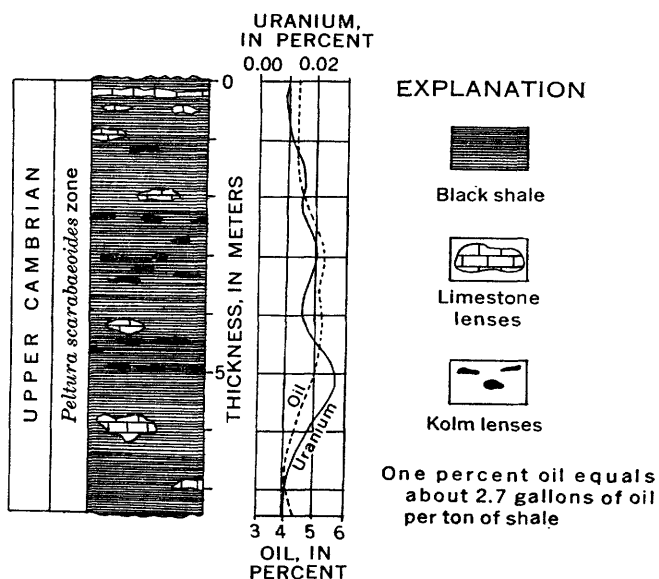


FIGURE 17.—Approximate relation of oil yield to uranium content of part of the kolm-bearing black shale of Late Cambrian age in the Kvarntorp district, Sweden. (Modified from information obtained from and used with permission of staff of Geological Survey of Sweden.)

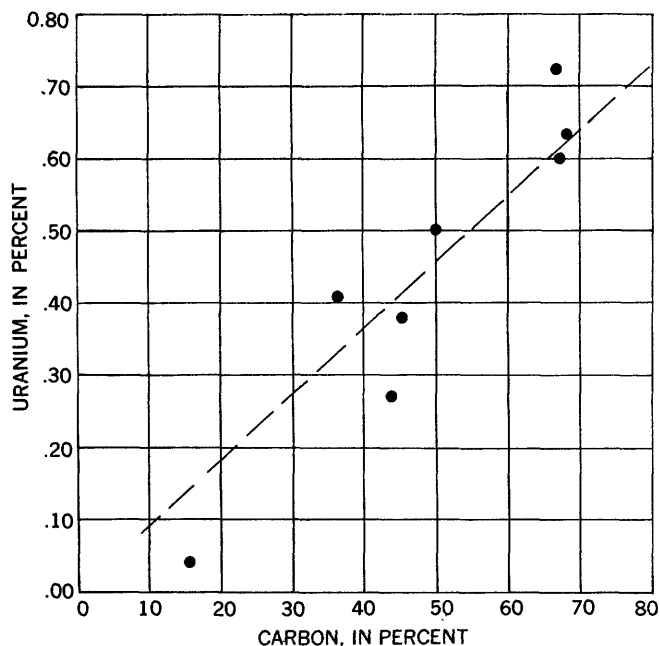


FIGURE 18.—Relation of uranium and carbon content in eight samples of kolm from the Upper Cambrian shale near Billingen, Västergötland, Sweden. (Data from Bates and others, 1956, p. 89.)

these kolm samples are lacking, so the relation of oil yield to uranium is not known. The oil yield of kolm is relatively small, according to Dr. Gosta Salomonson (oral communication, 1957) of the Swedish Shale Oil Co. A sample of kolm collected by Dr. Curt Teichert from the Upper Cambrian alum shale at Stolan, in the Billingen area, contained 0.58 percent uranium, yielded 1.1 percent or 2.9 gallons of oil per ton of rock, and had an ash content of 16.55 percent (U.S. Geological Survey sample 154140, Joseph Budinsky, analyst; oil determination by volumetric method of Cuttitta, 1953b).

THEORETICAL ROLE OF ORGANIC MATTER IN OIL YIELD AND URANIUM CONCENTRATION

The organic matter in the shale is the most important factor to be considered in understanding the oil yield and uranium content of any black shale. All the relations brought forward in discussing shales in this paper either directly or indirectly concern the carbonaceous matter in these shales.

The oil that can be distilled from organic matter can be related directly to the amount and type of organic matter in the shale. The uranium present in shales, however, is not for the most part an inherent original constituent of the organic matter; rather it is attached to the organic matter externally at some stage in the decay and sedimentary cycle of the organic matter. Thus, the amount and manner of fixation of uranium in a black shale involves many

more variables and is less understood than the origin of the recoverable oil.

It is generally true that the more carbonaceous material present in a shale, the greater will be the oil yield; but a simple direct relation between the two certainly does not hold for all shales. For example, a Pennsylvanian black shale in the midcontinent area and an oil shale from the Green River formation of Colorado may both have 25 percent organic matter; on distillation, the former yields only 7 gallons of oil per ton, but the latter yields 40 gallons per ton. The obvious conclusion is either that the oil yield is dependent on the original type of organic matter or that diagenetic processes drastically alter the organic substance to increase the oil yield. Both probably are of fundamental importance.

The oil yields of the wide variety of organic substances can be determined empirically, and thus the components of plants and animals can be shown to differ widely in the amount of oil they yield on destructive distillation. The resin of a tree, for example, yields over ten times the oil that the cellulose does (Francis, 1954, p. 351, 400); and, ignoring alteration for the moment, the shale whose organic matter consists predominantly of resins yields a far greater proportion of oil on destructive distillation than a shale whose organic matter consists largely of cellulose.

It is beyond the scope of this paper to list the oil yield and to evaluate the possible geologic significance of each of the many kinds of organic substances, as to its relative abundance and resistance to weathering, erosion, and diagenetic processes. Such a study would be necessary to the basic understanding of the amount of oil that can be extracted from a rock and the accurate determination of what kerogen (p. 6) actually is.

For this discussion, the organic matter in shales is simply divided into two main types—the sapropelic type and the humic type (Twenhofel, 1950, p. 463; Bell, 1954, p. 107). Each type has different paleobiologic, chemical, and geologic characteristics, and the significance of each type in controlling the oil yield and the uranium content of a black shale can be better described and understood in light of these differences.

The sapropelic type of organic matter in shales was derived principally from algae, spores and pollen, cuticles, and, probably to a lesser extent, from plant resins and waxes and from the fatty tissues of animals. Only the first two are commonly recognized in shales. Most of the humic type of organic matter in shales was derived from the woody parts of plants, composed mainly of cellulose and lignin. The sapro-

pellic and humic types of organic material may be distinguished on the basis of their hydrogen and oxygen contents (White, 1926, fig. 44, table 34; Francis, 1954, p. 329). The sapropelic type generally contains 10 percent or more hydrogen and 10 percent or less oxygen on an ash-free basis, whereas the humic type generally contains only a few percent hydrogen but as much as 50 percent oxygen.

The hydrogen content of organic matter may be considered as a crude index of oil yield, so that the greater the amount of hydrogen in organic matter, the greater the amount of recoverable oil (fig. 10; Francis, 1954, p. 400; Kinney and Schwartz, 1957, p. 1125). The sapropelic type of organic matter is, in general, greatly resistant to chemical and bacterial decay (White and Stadnichenko, 1923, p. 243) and thus retains its originally high hydrogen content; this more stable type of organic matter explains the high yields of oil from a shale, but it probably has little significance in the postulated processes controlling uranium concentration in shales.

The geologic significance of the two types of organic matter in shales and the changes that the precursory plant or animal substances have undergone under a variety of natural conditions are, of course, complex and therefore difficult to generalize. Though algae are more prevalent in marine waters, they were and are heavy contributors to the organic sediment in lakes and swamps. Spore exines and pollen grains, because they are easily transported by wind and as a fine-grained sediment by water, also are widely distributed; but because they are derived mainly from land plants, they would be expected to be more abundant near land. The humic type is more commonly confined to terrestrial or near-shore marine deposits. Thus, in a marine shale, the amount of the humic type of material would be expected to decrease with increasing distance from an ancient shore line (Uspenskiy, 1938). The importance of this latter observation on the distribution and subsequent alteration of hydrocarbon-forming materials in modern and ancient sediments was emphasized by Strakhov and Rodionova (1954).

The organic matter from which humic material is derived is generally much less resistant to chemical and bacterial decomposition than the plant substances from which sapropelic material is derived (Francis, 1954, p. 144-147). Most of the plant substances which are the progenitors of the humic type of organic matter are immediately attacked and are completely destroyed under most terrestrial conditions, and their rate of decay is partly arrested only under rather extreme natural conditions. Many of the plant or animal substances that end as sapropelic matter can

be exposed to aerobic conditions, transported, deposited, and preserved while the corresponding progenitors of humic matter, which initially might have been much more abundant, would be almost wholly destroyed. The resulting concentration of the sapropelic type of organic matter, if not too much diluted by mineral sediment, produces a rich oil shale.

The sapropelic type of organic matter on the other hand is believed to be almost inactive in the process of syngenetically concentrating uranium; being resistant to the natural forces of decomposition and almost chemically inert, it does not ordinarily produce the chemical environment or products of decomposition believed essential to uranium precipitation. This fact may be the most important reason why some rich oil shales contain less uranium than many other types of rock and may also explain the lack of correlation between oil yield and uranium content of some of the shales discussed in this report.

The exact method or methods by which uranium is incorporated with the organic matter in black shales is unknown. By laboratory experiments, uranium can be shown to be readily and irreversibly removed from solution by organic substances (Tolmachev, 1943; Szalay, 1954; Moore, 1954; Manskaya, Drozdova, and Emelyanova, 1956); but whether the uranium is held as adsorbed metal, as uranium-organic complexes, as finely disseminated uraninite, or as all three is not known. The general geochemistry of uranium is, however, fairly well known (McKelvey, Everhart, and Garrels, 1955, p. 466-472), and some very probable means by which uranium may be concentrated by organic matter are suggested here: namely, simple reduction and precipitation by hydrogen sulfide, and assimilation (either adsorption or complexing).

The humic type of organic matter readily undergoes a radical and complex chemical change on decay. It is postulated that this change is the critical basis for creating the chemical environment in which uranium will be removed from natural waters. After deposition of the humic type of organic matter in stagnant or poorly circulated water, the period of oxidation and attack by aerobic microbial action is very short; subsequent decomposition in the resulting toxic waters is accomplished at a much reduced rate by anaerobic bacteria, which are dependent upon the bound oxygen of the humic matter for survival. The overlying and surrounding water becomes increasingly reducing and acidic in character (Krumbein and Garrels, 1952, fig. 8) with the continued release of the decay products CO_2 , hydrogen sulfide, and methane.

The uranium that is soluble and transportable in natural waters is in the hexavalent form, but on the entry of these waters into the environment just de-

scribed, the uranium is reduced to its relatively stable tetravalent form and is probably precipitated directly or sorbed onto the organic matter. A possible mechanism of this precipitation process, suggested specifically for black shales by Strøm (1948) and by Goldschmidt (1954, p. 566-567), has been accomplished experimentally (Gruner, 1952; Miller, 1958), where tetravalent uranium oxide, or uraninite, can be precipitated from a uranyl solution by the introduction of hydrogen sulfide gas into the solution; as is well known, hydrogen sulfide is a common decomposition product of humic matter under anaerobic conditions; it is also formed by reduction of sulfate ions in sea water by bacteria. Strøm (1948) reported as much as 199.5 cubic centimeters of hydrogen sulfide per liter in the stagnant bottom waters of fjords on the coast of Norway, where black muds containing as much as 0.006 percent uranium are now accumulating.

The theory of slow but continuous precipitation of ultramicroscopic uraninite in the presence of hydrogen sulfide in the black mud environment seems very plausible, but it remains to be verified by duplication of this environment in the laboratory. Support for this postulated genesis of uranium in the Chattanooga shale is indicated by the findings of Deul (1955, 1957). After physically separating the shale into several fractions, he found that the fraction consisting of the finest particles contained the most uranium. He concluded (1955) that the uranium "... exists largely as a colloidal phase dispersed through the organic matrix and that most of the uranium is not now combined with the organic material or with the minerals." In 1957 (p. 218), on the basis of additional experimental data, he stated that the uranium was probably derived from the Chattanooga sea by reduction of the uranyl ion to uranium dioxide.

The amount of uranium precipitated by hydrogen sulfide would be controlled by the amount of uranium in the water and the rate of overturn of this water in the relatively stagnant environment. Sea water, with which we are mainly concerned, has an average uranium content of only 3.3 parts per billion, or 0.00000033 percent (Rona, Gilpatrick, and Jeffrey, 1957, p. 700), and there is little reason to believe ancient sea water contained appreciably more (Holland and Kulp, 1954, p. 204; Koczy, Tomic, and Hecht, 1957). Obviously, with so dilute a source and with the limited rate of overturn of water necessary to maintain the environment for the precipitation of uranium, the thorough dispersal of submicroscopic uranium on and within the organic matter of a black shale, and even on adjacent mineral particles, is more understandable. The probable slow but continual rain of detrital mineral particles and more organic sedi-

ment further makes the likelihood of a large amount of uranium being incorporated on or within any particular layer extremely small. It is for this latter reason that the interpreted slow rate of deposition is a key characteristic of uraniferous black shales.

It has also been shown experimentally that solid organic matter such as peat and lignite, which are predominantly humic in type, can extract large quantities of uranium from pregnant solutions (Szalay, 1954; Moore, 1954). The Devonian woody plant *Calliawylon*, mentioned in connection with the Chattanooga shale (p. 11), probably obtained its relatively large percentage of uranium (0.033 percent) in this manner, and this may have been an important method of concentration of uranium in this shale.

Another and slightly more complex mechanism whereby uranium is related specifically to the humic type of organic matter involves the decay products commonly termed humic acids (Vine, Swanson, and Bell, 1958). These "acids," which are released from decaying organic matter of the humic type and transported in a colloidal state by slightly alkaline solutions, are capable of adsorbing as much as 10 percent uranium by weight (Szalay, 1954, p. 304). If the pH of the aqueous medium is lowered, the humic acids, with the adsorbed uranium, readily coagulate to a gel, beginning at a pH of about 7.0 (Manskaya, Drozdova, and Emelyanova, 1956). It is conceivable that humic acids may have been carried by streams from land into black shale seas, or possibly were even derived from decomposing matter of the humic type on parts of the sea bottom. Adsorbing uranium enroute, these organic colloids may have been coagulated and deposited in the acidic waters where the organic-rich muds accumulated. The high uranium content (0.1 to 0.7 percent), the apparently low oil yield, and an appearance similar to both natural and artificial humates suggest that the kolm in the Upper Cambrian shales of Sweden originated as coagulated humic acids. On the sea bottom, humic acids may also form from and accumulate in the decomposing humic matter, earlier described as creating the chemical environment conducive to uranium precipitation from sea water; thus in themselves they may adsorb uranium without being transported. If these humic acids, which on hardening appear in thin section as structureless dark yellowish-brown to almost black translucent matter, make up only 0.1 percent of a black shale but contain 5 percent uranium, they could be the explanation for all the uranium in a shale having 0.005 percent uranium.

As previously cited, Deul (1955, 1957) found that of the several fractions of Chattanooga shale physically separated in the laboratory, the colloidal fraction

contained the most uranium, as much as 0.08 percent. It is possible, though apparently not considered by Deul, that this colloidal fraction may have contained several percent humic acids; either the solid humic acids may have been pulverized to colloidal-size particles, or, as a result of slight oxidation during grinding, the humic acids may have been made amenable to resuspension by chemical means.

The separation and analysis of humic acids from the Chattanooga shale by chemical methods were described by Kinney and Schwartz (1957); however, the original uranium content of the acids is not known because most of the uranium is chemically released during treatment of the shale for separation of the humic acids.

No specific study has been made of the effect of postdepositional or diagenetic processes on the present oil yield and uranium content of carbonaceous shales, but the results of other studies on these processes may be applied here. Simple physical compaction, which in muds, for example, may result in a volume loss of as much as 90 percent by loss of porosity (Hedberg, 1926, p. 1036), probably involves no real gain or loss of these components. But the compaction, once completed, does have a sealing effect; porosity and permeability are reduced to the point where the migration of any constituents is minimal, and the organic matter, with its uranium and its oil-yielding components, probably remains unchanged except under later conditions of extreme metamorphism or exposure to weathering.

In the earliest stages of diagenesis, before burial to depths of more than a few tens of feet, some chemical reorganization undoubtedly takes place—for example, the intrasediment precipitation of iron sulfides and possibly phosphate from the upward-moving interstitial solutions. But once the organic matter is buried, its decay is slowed and almost terminated, and subsequent changes, other than compaction, in it and its associated uranium are believed negligible. If at some later geologic time the shale is subjected to forces other than simple gravitational compaction, such as heat and pressures resulting from dynamic metamorphism, natural distillation of the organic matter, mainly of the sapropelic type, will result in the formation and possible expulsion of gaseous and liquid hydrocarbons. The oil yield of the rock will be correspondingly diminished; but, as shown by experiment by Breger, Meyrowitz, and Deul (1954) and further documented by McKelvey, Everhart, and Garrels (1955, p. 519–520), the uranium remains in the residual part of the organic matter.

In summary, it is here concluded that the fraction of the total organic matter in a shale genetically

responsible for most of the uranium is of the humic type. Though this same fraction contributes a small part, it is the sapropelic type of organic matter that is the source of most of the oil extractable from a shale.

It is obvious from the preceding discussion that a quantitative evaluation of all the factors that combine to result in a uraniferous oil shale would be extremely difficult. It is apparent that a given shale having, say, 20 percent organic matter throughout its extent might yield rather widely different amounts of oil and uranium from place to place; and, theoretically, at least, the two derivatives could actually be shown to have an inverse relation. Thus, other factors being constant, only where the proportion of sapropelic to humic type of organic matter remains constant would the oil yield and uranium content be expected to have a positive relation and be a simple function of the increase or decrease of total organic matter.

Because few data are available to prove specifically or to modify these theoretical relations, figures 19 and 20 are presented as illustrations of the possible control that the 2 types of organic matter have on the variable oil yield and uranium content of a black shale. Figure 19 is actually an extrapolation of the analytical data on the samples of the alga *Foerstia* and the wood fragments of *Calliavylon* from the Chattanooga shale, sapropelic and humic type of organic matter, respectively (p. 11). The positive relation of the uranium content to the specific gravity of the oil gives additional support to the theory that the type of organic matter controls the uranium content and oil yield of the shale. (See fig. 8; p. 12–13.)

As shown in the diagram on the left in figure 19, a marine black shale whose organic matter consists predominantly of the sapropelic type, probably has a very small amount of uranium, regardless of the amount of total organic matter in the rock; if, on the other hand, the humic type of organic matter predominates, relatively small increases in percent of organic matter can reflect a large increase in the uranium content of the rock. As shown in the diagram on the right in figure 19, almost the reverse situation is true where the sapropelic type of organic matter is responsible for much larger oil yields than a corresponding amount of the humic type of organic matter. Because most marine black shales contain mixtures of the two types of organic matter, it follows that the amount of uranium and the oil yield of these shales are related not only to the amount of organic matter in the rock, but also to the proportion of the sapropelic to the humic material making up that organic matter. Examples *a*, *b*, *c*, and *c'* in figure 19 show these relations. If additional analytical data

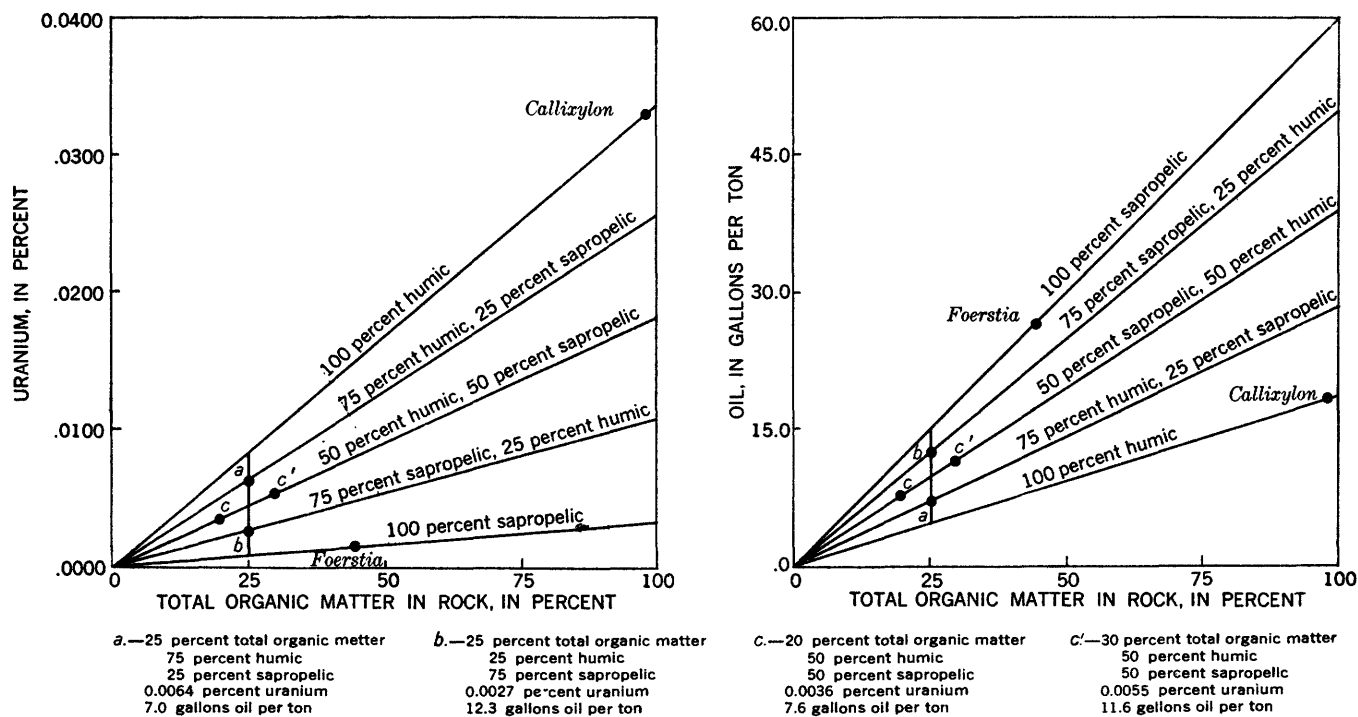


FIGURE 19.—Diagrams showing possible relation of uranium content to oil yield of a marine black shale, as controlled by total organic matter and the proportions of humic and sapropelic material making up the organic matter.

on isolated materials of the sapropelic and humic types of organic matter were obtained, they undoubtedly would modify the lines shown in figure 19, but the general pattern shown would probably hold for the Chattanooga shale.

In any black shale, the percent of organic matter and the proportion of sapropelic to humic type making up that organic matter probably change in a systematic manner in both a lateral and a vertical direction. The reason for these changes can be visualized by reconstructing the paleogeography of the basin or area in which the black muds were deposited. The amount of organic matter in the sediment at any locality probably can be related to the paleogeographic distance of the deposited sediment from the source area. Similarly, the ratio of sapropelic to humic matter probably increases with increasing distance from land areas. These theoretical relationships are illustrated in figure 20 and, inasmuch as they are believed to be significant in controlling the uranium content and oil yield of the resulting rock, several positions (*a*, *b*, *c*₁, *c*₂, *c*₃, *c*₄, *d*, *e*, and *f* in fig. 20) in the theoretical black mud layer are indicated to illustrate the changes in uranium content and oil yield of the rock. The data on the shale at these several positions are utilized in the diagrams in figure 21 to illustrate the circumstances under which a relation between uranium content and oil yield is lacking and those under which a positive relation would exist.

As shown, a positive relation exists if the proportion of humic to sapropelic type of organic matter remains constant, regardless of the total amount of organic matter in the rock.

SUMMARY

No black shale in the United States is known to have sufficient extractable quantities of both oil and uranium to warrant its being considered as an important common source of both these commodities in the near future. The shales in the Green River formation of northwestern Colorado and adjacent parts of Utah and Wyoming, which yield in excess of 25 gallons of oil per ton, will undoubtedly be commercially processed for their oil in the near future, but their uranium content is negligible, generally less than 0.001 percent. Parts of the Chattanooga shale of the southeastern United States will yield about 10 gallons of oil per ton and contain about 0.006 percent uranium; the large tonnages of this shale warrant its being considered as a low-grade source of both commodities.

In attempting to understand the oil yield and uranium content of black shales, the following points should be considered:

1. The organic matter in black shales accounts for all the oil yield and for most of the uranium content. In some shales, a clear-cut positive relation can be shown between oil yield and uranium content, but in others such a relation is lacking or is even inverse.

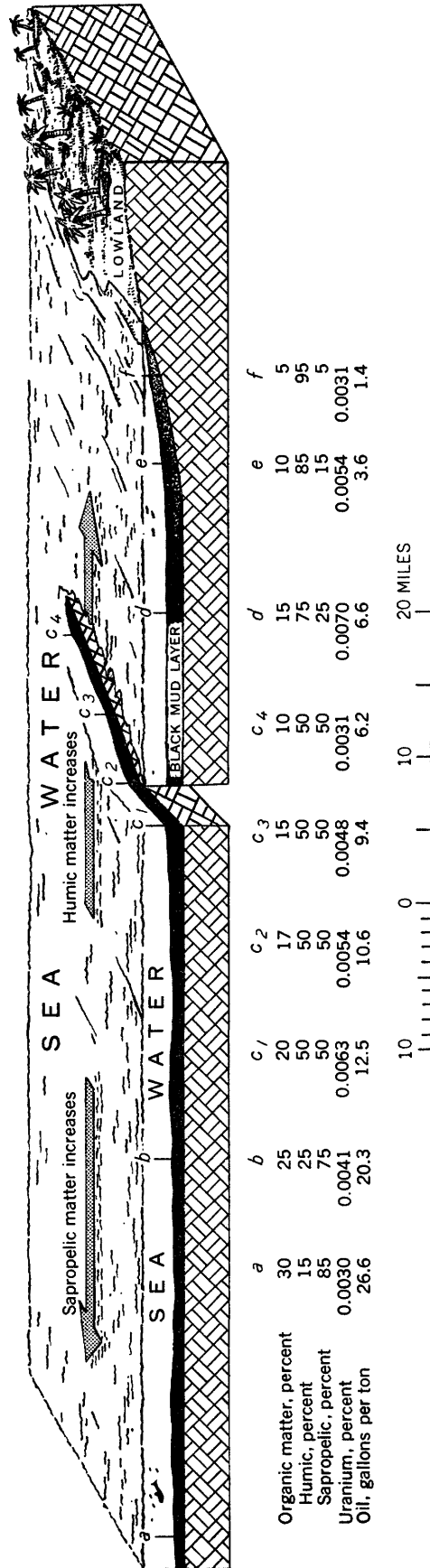


FIGURE 20.—Sketch showing theoretical distribution of humic and sapropelic materials in a shallow sea in which black muds are accumulating, and the estimated uranium content and oil yield of the resulting black shale. Increase of total organic matter seaward due chiefly to seaward decrease in amount of detrital sediment; proportional increase of sapropelic matter seaward due to decrease of humic land-plant debris and predominance of planktonic matter.

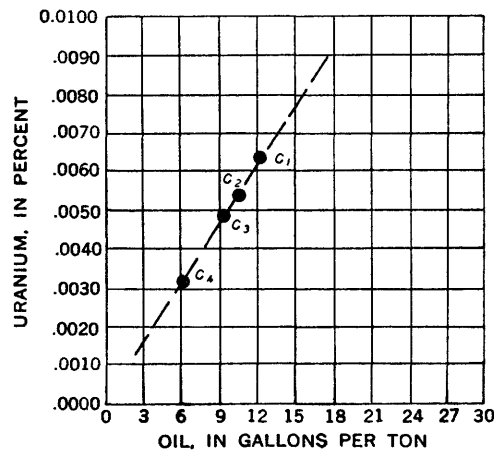
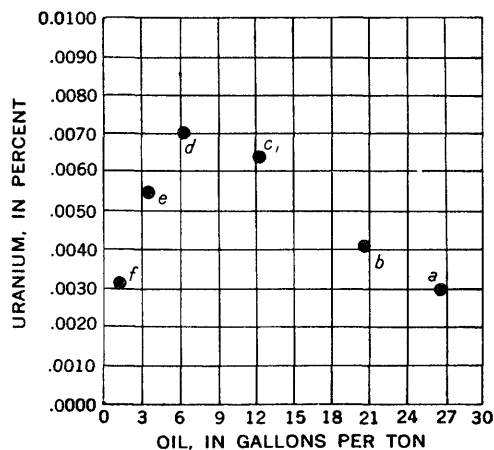


FIGURE 21.—Graphs showing relation of uranium content to oil yield in the theoretical black shale unit illustrated in figure 20.

2. Oil is derived directly from organic matter, whereas most of the uranium is not in the original organic matter but is later attached to or precipitated in the presence of organic matter.

3. Two main types of organic matter in black shales, the sapropelic and the humic, should be distinguished. The sapropelic type is derived from algae, spores, pollen, resins, cuticles, and analogous plant and animal remains. The humic type is derived from cellulose, lignin, and analogous woody parts of plants. Both types are present in varying proportions in most black shales.

4. The sapropelic type of organic matter yields 4 to 5 times more oil than does the humic type, whereas the humic type contains far more uranium than does the sapropelic type.

5. Some data indicate that as the uranium content of a black shale increases, the specific gravity of the oil derived from the shale by the Fischer method also increases. A tentative explanation of this linear relation is that both reflect an increase in the proportion of humic to sapropelic matter in the shale. This increase in the relative amount of humic matter also may be indicated by a decrease in the hydrogen content of the organic substances and a decrease in the percentage of organic matter converted to oil.

6. It is postulated that the uranium in shales is concentrated from sea water within, on, or near the humic type of organic matter by one or all of the following ways: direct precipitation (by simple reduction of the hexavalent to the tetravalent form) of uranium, probably by hydrogen sulfide; removal of uranium ions from solution by adsorption and complexing on solid humic materials; and adsorption or complexing of uranium by humic acids while in solution. The uranium in those black shales having an abundance of phosphatic materials generally is associated with the phosphate rather than with the organic matter; this uranium probably has substituted for calcium in the carbonate-fluorapatite structure.

7. Other factors being constant, only where the proportion of sapropelic to humic type of organic matter in a shale remains constant will the oil yield and uranium content have a high positive correlation. Because the humic type of organic matter is largely derived from land plants, this proportion would logically change with paleogeographic position, and the ratio of sapropelic to humic matter would increase with increasing distance from shore.

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TABLE 1.—Sampled localities and uranium content, oil yield, and other analyses of samples of black shales

[Source: Except where otherwise noted, all the data in this table were provided by U.S. Geological Survey personnel. The Survey geologists who were instrumental in obtaining these data are: E. C. Berry, Andrew Brown, J. H. Brown, Jr., W. B. Cassion, G. V. Conise, L. C. Conant, Walter Daanlichik, Wallace DeWitt, Jr., J. R. Donnell, D. C. Duncan, D. H. Earle, W. H. Hass, W. A. Heck, J. R. Houston, H. J. Hyden, J. M. Johnston, Charles Katlin, T. M. Kenn, R. C. Kelpferle, Chabot Kiburn, E. R. Landis, J. F. Pepper, J. C. Reed, Jr., R. C. Robeck, J. M. Schopf, L. E. Shirley, R. E. Smith, V. E. Swanson, H. A. Tournelot, L. D. Williams, and W. M. Zilbarsner. The Geological Survey chemists who made the analyses reported herein are: J. W. Budinsky, Alice Casenmetre, Chester Cox, Frank Curtitta, G. J. Daniels, M. H. Delevant, G. H. Dudley, D. L. Ferguson, Mona Frank, R. F. Gantner, F. S. Grimaldi, Norma Guttag, Carmen Hoy, B. L. Ingram, L. B. Jenkins, C. R. Johnson, J. Johnson, Mary Joslyn, Harry Levine, Irving May, B. A. McCall, J. P. McClure, Robert Meyrowitz, Roosevelt Moore, Wayne Mounjoy, W. W. Niles, J. W. Patton, Audrey Pietsch, Audrey Smith, Joan Smith, L. B. Steede, and W. F. Tucker]

Field No.	Locality	Sample		Oil (gallons per ton)	Water (gallons per ton)	Gas and loss (percent)	Sp gr of oil at 60° F compared with water at 60° F	Other analyses (percent)				
		Laboratory No.	Interval					Uranium (percent)	K ₂ O	P ₂ O ₅	Total S	Other
	Description		Thickness (feet)	Unit								
10J-9	Outcrop, Hurricane Creek, just below large dam at Cumberland Springs.	2143	2.04	g	7.5	10.1	0.899					
		2144	1.72	g	0.006	11.3	.882					
		2145	1.84	g	.005	8.0	.897					
		2146	1.78	g	.005	12.9	.892					
		2147	1.89	g	.005	5.1	.894					
		2148	1.83	g	.006	7.2	.906					
		2149	1.90	g	.006	9.3	.902					

CHATTAHOOGA SHALE

TENNESSEE

[For each locality, sample data are arranged from top to bottom of formation. Mm indicates basal unit of overlying Maury formation; gu, gm, and gl indicate, respectively, channel samples from the upper, middle, and lower units of the Gassaway member of the Chattanooga shale; du and dl, the upper and lower units of the Dowelltown member; g and d, the undivided members. Order of localities is generally from south to north. Laboratory numbers in parentheses are not formal laboratory numbers but are field numbers used by the laboratory]

Moore County

10K-6	Outcrop, about 4 airline miles north-northwest of Tullahoma and 2.6 miles west-northwest of Ovoca, cut on Cascade Branch road.	2174	1.80	gu	0.0061	4.0	5.8	0.883	0.17	8.59		
		2175	1.83	gu	.0050	3.4	5.3	.882	.13	5.19		
		2176	1.74	gu	.0072	4.3	3.8	0.883	.14	3.87		
		2177	1.80	gu	.0056	4.3	5.0	.888	.12	2.03		
		2178	.79	gm	.0024	1.3	2.8		.21	3.39		
		2179	1.68	gl	.0033	1.1	6.0					
		2180	2.00	gl	.0042	3.8	5.5	.896				
		2181	2.00	gl	.0052	5.6	5.0					
		2182	2.09	dl	.0018	3.8	4.6					
		2183	1.47	dl	.0020	3.8	6.0					
		2184	1.77	dl	.0028	2.4	5.3					
		2185	2.00	dl		2.7	5.5					
		114274	6.64	gu	.0085	6.2						
		114275	1.97	gm	.0048	2.8						
		114276	6.19	gl	.0049	4.6						
		114277	9.25	du	.0011	3.0						
		114278	5.41	dl	.0035	4.3						
YB-44	Drill core, from hole about 2 airline miles west-northwest of Manchester.	3264	2.11	gu	.0089	6.4	6.2	.905				
		3265	2.11	gu	.0073	5.4	5.0	.886				
		3266	1.00	gm	.0063	8	8.2	5.6				
		3267	1.75	gm	.0063	1.9	6.5	1.3				
		3268	1.99	gl	.0062	6.5	5.8	.898				
		3269	1.95	gl	.0058	6.0	6.0	.886				
		3270	1.87	gl	.0034	3.4	7.4					
		3271	2.00	dl	.0022	6.9	5.5	.875				
		3272	1.90	dl	.0035	4.9	4.6	.874				
		3273	1.96	dl	.0044	7.0	5.3	.890				
		3274	1.95	dl	.0032	4.7	6.0	.862				

Coffee County

10K-6	Outcrop, about 4 airline miles north-northwest of Tullahoma and 2.6 miles west-northwest of Ovoca, cut on Cascade Branch road.	2174	1.80	gu	0.0061	4.0	5.8	0.883	0.17	8.59		
		2175	1.83	gu	.0050	3.4	5.3	.882	.13	5.19		
		2176	1.74	gu	.0072	4.3	3.8	0.883	.14	3.87		
		2177	1.80	gu	.0056	4.3	5.0	.888	.12	2.03		
		2178	.79	gm	.0024	1.3	2.8		.21	3.39		
		2179	1.68	gl	.0033	1.1	6.0					
		2180	2.00	gl	.0042	3.8	5.5	.896				
		2181	2.00	gl	.0052	5.6	5.0					
		2182	2.09	dl	.0018	3.8	4.6					
		2183	1.47	dl	.0020	3.8	6.0					
		2184	1.77	dl	.0028	2.4	5.3					
		2185	2.00	dl		2.7	5.5					
		114274	6.64	gu	.0085	6.2						
		114275	1.97	gm	.0048	2.8						
		114276	6.19	gl	.0049	4.6						
		114277	9.25	du	.0011	3.0						
		114278	5.41	dl	.0035	4.3						
YB-44	Drill core, from hole about 2 airline miles west-northwest of Manchester.	3264	2.11	gu	.0089	6.4	6.2	.905				
		3265	2.11	gu	.0073	5.4	5.0	.886				
		3266	1.00	gm	.0063	8	8.2	5.6				
		3267	1.75	gm	.0063	1.9	6.5	1.3				
		3268	1.99	gl	.0062	6.5	5.8	.898				
		3269	1.95	gl	.0058	6.0	6.0	.886				
		3270	1.87	gl	.0034	3.4	7.4					
		3271	2.00	dl	.0022	6.9	5.5	.875				
		3272	1.90	dl	.0035	4.9	4.6	.874				
		3273	1.96	dl	.0044	7.0	5.3	.890				
		3274	1.95	dl	.0032	4.7	6.0	.862				

Outcrop, about 1 mile northwest of Noah on U.S. Highway 41; deep highway cut.

TABLE 1.—*Sampled localities and uranium content, oil yield, and other analyses of samples of black shales—Continued*

Field No.	Locality	Sample		Uranium (percent)	Oil (gallons per ton)	Water (gallons per ton)	Gas and loss (percent)	Sp gr of oil at 60° F compared with water at 60° F	Other analyses (percent)				
		Laboratory No.	Interval Thickness (feet)						Unit	K ₂ O	P ₂ O ₅	Total S	Other
CHATTANOOGA SHALE—Continued													
TENNESSEE—Continued													
Cannon County													
R-C2	Outcrop, about 4 airline miles south of courthouse at Woodbury, 1.4 miles west of State Route 53 at Sheboygan; cut along road. Outcrop, 3.6 miles north of junction of U. S. Highway 70S and Auburntown road on west edge of Woodbury; cut on west side of road.	2076	0.94	0.0076	5.0	6.7	2.3	0.923					
		2077	1.50	0.0080	5.0	6.0	2.1	0.913					
		2078	1.22	0.0048	5.0	3.6	1.6						
		2079	1.22	0.0048	5.0	6.0	1.0						
		2080	2.00	0.0046	4.2	6.5	2.7						
		2081	2.00	0.0063	5.5	6.0	3.4						
		2082	2.00	0.0063	7.1	4.8	2.3						
		2083	1.10	0.0043	6.0	5.5	3.5						
		2084	2.00	0.0043	6.0	7.2	2.6						
		2085	2.00	0.002	3.5	7.4	1.6						
		2086	1.50	0.003	6.0	6.0	2.3						
		2087	1.98	0.002	4.9	5.5	1.4						
		2088	1.98	0.002	4.9	4.6	1.4						
		2119	1.75	0.0040	7.3	4.6	2.1						
R-C6			2120	1.50	0.0073	5.1	7.2	2.1					
		2121	1.50	0.0073	8.7	4.3	3.9						
		2122	1.27	0.0074	7.1	4.8	2.3						
		2123	1.22	0.0047	9.1	4.1	1.9						
		2124	1.50	0.0054	11.2	4.1	2.2						
		2125	1.57	0.0058	9.8	3.8	3.8						
		2126	1.50	0.0052	10.4	3.8	2.0						
		2127	1.54	0.0043	9.1	4.8	2.6						
		2128	2.00	0.0028	2.1	8.6	2.1						
		2129	2.00	0.0044	2.9	9.6	2.4						
		2130	1.50	0.0063	6.0	7.2	1.2						
		2131	1.83	0.001	6.0	3.8	1.3						
Bledsoe County													
WR-49	Drill core, from hole on east side of Sequatchie Valley, east of Pikeville.	114280	4.00	0.0029	1.0					4.56	0.27	3.86	
		114281	4.00	0.0038	3.8					3.66	1.35	9.97	
		114282	5.40	0.0092	5.3					3.68	1.27	7.83	
		114283	1.72	0.0061	1.7					4.24	.16	5.17	
		114284	2.85	0.0063	2.8				4.24	.14	4.25		
		114285	6.46	0.0012	.5				4.90	.17	2.19		
White County													
LC-113A	Drill core, from hole about 8 airline miles southeast of Sparta; about 300 feet east of Dodson store, 75 feet north of road, and 70 feet east of Caney Fork River. (Fig. 4, loc. 5).	5270	2.1	0.0084	9.2	2.9	3.2	0.934					
		5271	1.1	0.0064	7.0	2.2	2.4	2.4	.926				
		5272	2.5	0.0053	6.5	2.6	2.0	2.0	.921				
		5273	1.0	0.0037	8.0	2.6	2.8	2.8	.922				
		5274	2.0	0.0060	7.9	2.4	1.8	1.8	.968				
		5275	1.0	0.0060	11.3	2.9	2.3	2.3	.936				
		5276	1.8	0.0058	10.9	3.4	1.9	1.9	.926				
		5277	1.3	0.0012	2.1	2.9	1.5	1.5					
		5278	2.0	0.0010	1.9	2.9	1.1	1.1					
		5279	1.5	0.0011	2.4	3.1	1.8	1.8					
		5280	1.6	0.0011	2.4	2.9	1.4	1.4	.890				
		5281	2.0	0.0007	1.9	2.6	1.7	1.7					
		5282	2.0	0.0026	9.8	3.1	1.5	1.5	.915				
			64	2.00	0.007	7.8	10.8	1.5	.921				
LC-11		Outcrop, about 4.8 airline miles west-northwest of Walling; south bank at northernmost part of Horseshoe Bend of Caney Fork; now below water level of Center Hill Reservoir.	267	1.38	0.005	5.6	11.3	1.2	.903				
	235		1.00	0.005	4.3	13.4	2.6						
	236		2.00	0.005	7.6	11.8	2.2						
	(11-21)		1.67	0.005	13.8	7.0	1.8		.920				
	(11-22)		2.00	0.006	13.0	6.5	2.3		.921				
	(11-31)		1.37	0.006	11.2	6.9	2.3		.923				
	(11-32)		1.23	0.006	12.6	5.0	2.0		.933				
	(11-61)		1.23	0.001	13.3(?)	5.0	2.0		.879				
	(11-62)		1.25	0.003	11.4	3.6	1.0		.888				

TABLE 1.—*Sampled localities and uranium content, oil yield, and other analyses of samples of black shales—Continued*

Field No.	Locality	Sample		Uranium (percent)	Oil (gallons per ton)	Water (gallons per ton)	Gas and loss (percent)	Sp gr of oil at 60° F compared with water at 60° F	Other analyses (percent)					
		Laboratory No.	Interval Thickness (feet)						Unit	K ₂ O	P ₂ O ₅	Total S	Other	
LC-102	Drill core, from hole about 0.3 mile northeast of previously described outcrop (LC-10); 100 feet west and 30 feet above road. (Fig. 4, loc. 2.)	(102-1)	0.50	Mm	0.002	None	Percent	0.1						
		131	1.25	Mm	.0072	2.2	2.0	3.9	0.922					
		132	1.95	gu	.0072	11.7	2.1	3.9	0.919					
		133	2.00	gu	.0075	12.5	2.0	3.0	.911					
		134	1.90	gu	.0071	6.7	1.4	1.9	.901					
		135	1.30	gm	.0048	3.1	1.2	1.6						
		136	1.20	gm	.0036	4.2	1.3	2.5	.926					
		137	1.80	gl	.0052	10.6	1.3	3.1	.928					
		138	1.80	gl	.0048	12.4	1.3	2.5	.927					
		139	1.80	gl	.0055	13.7	1.4	1.7	.929					
		140	2.00	du	.0060	3.0	1.4	1.0						
		141	2.00	du	.0016	8.6	1.6	0						
		142	1.80	du	.0011	1.2	1.7	0						
		143	2.00	du	.0011	5.2	1.6	1.1						
		144	2.00	du	.0010	1.7	1.5	1.1						
		145	1.81	du	.0010	12.4	1.3	1.7	.906					
		146	1.24	dl	.0024	10.5	1.3	3.1	.911					
		147	1.90	dl	.0034	7.7	1.5	.9	.906					
148	2.60	dl	.0021											
LC-101	Drill core, from hole on east side of State Route 56, 1.1 miles south of courthouse at Smithville.	(101-14)	4.0	gu	.009	11.7	2.5	.959						
		(101-15)	1.5	gu	.006	8.9	2.4	.949						
(101-21)	2.0	gm	.005	5.5	2.6	.8								
Putnam County														
13M-1	Outcrop at Burgess Falls, about 10 airline miles south-southwest of courthouse at Cookeville; about 0.8 mile upstream from old Cookeville power plant on Falling Water River.	1943	0.72	Mm	0.0016	4.2	Percent	0.2						
		1944	1.85	Mm	.0020	13.4	1.7	2.3	0.911					
		1945	1.98	gu	.0031	10.9	2.0	3.0	.920					
		1946	2.00	gu	.0047	11.6	3.6	3.0	.930					
		1947	2.00	gu	.0047	11.1	4.1	3.0	.924					
		1948	2.00	gu	.0060	11.9	2.5	1.3	.926					
		1949	1.80	gu	.0050	11.3	3.5	1.0	.935					
		1950	.85	gm	.0034	5.8	2.5	1.7	.905					
		1951	1.99	gm	.0042	8.3	2.1	1.1	.898					
		1952	1.94	gl	.0049	11.9	2.7	1.8	.919					
		1953	1.69	gl	.0044	12.4	2.5	1.2	.931					
		1954	1.69	gl	.0049	12.9	2.6	1.8	.926					
		1955	1.69	gl	.0057	16.6	1.7	3.4	.925					
		1956	2.07	dl	.0026	13.0	1.1	1.4	.903					
		1957	1.76	dl	.0028	12.4	1.4	1.4	.907					
		1958	1.76	dl	.0016	6.1	1.6	.4	.905					
		13L-11	Outcrop, on road to Center Hill Dam, 2.5 miles west of Silver Point.	2000	1.57	Mm	.001	None	Gallons per ton	1.1				
				2001	1.17	Mm	.002	None	6.7	1.1				
2002	1.71			Mm	.004	3.7	3.8	.36						
2003	1.80			Mm(?)	.006	5.8	9.6	.6	.907					
2004	1.90			gu	.006	8.2	5.8	1.4	.918					
2005	1.78			gu	.006	8.6	5.0	2.5	.926					
2006	1.63			gu	.008	8.2	5.0	1.8	.926					
2007	1.32			gu	.007	1.3	7.0	1.8						
2008	1.31			gm	.005	2.4	5.3	.4						
2009	1.55			gl	.005	Trace	9.6	1.8	.930					
2010	1.55			gl	.005	8.7	5.3	2.2						
2011	1.55			gl	.005	Trace	10.3	5.3						
2012	2.02	dl	.003	6.3	7.2	.5	.907							
2013	2.01	dl	.004	2.6	7.7	.3								
2014	2.02	dl	.003	1.6	8.4	.1								

TABLE 1.—Sampled localities and uranium content, oil yield, and other analyses of samples of black shales—Continued

Field No.	Locality	Sample		Uranium (percent)	Oil (gallons per ton)	Water (gallons per ton)	Gas and loss (percent)	Sp. gr. of oil at 60° F. compared with water at 60° F.	Other analyses (percent)			
		Laboratory No.	Interval Thickness (feet)						Unit	K ₂ O	P ₂ O ₅	Total S
CHATTANOOGA SHALE—Continued												
TENNESSEE—Continued												
Jackson County												
14M-16	Outcrop, about 6 airline miles northeast of Gainesboro and about 1 mile south of Pleasant Hill School along road leading to Sugar Creek.	3353 3354 3355 3356 3357 3358 3359	1.85 2.00 2.00 2.00 2.00 2.00 2.00	.001 .002 .004 .004 .004 .002 .003	3.8 3.8 6.8 4.2 8.0 10.7 6.0	9.4 7.4 8.6 12.0 7.2 5.0 6.5	1.2 1.7 1.4 2.6 2.3 2.0	0.893 .896 .896 .897 .925 .920 .912				
Clay County												
15N-12	Outcrop, about 3 miles east of courthouse at Celina and about 260 yards west of north end of Dale Hollow Dam; cut on north side of road.	2269 2270 2271 2272 2273 2274 2275 2276 2277 2278	2.00 2.00 2.00 2.00 1.50 1.51 1.82 1.82 1.18	0.0028 .0054 .0055 .0060 .0043 .0054 .0073 .0060 .0043 .0021	6.2 8.7 6.1 4.0 1.6 5.2 6.5 7.2 5.3	7.0 5.3 5.5 7.9 10.6 7.0 4.3 3.6 5.3	1.3 1.6 .9 .7 1.0 1.7 2.3 2.3 1.5	0.888 .890 .899 .891 .892 .889 .897 .896			3.4 .2 .1 .1 .1 .1 .2 .4	
KENTUCKY												
Russell County												
16P-1	Outcrop, about 9.5 airline miles southwest of courthouse at Jamestown; cut for the west end of Wolf Creek Dam, now concealed by dam. Vertically contiguous samples of entire formation, except for lower 5.1 feet; upper 4.0 feet of shale contain scattered phosphatic nodules.	17291 17292 17293 17294 17295 17296 17297 17298 17298-A 17299 17300 17301	2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0 2.0	0.003 .003 .003 .005 .006 .005 .005 .005 .005 .005 .005 .005	15.9 11.4 11.9 13.2 10.5 8.6 8.0 8.2 9.1 9.1 9.1 10.1	4.6 4.1 3.8 4.3 3.8 3.8 3.8 3.6 3.8 3.8 4.3	2.2 2.4 1.9 3.1 2.4 2.2 2.4 2.9 2.5 3.3 3.4	0.887 .905 .909 .926 .915 .896 .895 .905 .900 .904 .904 .901				
Pulaski County												
17R-6	Outcrop, about 7.5 airline miles northwest of courthouse at Somerset; at Hogue on east bank of Fishing Creek and cut in north side of road. Vertically contiguous channel samples of entire formation; upper 6.25 feet contain scattered phosphatic nodules.	17320 17321 17322 17323 17324 17325 17326 17327 17328 17329 17330 17331 17332 17333 17334 17335 17336 17337 17338	2.00 2.00 2.00 2.25 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.00 2.50	0.003 .003 .002 .004 .004 .005 .003 .004 .004 .004 .004 .004 .004 .004 .004 .005	17.8 15.4 13.7 11.3 11.9 7.4 6.7 6.2 7.3 8.0 8.0 8.5 7.7 8.4 11.1 12.1	6.5 6.6 7.2 7.0 6.8 6.8 8.4 6.2 6.5 5.8 6.2 5.8 7.7 8.2 8.2 5.8	5.1 2.4 1.8 1.8 2.1 2.2 1.0 1.8 2.1 2.2 1.4 1.4 1.9 2.1 1.2 1.5	0.906 .913 .912 .910 .910 .895 .903 .897 .898 .893 .890 .871 .902 .908 .919 .928 .912 .911				

TABLE 1.—*Sampled localities and uranium content, oil yield, and other analyses of samples of black shales—Continued*

Field No.	Locality		Sample		Uranium (percent)	Oil (gallons per ton)	Water (gallons per ton)	Gas and loss (percent)	Sp gr of oil compared with water at 60° F	Other analyses (percent)			
	Description	Laboratory No.	Interval	Unit						K ₂ O	P ₂ O ₅	Total S	Other
	Outcrop of type section of Dunkirk shale at Dunkirk Harbor...		12	pd	0.001	3.0							
Chautauque County, N.Y.													
Wyoming County, N.Y.													
	Outcrop, Beaver Meadow Creek, Java Village, Java Township; crude channel sample about 10 feet above base near middle of formation.		32680	1	hp	0.003	2.4	3.6	0.4				
OKLAHOMA AND TEXAS													
[c, indicates Chattanooga shale; w, Woodford shale; hd, Doublehorn shale member of Hony formation; we, Woodford shale of Ellison (1950)]													
Cherokee County, Okla.													
Murray County, Okla.													
	Outcrop SE¼ sec. 24, T. 18 N., R. 22 E., 11 vertically contiguous channel samples of lowermost 111 feet of black shale. Total thickness of formation, about 35 feet.		147374 147172 147173 147174 147375	1 1 1 1 1	c c c c c	0.001 .004 .005 .005 .003	1.4 1.7 1.9 1.4 1.4	4.3 4.3 4.3 3.3 4.8	0.5 4.0 2.0 1.9 2.5				4.6 organic C 4.5 organic C
	Outcrop SE¼ sec. 35, T. 1 S., R. 3 E.; channel samples of black shale. Laboratory No. 147211 of top foot, No. 147205 of foot, No. 147206 of 2nd foot, No. 147207 of 3rd foot, No. 147208 of 4th foot, No. 147209 of 5th foot, No. 147210 of 6th foot, No. 147207 of unit, 32.3 to 37.3 feet from top, and remaining samples of contiguous 6-foot limits below No. 147207 (fig. 13).		147211 147205 147206 147207 147208 147209 147210	1 4 5 5 5 5 5	w w w w w w w	0.004 .007 .006 .004 .004 .004 .002	12.5 15.3 11.5 12.0 14.4 12.0 3.8	5.3 7.2 8.6 7.2 4.8 7.2 10.5	2.0 2.5 1.0 3.0 1.0 1.5 2.0	0.984 1.014 1.033 .893 .888 .891			
Burnet County, Tex.													
	Outcrop, Doublehorn Creek, Hony ranch, about 6 airline miles south-southeast of Marble Falls, Tex.; channel sample of about 5 feet of black shale. Total thickness of member here 8 to 8½ feet (Clout, Barnes, and Hass, 1937, p. 815).		209211	5±	hd	0.009	21.8	7.2	5.0	0.991			3.2 K

Andrews County, Tex.

Core, Sinclair Prairie Oil University 6 "154"; Laboratory Nos. 211045 and 211049 spot samples from parts of core at 9,245.2 and 9,246.4 feet depths, respectively. Nos. 211051 through 211057 from parts of core representing successive 1-foot depths from 9,247 to 9,253 feet; No. 211057, 9,253 to 9,255.3 feet; samples provided by S. P. Ellison, Jr. (Ellison, 1950).	211045 211049 211051 211052 211053 211054 211055 211056 211057	we we we we we we we we we	0.003 .002 .003 .003 .002 .003 .003 .001 .005	7.7 9.2 7.0 7.0 8.2 8.2 11.3 10.1 5.3	4.1 3.8 5.3 4.1 4.1 3.8 3.6 4.8 4.8	1.7 1.0 .5 2.5 1.0 3.0 1.5 2.0 	0.968 1.172 .951 .961 .970 .959 .967 .962 .955	3.4 K
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PENNSYLVANIAN SHALES

ILLINOIS, KANSAS, AND OKLAHOMA

[sc, indicates shale below Shoal Creek limestone of McLeansboro group; cs, shale above Spaniard limestone member of Savanna formation; ts, black shale in Senora formation, the black shale unit above the coal in the Tebo formation of Seaight and others (1953, p. 2749); sb, uppermost black shale unit of Senora formation; cb, uppermost black shale unit of Cherokee shale; fs, black shale in the Fort Scott limestone; pb, black shale at base of Favnes limestone; l, black shale in the Lenap limestone; co, black shale near base of Coffeyville formation]

ILLINOIS

	Inches		Percent		0.973		0.6
Outcrops D10, SE $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 17, T. 7 S., R. 10 E., D11, SW $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 21, T. 7 N., R. 4 W., D21, NE $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 33, T. 8 S., R. 6 E.; D70, NW $\frac{1}{4}$ NE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 3, T. 13 N., R. 5 W.; D72, SW $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 36, T. 10 N., R. 7 W.; D92, SE $\frac{1}{4}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 3, T. 9 N., R. 12 W.; D94, SW $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 22, T. 2 N., R. 6 W.; Collected and reported by Ostrom and others (1955) and Lamar and others (1956). Data on oil yield from Lamar and others (1956, table 3); uranium and P ₂ O ₅ analyses by U.S. Geological Survey (fig. 16).	12 18 18 10 17 36 10 26	sc sc sc sc sc sc sc	15.5 11.3 9.1 11.7 12.3 8.8 8.8	0.0651 .0073 .0049 .0106 .0091 .0052 .0091	4.0 5.5 3.5 4.0 4.0 3.0 5.2	3.8 2.8 1.0 3.7 3.7 2.4 2.5	0.6 1.5 1.9 .6 2.3 1.0 1.9
Outcrops D22L, SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 5, T. 10 S., R. 7 E.; D42, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 17, T. 5 N., R. 4 E.; D56, SE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 3, T. 32 N., R. 2 E.; D58, NE $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 3, T. 33 N., R. 1 E.; D68, center sec. 36, T. 2 N., R. 1 W.; D75, SW $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 24, T. 12 N., R. 11 W.; D101, SW $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 11, T. 18 N., R. 11 W.; Collected and reported by Ostrom and others (1955) and Lamar and others (1956). Data on oil yield from Lamar and others (1956, table 3); uranium and P ₂ O ₅ analyses by U.S. Geological Survey (fig. 16).	18 24 24 34 38 30 26	cs cs cs cs cs cs	12.9 13.1 28.8 5.0 17.0 18.6 16.2	.0074 .0086 .0067 .0082 .0071 .0057	3.0 3.5 4.3 4.0 3.0 4.2	4.9 .5 4.3 3.9 3.0 4.2	.8 1.2 4 1.1 4.0 1.5

Craig County, Okla.

Outcrop NE $\frac{1}{4}$ sec. 3, T. 26 N., R. 21 E.; channel sample from part of unit 10 feet thick.	146101	sp	0.002	0.2	0.5	0.5	
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Rogers County, Okla.

Outcrop SW $\frac{1}{4}$ sec. 12, T. 21 N., R. 16 E.; channel sample. Outcrop center of south line sec. 3, T. 23 N., R. 16 E. Channel sample of upper 4 feet of this unit, which is 7 feet thick (included in fig. 14).	146048 146082	ts sb	0.002 0.002	<0.2 8.1	9.6 11.5	1.0 2.5	0.981
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Bourbon County, Kans.

Outcrop NE $\frac{1}{4}$ sec. 19, T. 25 S., R. 25 E. Laboratory No. 148035 channel sample of upper gray shale; No. 148034 of lower black shale; Nos. 148038, 148039, 148041, and 148042 channel samples taken 6, 12, 54, and 72 feet, respectively, horizontally away from No. 148034 (fig. 14).	148035 148034 148038 148039 148041 148042 148053	cb cb cb cb cb cb fs	0.0022 .0088 .0093 4.6 .0049 .0042 .0040	0.2 2.9 4.6 7.2 7.2 12.7	4.8 5.8 6.7 5.3 5.3 4.3	1.0 1.5 .5 1.0 2.0 2.0	1.5 3.4 5.3 4.6 3.3 2.2 2.4
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Linn County, Kans.

Laboratory No. 146999 channel sample from outcrop SW $\frac{1}{4}$ sec. 26, T. 21 S., R. 25 E. No. 147000 spot sample from outcrop center of west line sec. 18, T. 23 S., R. 25 E. Outcrop center of sec. 6, T. 21 S., R. 25 E.; channel sample.	146999 147000 146981	pb pb l	0.004 .006 .003	14.6 6.7 12.0	10.1 16.3 7.2	3.5 4.0 4.0	0.947 .951 .957	2.3
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INDEX

	Page		Page
A			
Acknowledgments.....	3, 31	Green River formation, analyses.....	41
Albert formation.....	2, 21	Laney shale tongue.....	20
Alum shales of Sweden.....	4, 21	locality.....	2
Analytical methods.....	7	Mahogany ledge.....	7, 20, 41
Analyses of black shales.....	31-41	oil shales.....	6, 19-21
Ancient sea water, source of uranium.....	5, 24	uranium content.....	20-21, 26
Antrim shale, analyses.....	37	H	
correlative of Chattanooga shale.....	7	Hanover shale, Pipe Creek member, analyses.....	38
locality.....	2	Heebner shale member, Oread limestone.....	16
oil yield and uranium content.....	14-15	Houy formation, Doublehorn shale member, analyses.....	38
Australia, shales, relation of specific gravity of oil to oil recovery.....	13	locality.....	2
Averages, uranium content of shales.....	4	oil yield and uranium content.....	16
B			
Black shale, definition.....	3	Humic acid, role in concentrating uranium.....	24-25, 28
Brazil, shales, relation of specific gravity of oil to hydrogen content and to oil recovery.....	13	Humic organic matter, defined.....	6
Byproducts of oil distillation.....	3	decay process.....	23
C			
<i>Callixylon</i>	11-12, 14, 24, 25	derivation.....	22-23
Canada, Albert formation.....	21	relation to oil yield and uranium content.....	11-12, 25-27
Carbon content, relation to uranium content.....	11, 15, 16, 21-22	Hydrogen content of organic matter, index of oil yield.....	13, 23
Carbonaceous shale, definition.....	3, 4	Hydrogen sulfide, in environment of marine black shale deposition.....	4, 5, 23
Carbonate minerals.....	4, 8, 20	role in precipitation of uranium.....	24, 28
Chattanooga shale, analyses.....	31-37, 38-39	K	
in the midcontinent area.....	15-16	Kerogen.....	6, 22
in the Southeastern States.....	8-14	Kolm.....	4, 21, 22, 24
oil yield.....	3, 7, 9-11, 12	Kukersite.....	21
organic matter.....	8, 11-12	L	
sampled localities.....	2, 7, 31-37, 38-39	Laney shale tongue, Green River formation.....	20-21
uranium content.....	3, 4, 7, 8, 9-11, 12	Lenapah limestone, black shale in, analyses.....	39
Chattanooga shale and correlatives, in eastern and central United States.....	7-15	oil yield and uranium content.....	16
Oberokee shale, analyses.....	39	Literature cited.....	28-30
oil yield, phosphate and uranium contents.....	16-17	M	
Clay, in marine black shales.....	4	Mahogany ledge, Green River formation.....	7, 20, 41
Coffeyville formation, black shale near base, analyses.....	40	Manchuria, shales, relation of specific gravity of oil to oil recovery.....	13
Conclusions.....	25-28	Maury formation.....	9, 31, 33, 34, 35
Criteria, for locating shale with most uranium.....	4, 8, 9	Mississippian shales. <i>See</i> Albert formation, Maury formation.	
D			
Definition of terms.....	3, 6	N	
Devonian shales, localities.....	2	Nashville Basin. <i>See</i> Eastern Highland Rim.	
oil yield and uranium content.....	7, 14, 16, 31-39	New South Wales, torbanite oil shales.....	6, 13, 21
Diagenesis, effect on oil yield and uranium content of shales.....	22, 25	O	
<i>Dictyonema</i> shales of Estonia and U.S.S.R.....	21	Ohio shale, analyses.....	11, 37
Doublehorn shale member, Houy formation.....	16, 38	correlative of Chattanooga shale.....	7, 11
Dowelltown member, Chattanooga shale.....	8, 9-10, 31-35	locality.....	2
Dunkirk shale member, Ferrysburg formation.....	7, 37-38	Oil shale, definition.....	3, 6
E			
Eastern Highland Rim, locality of Chattanooga shale.....	3, 8	Oil yield, Albert formation.....	21
Economic significance.....	3-4	alum shales of Sweden.....	21
Eudora shale member, Stanton limestone.....	16	analyses.....	31-41
F			
Fischer retort assay method, used for oil yield determinations.....	7, 12	Antrim shale.....	14-15, 37
Fluorometric method, for uranium analyses.....	7	black shale in Coffeyville formation.....	40
<i>Foersta</i>	11-12, 25, 26, 37	black shale in Fort Scott limestone.....	16, 39
Fort Scott limestone, black shale in, analyses.....	39	black shale in Lenapah limestone.....	16, 39
oil yield and uranium content.....	16	black shale in Pawnee limestone.....	16, 39
G			
Gassaway member, Chattanooga shale.....	3, 4, 8-12, 31-35	black shale in Phosphoria formation.....	18-19, 40
Geochemistry of uranium concentration.....	23-25	black shale in Savanna formation.....	39
Glen Davis mine, Australia.....	21	black shale in Senora formation.....	39
		black shales of Pennsylvanian age.....	16-18, 39-40
		Chattanooga shale.....	8, 15, 31-37, 38
		Cherokee shale, uppermost black shale unit.....	17, 39
		Devonian shales.....	7-16, 31-39
		Doublehorn shale member of Houy formation.....	16, 38
		Dunkirk shale member of Ferrysburg formation.....	37-38
		Eudora shale member of Stanton limestone.....	16

	Page		Page
Oil yield, Albert formation—Continued			
Green River formation.....	20, 41	South Africa, oil shales.....	13, 21
Heebner shale member of Oread limestone.....	16	Specific gravity of oil, relation to hydrogen content.....	13
Houy formation.....	16, 38	relation to oil recovery.....	13
kolm from Cambrian shales of Sweden.....	22	relation to uranium content.....	12-14, 15, 28
Maury formation.....	33-35	Stanton limestone, Eudora shale member.....	16
Ohio shale.....	37	Summary.....	26-28
Pipe Creek member of Hanover shale.....	37	Sweden, alum shales.....	4, 21-22
relation to uranium content.....	8-10, 14, 15, 18-19, 21-22, 25-26		
role of organic matter.....	6, 22-26	T	
shale above No. 2 coal, Carbondale group.....	17-18, 39	Tebo formation, black shale unit, analysis.....	39
shales in foreign countries.....	21-22	Torbanite oil shales, New South Wales, yield.....	6
Sharon Springs member of Pierre shale.....	19, 41		
Shoal Creek limestone, shale below.....	17-18, 39	U	
Woodford shale.....	15, 16, 38-39	Upper Devonian shales, analyses.....	37-38
Oread limestone, Heebner shale member.....	16	Uranium, lateral distribution in black shales.....	4, 8
Organic matter, "blackness" as measure of amount in shale.....	9-10	methods of emplacement in marine black shales.....	4-6, 23-24
genetic interrelation to uranium and phosphate in Pennsylvanian shales.....	16-17	Uranium concentration, geochemistry.....	23-25
in marine black shales.....	4, 5	Uranium content, Albert formation.....	21
proportion of humic to sapropelic as indication of oil yield and uranium content.....	11-14, 25-28	alum shales of Sweden.....	21
relation to oil yield.....	6, 22-23	analyses.....	31-41
relation to uranium content.....	4-5, 23-28	Antrim shale.....	14-15, 37
sapropelic and humic, defined.....	6, 22	black shale in Coffeyville formation.....	40
P		black shale in Fort Scott limestone.....	16, 39
Parachute Creek member, Green River formation.....	20, 41	black shale in Lenapah limestone.....	16, 39
Pawnee limestone, oil yield and uranium content.....	16, 39	black shale in Pawnee limestone.....	16, 39
Pennsylvanian shales, analyses.....	39-40	black shale in Phosphoria formation.....	18-19, 40
localities.....	2	black shale in Savanna formation.....	39
oil yield and uranium content.....	16-18	black shale in Senora formation.....	39
Perrysburg formation, Dunkirk shale member, analyses.....	37-38	black shales of Pennsylvanian age.....	16-18, 39-40
Phosphate, analyses, in black shales.....	31-40	Chattanooga shale.....	8, 15, 31-37, 38
component of marine black shales.....	4-5	Cherokee shale, uppermost black shale unit.....	17, 39
relation to uranium in Green River formation.....	21	Devonian shales.....	7-16, 31-39
relation to uranium in Pennsylvanian shales.....	16-17	Doublehorn shale member of Houy formation.....	16, 38
relation to uranium in Phosphoria formation.....	18-19	Dunkirk shale member of Perrysburg formation.....	37-38
relation to oil yield and uranium content.....	17, 18-19, 28	Eudora shale member of Stanton limestone.....	16
Phosphoria formation, analyses.....	40	Green River formation.....	20, 41
locality.....	2	Heebner shale member of Oread limestone.....	16
oil yield and uranium content.....	18-19	Houy formation.....	16, 38
Photometric method of Cuttitta, used for oil determinations.....	7	kolm from Cambrian shales of Sweden.....	4, 21, 22, 24
Pierre shale, locality.....	2	Maury formation.....	33-35
oil yield and uranium content.....	19, 41	Ohio shale.....	37
Pipe Creek member, Hanover shale.....	37, 38	Pipe Creek member of Hanover shale.....	37
		relation to carbon content.....	11, 15, 16, 21-22
R		relation to oil yield.....	8-10, 14, 15, 18-19, 21-22, 25-26
Radioactivity. See Uranium content.		relation to organic matter.....	4-5, 23-28
Resistates, in marine black shales.....	4, 5	relation to phosphate content.....	4-5, 16-17, 18-19, 28
		relation to specific gravity of oil.....	12-14, 15, 28
S		role of organic matter.....	22-26
Sampled localities.....	2, 31-41	shale above No. 2 coal, Carbondale group.....	17-18, 39
Sampling methods.....	6-7	shales in foreign countries.....	4, 21-22
Sapropelic organic matter, defined.....	6, 22	Sharon Springs member of Pierre shale.....	19, 41
derivation.....	22-23	Shoal Creek limestone, shale below.....	17-18, 39
relation to uranium content and oil yield.....	23, 25-27	Woodford shale.....	15, 16, 38-39
Senora formation, black shale units, analyses.....	39		
Shales in foreign countries.....	21-22	W	
Sharon Springs member, Pierre shale.....	19, 41	Weathering, effect on oil yield and uranium content.....	7
Shoal Creek limestone, black shale below.....	17-18, 39	Woodford shale, analyses.....	38-39
		localities.....	2
		relation of uranium content to oil yield and specific gravity of oil.....	15-16