Contributions to the Geology of Uranium and Thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland 1955

Compiled by LINCOLN R. PAGE, HOBART E. STOCKING, *and* HARRIET B. SMITH

GEOLOGICAL SURVEY PROFESSIONAL PAPER 300

Prepared as a cooperative effort of the United States Geological Survey and the United States Atomic Energy Commission and published with the permission of the Commission

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1956

URANIUM IN MARINE BLACK SHALES OF THE UNITED STATES

By VERNON E. SWANSON, U. S. Geological Survey

CONTENTS

	Page
Abstract	451
Introduction	451
Lithologic and chemical characteristics	452
Chattanooga shale	453
Midcontinent shales of Pennsylvanian age	454
Phosphatic carbonaceous shales, Phosphoria formation	455
Other uraniferous shales	455
Geologic significance of abnormally radioactive shales	456
References cited	456

ILLUSTRATION

	Page
FIGURE 158. Distribution of significantly uraniferous black shale	452

ABSTRACT

Uranium is disseminated in minor amounts, generally not exceeding 0.02 percent, in many of the marine organic-rich black shales in the United States. Two hundred or more stratigraphic units, ranging in age from Precambrian to Tertiary, consist wholly or in part of black shale, and one or more of these units are present in nearly every State. Broad reconnaissance and scattered sampling of many of these units and also a few detailed geologic studies have been made; several thousand samples of black shale have been analyzed for uranium, and many for organic content, oil yield, and specific chemical constituents.

The most uraniferous shales are those rich in organic matter (mainly plant debris), pyrite, and phosphatic matter. They are also low in calcium carbonate content, and yield oil by destructive distillation. Most uraniferous black shale units are thin blanketlike deposits of Paleozoic age that have very little variation in thickness or lithology over wide areas and were deposited at an exceedingly slow rate. The Chattanooga shale and its equivalents, such as the New Albany, Ohio, and Woodford formations, which range from Late Devonian to early Mississippian age, make up such a blanket deposit that was laid down in the eastern and central parts of the United States; this shale averages about 50 feet in thickness over much of this area and contains between 0.001 and 0.035 percent uranium. Several thin and widespread black shales of Pennsylvanian age in the Midcontinent and thin beds of phosphatic black shales in the Phosphoria formation of Permian age in Idaho, Montana, and Wyoming have comparable uranium contents.

Both field and laboratory studies show that uranium is evenly disseminated throughout the black shale and is believed to have accrued contemporaneously with the deposition of the enclosing organic-rich muds. Areal variations in uranium content are related directly to regional paleogeographic trends; vertical variations are related directly to lithologic changes, particularly in the ratio of organic matter to detrital minerals. The form of the uranium in the shale is not completely known and no uranium-bearing minerals have been identified; however, laboratory studies indicate that uranium ions in the sea water were adsorbed by the organic matter.

In order to evaluate the uranium potential of marine black shales, they may be classified by the tectonic and paleogeographic setting of the area during time of accumulation of organic-rich muds. Thus, four general categories are considered: epicontinental areas similar to the Chattanooga, geosynclinal-fringe areas similar to the Marcellus, miogeosynclinal areas similar to the Normanskill, and eugeosynclinal areas similar to the Mariposa. As inferred from geologic studies, each is characterized by definite water conditions (chemistry, depth, circulation, life regimen), climatic conditions, rate and amount of subsidence, and relation to the source of sediments (distance, topography and drainage, rock composition). The more uraniferous shales known in the United States were deposited in epicontinental seas. Further study and refinement of these or similar characteristics that serve to identify uraniferous shales may result in the finding of additional marine shales of higher grade.

INTRODUCTION

For the past decade black shales have been regarded as possible low-grade sources of uranium, and numerous black shale units in the United States have been tested for their uranium content. Of those tested, a few widespread shales of Paleozoic age contain about 0.007 percent uranium.

To date, the search for uraniferous shales has been mainly a broad-scale surface reconnaissance, utilizing radiation-detecting instruments. The general radioactivity of many black shales in the subsurface has been determined from gamma-ray logs of oil and gas wells (Gott and Hill, 1953), and many well cores have been scanned radiometrically and analyzed chemically for uranium. Hundreds of exposed black shale units that range in age from Precambrian to Tertiary, and from a few feet to several thousand in thickness, have been cursorily examined. Several have been studied in detail and hundreds of samples collected and chemically analyzed for uranium and other constitutents; many are represented by only a few samples that have been measured chemically or by field radioactivity methods. The possibilities in the United States for finding black shales more uraniferous than those now known certainly have not been exhausted; and it is believed that further study of the paleogeology of marine shales may be of help in finding shales of higher uranium content than are now known.

No uranium has been produced from black shale in the United States, because a large number of high-grade deposits of other types have been discovered and because black shale units of sufficiently high grade and large volume have not been found. Despite the low uranium content of black shales, the tonnage of metallic uranium in shales is extremely large, and it is possible that the amount of uranium required in the future may necessitate developing this large low-grade reserve. For example, central Tennessee and parts of adjoining states have about 85 billion (85×10^9) tons of shale averaging slightly more than one-tenth of a pound of uranium per ton; this represents a reserve of 5 to 6 million tons of uranium (Johnson, 1955).

Many references to the radioactivity of black shales exist in the literature. An extensive bibliography is listed by McKelvey and Nelson (1950), and a comprehensive review of theories on the depositional origin of black shales is given by Twenhofel (1939). The distribution of significantly uraniferous black shales is shown in figure 158.

LITHOLOGIC AND CHEMICAL CHARACTERISTICS

With few exceptions the uranium content of known marine black shales of the United States does not exceed 0.02 percent, and the contents of few shale units having a thickness of more than 2 feet exceed 0.005 percent uranium. Black vitreous layers of coalified plant tissue that are fractions of an inch thick and abundant in black shales of Devonian age contain as much as 0.035 percent uranium. Specially selected

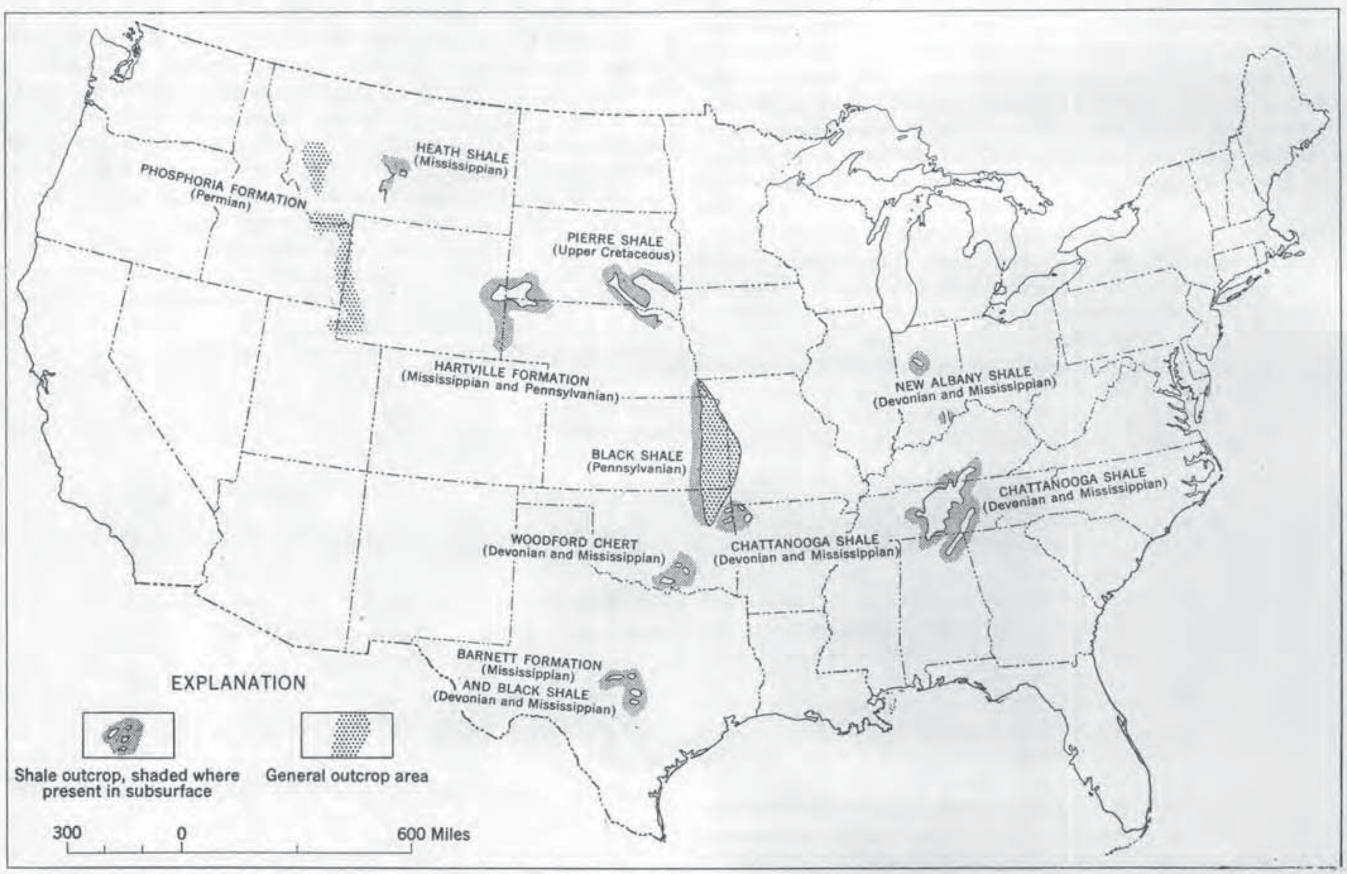

FIGURE 158.—Distribution of significantly uraniferous black shale.

samples of highly phosphatic material in some black shales may have more than 0.035 percent uranium. These and a few secondarily mineralized shales, which have sporadic uranium concentrations, are the only ones known to have more than 0.02 percent uranium.

Several marine black shales are almost nonradioactive, having uranium contents comparable to the average sedimentary rock. Parts of the Eagle Ford shale of Late Cretaceous age in east-central Texas, for example, contain less than 0.001 percent, though this formation has several lithologic characteristics typical of other uraniferous shales (Eargle, written communication, 1955).

The total radioactivity of the more uraniferious black shales is primarily due to uranium, though thorium and the radioactive isotope of potassium are probably important constituents of some radioactive shales.

To date, laboratory experiments have failed to isolate and identify the uranium mineral or minerals in black shales. The uranium is apparently thoroughly disseminated in the shale but is associated most closely with the contained organic matter which is also finely dispersed. The rapid adsorption of uranium by carbonaceous material immersed in a uranyl solution (Szalay, 1954; Moore, 1954) supports the theory that uranium in the sea water was adsorbed by the organic debris contemporaneously with the deposition of the enclosing muds (Conant, p. 463, this volume). The mineralogical association of the uranium and the phosphatic material common to many black shales is discussed in detail by McKelvey (p. 477, this volume).

In addition to the organic matter, other common components of uraniferous shales are pyrite lenses, nodules, and minute crystals and phosphate as nodules as much as a foot in diameter or as disseminated particles. Also, abnormal amounts of certain trace elements, such as copper, nickel, vanadium, germanium, and molybdenum, are common in some uraniferous black shales. The uranium content generally decreases sharply with small increases of calcium carbonate.

Many uraniferous black shales have long been known as oil shales. The marine Chattanooga shale, noted for its comparatively high radioactivity, is a low-grade oil shale, yielding on the average 5 to 10 gallons of oil per ton of shale by destructive distillation methods; further, a crude relationship can be shown between the increase of oil content and uranium content in this formation. Some oil-bearing shales, however, are not particularly uraniferous. For example, the oil shale units of the nonmarine Green River formation in Colorado and Utah contain 0.001 percent uranium or less.

CHATTANOOGA SHALE

Among the radioactive marine black shales that have been studied in the United States, the Chattanooga shale of Late Devonian and early Mississippian age in central Tennessee is best known and is currently considered as a possible low-grade source of uranium. Other shale units in the United States locally contain more uranium, but such shales are less extensive, thinner, or are deeply buried. The reader is referred to papers by Brown (p. 457, this volume), Conant (p. 463, this volume), and Hass (1956) for more detailed descriptions of the Chattanooga shale.

The Chattanooga shale in Tennessee, Kentucky, and Alabama is the generally more radioactive part of a thin blanket of black shale that once covered a large part of eastern and central United States. Correlatives of the Chattanooga, all slightly radioactive, are the New Albany shale of Illinois, Indiana, and Kentucky; the Antrim shale of Michigan; the Sunbury and Ohio shales of Ohio and Kentucky; the Genessee group, the Dunkirk member of the Perrysburg formation, and other thin shales of New York; the Chattanooga shale of Kansas, northern Arkansas, and northern Oklahoma; and the Woodford chert of Oklahoma and Texas. Except in mountainous areas, these shales are flat-lying or locally warped into gentle folds.

The thickness of these Upper Devonian and lower Mississippian shales ranges from a feather edge to several hundred feet, but in central Tennessee, where mining of the shale is most feasible, the Chattanooga shale is less than 35 feet thick. These shales consist chiefly of black siliceous shale and gray claystone, and locally include thin sandstone beds, calcareous lenses, chert layers, and phosphatic nodules. They contain abundant plant remains (such as stems, spores, and macerated debris) as well as linguloid brachiopods, conodonts, and fish bones.

The more radioactive black shale units of the Chattanooga in central Tennessee are composed of silt-sized grains of quartz (about 25 percent), clay, feldspar, and mica (about 35 percent), organic matter (about 20 percent), pyrite (about 15 percent), and minor amounts of chlorite, phosphatic material, calcite, and heavy minerals. The rock yields 3 to 15 gallons of oil per short ton by destructive distillation.

The uranium content ranges from 0.001 to 0.035 percent and is remarkably persistent and uniform, as are the lithologic units, over large areas. In central Tennessee an upper member of predominantly black shale, about 15 feet thick, averages about 0.007 percent uranium, and a coalified plant fragment from this area contained 0.035 percent uranium. Parts of the Woodford chert in southeastern Oklahoma contain as much as 0.008 percent uranium, but the average content of known units of minable thickness does not exceed 0.005 percent uranium. In central Texas an irregularly distributed unit of black shale, correlated with and megascopically similar to the Chattanooga shale, is about 5 feet thick and contains an average of 0.008 percent uranium. Phosphate nodules in the Chattanooga and its equivalents contain as much as 0.013 percent uranium, but, at least in the Southeastern States, their average content is less than that of the enclosing shale. In areas where gray shales are more abundant, and where sandstones, calcareous siltstones, or limestone lenses are common, the formation generally contains 0.001 to 0.003 percent uranium. A direct relationship appears to exist between the uranium and organic content, and between the uranium and the pyrite (although the uranium is not contained in the pyrite).

The Chattanooga shale and its correlatives accumulated in a widespread, relatively shallow, epicontinental sea that covered a vast area of the North American continent. It was deposited under conditions that resulted in extremely slow accumulation of mineral-bearing detritus and proportionately high accumulation of carbonaceous debris. Presumably uranium in solution in the sea was absorbed by the organic debris.

MIDCONTINENT SHALES OF PENNSYLVANIAN AGE

Approximately 2,500 feet of gently dipping rocks of Pennsylvanian age are exposed in eastern Kansas (Moore and others, 1951) and parts of Oklahoma and Missouri nearby. Marine black shale beds, generally only a few feet thick, are scattered throughout the sequence; many of them are units of cyclic deposition that include sandstone, coal, and limestone.

About 20 of these black shale beds are abnormally uraniferous, containing more than 0.003 percent uranium; several contain 0.010 percent uranium; and, locally at least, beds of black shale 0.5 to 2.0 feet thick contain as much as 0.017 percent uranium, as in the Pleasanton group of late Pennsylvanian age. Most of the thin coal beds are practically nonradioactive, the highest known uranium content being 0.002 percent. The rest of the lithologic units are in effect non-uraniferous.

Many of these black shales of Pennsylvanian age are characterized by irregularly distributed small phosphatic concretions or nodules, containing as much as 30 percent P_2O_5, and, at some localities, making up as much as 5 percent of the thin shale beds. The radioactivity of the nodules is generally higher than that of the enclosing shale, their average equivalent uranium content being about 0.035 percent and the average uranium content 0.015 to 0.020 percent. A few samples of phosphatic nodules contained slightly less than 0.1 percent uranium. Except for the general observation that the nodules are typically present in the uraniferous black shales, no correlation appears to exist between the abundance of the nodules and their uranium content; nor does their uranium content appear to be related to the thickness, lithology, and uranium content of the enclosing shales.

Of the several black shales of Pennsylvanian age in the southeastern Kansas area that are abnormally uraniferous, only two are mentioned here to illustrate their geologic characteristics and distribution.

The Hushpuckney shale member of the Swope limestone (upper Pennsylvanian) of Moore (1933) is composed of an upper unit of almost nonradioactive greenish clay shale about 4 feet thick, and a lower unit of black fissile shale, devoid of phosphatic nodules, about 2 feet thick; the member is both overlain and underlain by persistent but thin limestone units. This uraniferous black shale crops out from southeastern Kansas north-northeastward into Missouri, and analyses of scattered samples suggest that this shale contains about 0.010 percent uranium throughout most of this area. It is present westward in the subsurface for 100 or more miles, but its radioactivity beyond the outcrop is not known.

The Cherokee formation of middle Pennsylvanian age is exposed in a belt about 25 miles wide cutting across the southeastern corner of Kansas and into adjacent parts of Missouri and Oklahoma. It is of cyclic deposition, the cycle being crudely repeated about 14 times and generally consisting of sandstone, "underclay," coal, black shale, limestone, and claystone. Although the radioactivity of the Cherokee has not been systematically studied, most of the black shale units are uraniferous, and channel samples of a few beds as much as 2 feet thick contained 0.009 to 0.013 percent uranium; adjacent units, regardless of lithology, contain less than 0.002 percent uranium.

The thin but persistent units of black fissile shale in the Pennsylvanian indicate deposition in extremely shallow water, too shallow for circulation and effective wave or tidal action (Moore, 1929, p. 459–487). The influx of sediment into the wide expanse of the shallow seas was apparently meager, and the reducing environment in the lower waters of the sea permitted the slow accumulation and preservation of organic debris. Available uranium in the sea water was adsorbed in this bottom sludge, and a chemical exchange bonded the uranium and the phosphate during the accretionary growth of the nodules. Apparently, slight but widespread, tectonic movements permitted oxygenation of the waters, destroying the environment favorable for the accumulation of carbonaceous material and uranium and permitting the deposition of calcium carbonate.

Several thin beds of marine black shale in the subsurface Hartville formation of Pennsylvanian age in eastern Wyoming and western Nebraska contain as much as 0.019 percent uranium. The most radioactive shales are several thousand feet below the surface in eastern Niobrara and Goshen Counties of easternmost Wyoming and western Sioux County in westernmost Nebraska, as indicated by samples and gamma-ray logs from a few wells. The subsurface distribution of these abnormally radioactive shales has not been fully defined, but they are not present in the outcrop area of the Hartville uplift 25 to 50 miles to the west in Wyoming, where their stratigraphic equivalents are dolomitic rocks.

Available data show that the midcontinental black shale beds less than 1 foot thick generally contain more than 0.01 percent uranium, but the thicker beds, which may be as much as 10 feet thick, generally contain 0.005 percent uranium or less. This relationship between uranium content and thickness and the lateral change from black shale into dolomitic facies in Nebraska and Wyoming probably are the significant guides to the more uraniferous parts of these shales of Pennsylvanian age.

PHOSPHATIC CARBONACEOUS SHALES, PHOSPHORIA FORMATION

The rocks of the Phosphoria formation of Permian age, which are present in an area of some 100,000 square miles in Idaho, Montana, and Wyoming, are marine sediments that are significant because of their contained phosphate and uranium (McKelvey and Carswell, p. 483, this volume).

Two dark phosphatic shale members characterize the Phosphoria formation; chert, sandstone, and limestones make up the rest of it. The lower member is about 150 to 200 feet thick and contains as much as 38 percent P_2O_5 in southeastern Idaho, but the member pinches out in southern Montana, central Wyoming, and eastern Utah. Its average uranium content is about 0.010 percent, but some thin units contain as much as 0.033 percent uranium. The upper member is about 75 feet thick in southwestern Montana, but thins in most directions away from this area. The P_2O_5 content of minable beds is about 30 percent, and the uranium content is about 0.010 percent. Pyrite is an important constituent of both members.

The Phosphoria formation (Swanson, McKelvey, and Sheldon, 1953) may be roughly divided into a miogeosynclinal facies (Kay, 1947) on the west and a platform facies on the east. In the western facies the rocks are generally finer grained, principally dark phosphatic shales and cherts, and are thicker than in the eastern platform facies where conspicuous unconformities are common.

The organic and phosphatic material are apparently the constitutents that contain the uranium in the Phosphoria formation (Thompson, 1953); and as the phosphate and carbonaceous matter increase together, the uranium content increases also.

Although ideas of the configuration and depth of the Phosphoria sea differ, the coincidence of abnormal phosphate accumulation, preservation of carbonaceous matter, limited supply of fine-grained sediment, and high uranium content unmistakably suggest a genetic similarity to the other black shales described. Presumably the sediments accumulated more rapidly than most uranium-bearing shale, but possibly an accelerated supply of phosphate and plant material resulted in concentrations comparable to those in other uraniferous shales.

OTHER URANIFEROUS SHALES

The Sharon Springs member of the Pierre shale of Cretaceous age—a hard, black, pyritic, organic-rich shale similar to the Chattanooga shale—is slightly radioactive throughout a large part of South Dakota, Nebraska, northern Kansas, and northeastern Colorado (Tourtelot, 1956). The unit ranges in thickness from a few feet to about 500 feet. Thin beds of the shale locally contain as much as 0.01 percent uranium, but generally the content is less than 0.003 percent.

Several thin black shale beds in the Hermosa formation including the Paradox members of Pennsylvanian age in western Colorado contain from 0.003 to 0.004 percent uranium.

In the predominantly calcareous rock of Mississippian age in Montana and Utah, thin black shale beds are commonly present at the base of thick limestone units and in places contain 0.005 percent uranium or more (Mapel, p. 469, this volume).

In central Montana parts of the Heath shale of late Mississippian age contain as much as 0.009 percent uranium, the most highly uraniferous shale of any thickness being at one locality in Fergus County, where 4 feet of black shale near the top of the formation contains 0.006 percent uranium.

Along an abnormally radioactive outcrop area in central Texas the Barnett formation of middle Mississippian age includes thin beds of phosphatic black shale that contain about 0.015 percent uranium. One sample of phosphatic rock from this formation had as much as 33.8 percent P_2O_5 and 0.033 percent uranium.

Existing sample and analytical data on the many thick dark marine shales in the states bordering the Atlantic and Pacific Oceans are very meager, but, they, together with data obtained from radiometric traverses, indicate that these shales generally have less than 0.003 percent uranium. Those along the East Coast are mainly early Paleozoic in age, those along the West Coast chiefly late Paleozoic and Mesozoic.

GEOLOGIC SIGNIFICANCE OF ABNORMALLY RADIOACTIVE SHALES

The potential uranium content of marine black shales can be classified by their tectonic and paleogeographic environment during the time of accumulation. Four general categories of these shales correspond to four depositional environments: epicontinental areas, geosynclinal fringe areas, miogeosynclinal areas, and eugeosynclinal areas. The characteristics of each depositional area are described by Kay (1951).

Several formations composed in whole or in part of black shale can be assigned to each of the four categories of geologic environment. Those originating in epicontinental areas (or on the craton of Kay) are relatively thin formations having great horizontal extent, as exemplified by the Chattanooga shale and the shales of Pennsylvanian age already described. Between the epicontinental and miogeosynclinal areas is a belt where formations change rapidly in thickness and rock type; shales in the Hamilton and Marcellus formations of Devonian age in the eastern States can be considered typical of the geosynclinal-fringe deposits. Within the thick, predominantly clastic sequence of miogeosynclinal deposits, laid down in a belt lacking volcanism, the graptolitic shale of the Deepkill and Normanskill formations are examples. And, fourth, representative of the eugeosynclinal deposits, which typically are rapidly deposited sediments, measured in thousands of feet, that were laid down in belts of active volcanism, are the Mariposa slate and other dark argillites and siltstones common in the Mesozoic sequence in the West Coast region.

The general tectonic and paleogeographic category into which most uraniferous shales fall is that of the epicontinental area. This environment was common in much of the interior of the United States during several intervals of the Paleozoic. The long-term innundation of a broad expanse of a relatively flat surface, and the lack of a source of a large amount of clastic sediment made possible the development of specific geochemical conditions that controlled the accumulation and preservation of uraniferous carbonaceous muds.

REFERENCES CITED

Gott, G. B., and Hill, J. W., 1953, Radioactivity in some oil fields of southeastern Kansas: U. S. Geol. Survey Bull. 988–E, p. 69–122.

Hass. W. H., 1956, Age of the Chattanooga shale and Maury formation: U. S. Geol. Survey Prof. Paper 286 (in press).

Johnson, J. C., 1955, Uranium resources for industrial power: U. S. Atomic Energy Comm. press release (April 5, 1955).

Kay, G. M., 1947, Geosynclinal nomenclature and the craton: Am. Assoc. Petroleum Geologists Bull. v. 21, no. 10, p. 1289–1293.

——— 1951, North American geosynclines: Geol. Soc. America Mem. 48, 143 p.

McKelvey, V. E., and Nelson, J. M., 1950, Characteristics of marine uranium-bearing sedimentary rocks: Soc. Econ. Geologists Bull. 45, p. 35–53.

Moore, G. W., 1954, Extraction of uranium from aqueous solutions by coal and some other materials: Soc. Econ. Geologists Bull. v. 49, p. 652–658.

Moore, R. C., 1929, Environment of Pennsylvanian life in North America: Am. Assoc. of Petroleum Geologists Bull. v. 13, no. 5, p. 459–487.

——— 1933, A reclassification of the Pennsylvanian in the northern Midcontinent region: Kansas Geol. Soc. Guidebook, 6th Ann. Field Conf. p. 79–98.

Moore, R. C., and others, 1951, the Kansas rock column: Kan. State Geol. Survey Bull. 89, 132 p.

Swanson, R. W., McKelvey, V. E., and Sheldon, R. P., 1953, Progress report on investigations of western phosphate deposits: U. S. Geol. Survey Circ. 297.

Szalay, S., 1954, The enrichment of uranium in some brown coals in Hungary: Acta Geologica [Hungaricae], Magyar tudom. Akad. II, p. 299–310.

Thompson, M. E., 1953, Distribution of uranium in rich phosphate beds in the Phosphoria formation: U. S. Geol. Survey Bull. 988–D, p. 45–67.

Tourtelot, H. A., 1956, Radioactivity and uranium content of some Cretaceous shales, central Great Plains: Am. Assoc. Petroleum Geologists Bull. v. 40, no. 1, p. 62–83.

Twenhofel, W. H., 1939, Environments of origin of black shales, Am. Assoc. Petroleum Geologists Bull. v. 23, no. 8, p. 1178–1198.