Uranium and Other Trace Elements in Petroleums and Rock Asphalts

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and Rock Asphalts

By KENNETH G. BELL

URANIUM IN CARBONACEOUS ROCKS

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ABSTRACT

Uranium is a minor trace-element constituent of petroleums and their natural derivatives. The quantity of uranium in crude oils produced by primary-recovery processes generally ranges from none to 5 parts per billion (ppb) although some crude oils may contain as much as a few tens of parts per billion. The average uranium content for all crude oil is estimated to be about 1 part per billion (ppb), or about one third that of the average content of sea water. Paraffin-base crude oils have the smallest uranium content, less than 1 ppb. Mixed-base and asphalt-base crude oils, in general, contain a slightly greater quantity of uranium and show a rough positive correlation between specific gravity and uranium content. There is no correlation between uranium contents of crude oils and geologic ages of reservoir rocks. Crude oils from one region are no more uraniferous than those from any other, except perhaps as a result of local predominance of heavy aromatic and asphaltic constituents. As a group, the crude oils of the Colorado Plateau and Rocky Mountain regions, both being uraniferous provinces, contain less-than-average quantities of uranium, a condition that is attributed to predominance of paraffinic constituents. Crude oils produced by secondary-recovery processes utilizing water flooding and detergents apparently contain above-average quantities of uranium, possibly because they contain asphaltic residues that are removed from pore walls of reservoir rocks. The mode of occurrence of uranium in petroliferous materials and the source of the uranium have not been determined.

The bituminous constituents of rock asphalts contain as much as a few thousand parts per billion of uranium, the average being about 1,000 ppb, a concentration that is about a thousand-fold increase over that in crude oils and probably a somewhat smaller increase over that in petroleums. It is believed that the bitumens extract uranium from the host rocks. There seems to be a positive correlation between the uranium content of the bitumens and that of the host rocks.

There is no evidence that petroleum acts as an ore-forming fluid for uranium. Oil field waters containing dissolved organic substances extracted from petroleum, and hydrogen sulfide, may provide a reducing environment in which uranium brought in by ground water or hydrothermal solutions may be precipitated at the interface of the solutions.

Crude oil is not a practical source material for uranium; the total uranium content of the crude oil reserves of the United States does not exceed 5 tons. The bitumens of the rock-asphalt deposits of the United States contain several hundred tons of uranium, but, because these bitumens are dispersed in several billion tons of rock, they are not practical source materials for uranium.

INTRODUCTION

Petroleums, natural asphalts, and rock asphalts contain many elements in trace amounts. The trace-element content of crude oils has been the subject of considerable research because it might furnish possible clues concerning the origin and migration of petroleum and because some metals have deleterious effects upon catalytic-cracking processes and upon refinery and combustion equipment. The suite of trace-elements present in crude oils and natural asphalts consistently includes vanadium and nickel as major constituents, and copper, cobalt, chromium, manganese, iron, lead, and zinc as minor constituents. Arsenic, molybdenum, silver, rare-earth elements, uranium, and other elements are sporadic constituents. Although the suite of metals is quite consistent, the quantities of individual metals differ significantly in different crude oils and asphalts and even in the same type of crude oil from different localities. Metals other than vanadium and nickel are major trace-metal constituents of some crude oils. The geochemical factors that bring about minor concentrations of metals in petroleum have been investigated most extensively for those elements that form porphyrin complexes or are essential constituents of chlorophyll and hemoglobin. The principal metals in this group are vanadium, nickel, copper, iron and magnesium. Geochemical factors that bring about associations of other metals in petroleum have been subject of but little investigation.

Considerable data concerning the quantities of vanadium, nickel, and copper in petroleums and crude oils have been compiled in many laboratories, and some information concerning the manner in which these elements are held by the organic substances has been

published. Vanadium may be concentrated in asphalt-base crude oils in quantities as large as about 0.1 percent of the fluid, or about 75 percent of the ash. Nickel generally occurs in lesser quantities and may constitute as much as 10 percent of the ash. Nickel seems to be preferentially concentrated in paraffin-base crude oils. The copper content of crude oil generally ranges from 0.01 to 0.1 parts per million (ppm), but some crude oils may contain several parts per million of copper constituting as much as 10 percent of the ash. It has been established by Triebs (1934), Uspenskiy and Gorskaya (Успенский и Горская, 1938), Skinner (1952), and others that some of the vanadium in crude oils is held in porphyrin complexes; Gleboskaya and Vol'kenshteyn (Глебовская и Волькенштейн, 1948) have extracted and identified nickel-porphyrin complexes from crude oils of the U.S.S.R.; Dunning and others, 1953, 1954) have extracted and identified nickel-porphyrin complexes from California crude oils; copper-porphyrin complexes can be prepared synthetically, but there seems to be no published data showing them to have been identified in crude oil. Vanadium, nickel, and copper have been investigated because they are the most abundant trace-metal constituents of petroleums and other natural bitumens and, because, they have deleterious effects on catalytic cracking agents. Vanadium is also of interest because the oxide formed from it during combustion of fuel oils has deleterious effects on silica-brick furnace linings, turbine blades, and other equipment. Some bitumens are source materials for vanadium.

Some recent investigations have dealt with the variability in contents of trace metals in crude oils and petroleums and the geologic interpretations that can be deduced from them. Attempts have been made to use trace metals as an aid in correlating petroleums in different pools within a formation, to correlate petroleums with possible source materials and source beds, and to provide data pertaining to migration of petroleum. Some of these investigations have been described in papers by Smith (1954), Erickson and others (1954), Hodgson (1954), and Bonham (1956).

The association of radioactive elements with petroleum and other bitumens has been the subject of considerable research. Some of the more significant investigations have dealt with the radium content of crude oils and oilfield waters (Burton, 1904; Engler, 1907; Bohn, 1930; Nikitin and Komleff, 1930; Hahn and Born, 1935; Bell and others, 1940; Tiratsoo, 1941; Gott and Hill, 1953), the possible role of radioactivity in the origin of petroleum (Sheppard, 1944; Sheppard and Whitehead, 1946; Breger and Whitehead, 1951; Whitehead, 1954), and the role of radioactivity in the

formation of various natural bitumens and pyrobitumens, particularly thucholite, (Lind, 1928; Spence, 1932; Vernadsky, 1935; Davidson and Bowie, 1951).

The uranium content of petroleums and their natural derivatives, and the possible role of petroleums in the genesis of some uraniferous mineral deposits in sedimentary rocks, have been subjects of some research, much speculation, and a few geological interpretations of doubtful validity. Sedimentary formations that are good host rocks for uranium deposits generally are also equally good reservoir rocks for petroleums. In the Rocky Mountain region and the Colorado Plateau region, petroleum reservoirs and mineral deposits mined primarily for uranium are distributed throughout a sequence of sedimentary rocks ranging in age from Mississippian through Eocene. "Dead-oil" residues, tar sands, and deposits of rock asphalt are found in the vicinity of many uranium deposits. "Live-oil" seeps occur near uranium deposits and even within mines. The same conditions prevail along the western margin of the San Joaquin Valley, Calif., where small noncommercial uranium deposits are known. Some oil shales are uraniferous. These common occurrences of petroliferous substances and deposits containing uranium minerals in the same localities and formations have posed some intriguing problems.

Some solid carbonaceous mineraloids are highly uraniferous, but neither their compositions nor their origins are completely known. Some of these substances have been referred to in literature as "asphaltite", "hydrocarbon", "pyrobitumen", "dead-oil residue", and by other names. An origin from petroleum has been ascribed for them by some authors. Inasmuch as their identities and origins are uncertain, and because in their present forms they cannot properly be classified as petroliferous or asphaltic substances, they are discussed briefly in this report.

The purpose of this report is to summarize briefly current knowledge of the association of uranium with petroleums and asphalts, to survey the role, if any, that petroleums may play in the origin of uranium deposits, and to present analytical data compiled during the course of investigations by the U.S. Geological Survey. Quantitative analytical data on the uranium contents of petroleums and rock asphalts are presented in tables 2 and 3. Inasmuch as this report is concerned principally with uranium and petroleums and natural asphalts, the association of other trace elements with petroleums and natural asphalts is discussed only briefly in the text; semiquantitative spectrochemical analytical data on these elements accumulated during the course of the investigations are presented in tables 2 and 3.

DEFINITIONS

Inasmuch as the nomenclature of bituminous substances, including petroleums, is used with many meanings, it is essential that the individual terms as used in this report be defined. The classification and nomenclature used by Abraham (1945) are followed, and the definitions given below, unless otherwise indicated, are from this source.

All bituminous substances fall into two classes, native and pyrogenous. All bitumens occurring naturally in the earth's crust are native. Bituminous substances formed from various organic raw materials in industrial processes utilizing heat are classified as pyrogenous. This report is concerned only with native petroleums and asphalts.

Bituminous substances: A class of native and pyrogenous substances containing bitumens or pyrobitumens, or resembling them in their physical properties. (Abraham, 1945, p. 51).

Scope. This definition includes bitumens, pyrobitumens, pyrogenous distillates and tars, pyrogenous waxes and pyrogenous residues (pitches and pyrogenous asphalts).

Bitumen: A generic term applied to native substances of variable color, hardness, and volatility; composed principally of hydrocarbons, substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being *fusible* and largely *soluble* in carbon disulfide, yielding water-soluble sulfonation products.

Scope. This definition includes petroleums, native asphalts, native mineral waxes and asphaltites. (Abraham, 1945, p. 60).

Pyrobitumen: A generic term, applied to native substances of dark color; comparatively hard and non-volatile; composed of hydrocarbons, which may or may not contain oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituent being *infusible* and relatively *insoluble* in carbon disulfide.

Scope. This definition includes the asphaltic pyrobitumens (elaterite, wurtzilite, albertite and impsonite) also the non-asphaltic pyrobitumens (peat, lignite, bituminous coal and anthracite coal) and their respective shales (Abraham, 1945, p. 60).

Petroleum: A species of bitumen, of variable color, *liquid* consistency, having a characteristic odor; comparatively volatile; composed principally of hydrocarbons, substantially free from oxygenated bodies; soluble in carbon disulfide, yielding water-insoluble sulfonation products (Abraham, 1945, p. 60).

Scope. This definition includes paraffin-base, mixed-base, and asphalt-base petroleums.

Crude oil: The natural petroleum, unrefined, as it issues from the ground (Rice, 1953, p. 93).

In this report the term crude oil is used to designate the recoverable portion of petroleum.

Asphalt and *rock asphalt:* A term applies to a species of bitumen, also to certain pyrogenous substances of *dark color*, variable hardness, comparatively non-volatile; composed principally of hydrocarbons, substantially free from oxygenated bodies; containing relatively little to no crystallizable paraffins; sometimes associated with mineral matter, the non-mineral

constituents being *fusible*, and largely soluble in carbon disulfide, yielding water-insoluble sulfonation products.

Scope. This definition is applied to native asphalts and pyrogenus asphalts. Native asphalts include asphalts occurring naturally in a pure or fairly pure state, also asphalts associated naturally with a substantial proportion of mineral matter. The associated mineral matter may be sand, sandstone, limestone, clay, shale, etc. (Abraham, 1945, p. 61).

Native asphalts associated naturally with sandstone, limestone, and other rocks, commonly are called rock asphalts.

In the discussion that follows, the bitumens extracted from rock asphalts are called "asphalts."

Asphaltenes: The components of the bitumen in petroleum, petroleum products, malthas, asphalt cements, and solid native bitumens, that are soluble in carbon disulphide but insoluble in naphtha (petroleum spirit). (Rice, 1953, p. 25).

Asphaltenes are likewise insoluble in *n*-pentane.

Asphaltite: A species of bitumen, including dark-colored, comparatively hard and non-volatile solids; composed principally of hydrocarbons, substantially free from oxygenated bodies and crystallizable paraffins; sometimes associated with mineral matter, the non-mineral constituents being *difficulty fusible*, and largly soluble in carbon disulfide, yielding water-insoluble sulfonation products.

Scope. This definition includes gilsonite, glance pitch, and grahamite. (Abraham, 1945, p. 61–62).

Kerogen: There seem to be about as many definitions for kerogen as there are authors who have mentioned the substance. Perhaps these definitions can be summarized by saying, kerogens are fossil organic substance, or substances, that yield bitumens, or hydrocarbons, upon pyrolysis (destructive distillation). They are found in marine and lacustrine sedimentary rocks and are principal constituents of oil shales.

Dead oil: A dry residue formed from petroleum by inspissation, oxidation, polymerization, or some combination of these processes.

Live oil: A synonym for petroleum that commonly is used to designate noncommercial accumulations of fluid.

SOURCES OF SAMPLES AND SAMPLING METHODS

Most of the samples for which analytical data are listed in tables 2 and 3 were collected during the course of several Geological Survey investigations concerning possible associations of uranium with naturally occurring organic substances. Crude oils and rock asphalts from the uraniferous Colorado Plateau region were sampled and analyzed specially to provide data for this report. Of the 498 samples of crude oils and rock asphalts listed in the tables, 125 samples were collected by H. J. Hyden and N. W. Bass (Hyden, 1956), 28 samples were collected by A. P. Pierce and J. W. Mytton, 233 samples were collected by W. J. Hail, Jr., (Hail and others, 1956), 67 samples were collected by the author, and 45 samples were collected by other individuals. All samples of crude oil were collected from localities west of the Mississippi River. All samples

of rock asphalt, except three samples collected in northern Alabama, were collected in localities west of the Mississippi River.

The crude-oil samples are representative of parraffin-, mixed-, and asphalt-base oils. Also, the samples represent pools distributed in all types of petroleum-reservoir rocks that range in age from Cambrian through Miocene. Samples were collected from the Gulf coast, Texas Panhandle, Mid-Continent, Rocky Mountain, and Pacific coast regions. Wherever possible, crude-oil samples were taken directly from the wellhead, and preferably from wells that had been flowing or pumped for several hours prior to sampling. Some samples were taken from storage tanks. A few samples from the Colorado Plateau region were collected during swab tests. When fluid was taken from a wellhead, it was allowed to stand for a short time while gas and water separated from the oil, and the oil was recovered by decantation.

Most of the rock-asphalt samples were collected from major deposits, that is, those that are being or can be exploited profitably for their bitumen content or for paving material. The host rocks are sandstones and limestones. Where unweathered rock was exposed on quarry faces, channel samples were cut from the principal bituminous beds of the deposits, elsewhere spot samples were taken by digging into unweathered material.

The number of samples of crude oils and rock asphalts that could be collected was limited by the capacity of the laboratory to do the analytical work. As a consequence, the localities sampled are very sparsely distributed in relation to the abundance of source areas from which material can be collected. It is thought that the samples are sufficiently representative of petroliferous substances so that conclusions derived from this study are applicable to these substances as a group wherever they may be found.

ANALYTICAL PROCEDURES

The methods commonly used to identify metallic constituents of bituminous substances involve burning off the organic constituents and analyzing the ash. During the 1940's and 1950's spectroscopy came into common use for making quantitative and semiquantitative determinations of a large number of the elements that may be in the ash. Both dry- and wet-ashing techniques are used to eliminate organic constituents. Dry-ashing techniques consist of burning the sample in a suitable container and igniting the residue to constant weight. Standard methods of dry ashing are described under American Society of Testing Materials designation D482–46. Wet-ashing techniques consist of heat-

ing the sample in an excess of concentrated sulfuric acid, strong oxidizing acids, such as nitric or perchloric acid, or in mixtures of these acids, until organic constituents are broken down to carbon residue or eliminated, then evaporating the residue to dryness and igniting it to constant weight. Various procedures for wet ashing of organic materials are described by Southwick (1951), Milner and others (1952), Gamble and Jones (1955), and Horeczy and others (1955). The residues of either dry- or wet-ashing techniques may be analyzed spectrochemically for a large number of elements in one operation or may be analyzed for individual elements by wet chemical methods. Prior to the development of spectroscopy, it was necessary to analyze residues for individual elements, and as a consequence, only those metallic constituents of bituminous substances that occur in the greatest quantities were investigated thoroughly.

The development of analytical techniques for quantitative determinations of trace elements in crude oils and petroleum products has been the subject of much recent research. The accuracy of wet-ashing techniques compared to dry-ashing techniques in determining various elements still is not fully established. Some techniques and the magnitude of errors that can be expected for each have been discussed by Southwick (1951), Karchmer and Gunn (1952), Milner and others (1952), Gamble and Jones (1955), and Horeczy and others (1955). Techniques and probable errors for determination of vanadium, nickel, copper, and iron are more firmly established than for other metals. Research carried on in Geological Survey laboratories has resulted in a procedure for precise determination of very small quantities of uranium in bitumens and other organic substances. The organic constituents are eliminated by a dry-ashing technique, and uranium in the ash is determined by the fluorimetric method described by Grimaldi and others (1954). The accuracy of currently used techniques for other elements has not yet been discussed in published reports.

Spectrochemical analysis of ashes of bituminous substances provides a rapid method of determining the presence of a large number of elements simultaneously and gives satisfactory quantitative determinations for most of the elements. Accuracy depends principally upon the efficiency of two stages of the analytical procedure: First, there must be no losses by volatilization or entrainment during combustion and ignition; second, an element must be present in the ash in such quantity as to permit spectrochemical determination. Any modification of ashing technique and spectrochemical analysis that gives quantitative determinations of element A within limits of a given probable error does

not necessarily provide the same accuracy for element *B*. The simultaneous quantitative determinations of many elements by spectroscopy may, therefore, yield for different elements values having different probable errors.

There are many factors that cause incomplete spectrochemical analyses and large probable errors while determining the trace-element content of petroliferous substances. Volatilization during ashing and ignition results in partial or complete loss of some elements. Arsenic may be a rather common constituent of crude oils but is not often detected because its compounds volatilize readily during dry ashing and during ignition of residues, and furthermore, it has a low spectrochemical sensitivity (Ahrens, 1950, p. 208). Mercury and germanium are other metals subject to losses through volatilization (Ahrens, 1950, p. 206, 216). It has been shown by Horeczy and others (1955) that certain organic complexes of vanadium, nickel, and copper that exist in some crude oils or some refinery charge stocks and overhead fractions are subject to volatilization. Some other elements, such as cadmium, may be determined as less than the actual quantities because some of the element is subject to early volatilization in the arc of the spectrometer (Ahrens, 1950, p. 206).

Inadvertent contamination during analysis may result in high determinations of some elements. For example, trace amounts of metals have been extracted from nonmetallic laboratory apparatus (A. T. Myers, oral communication, 1956) and from porous-silica boiling chips (Southwick, 1951) during wet ashing of bitumens. Samples treated in glassware cleaned with chromic acid may become contaminated with chromium (A. T. Myers, oral communication, 1956). Improper preparation of samples may leave foreign material in the split analyzed. Some crude oils and other native bitumens carry suspended mineral matter, some of which may be so finely dispersed through the organic substance that it cannot be completely separated by mechanical means. A. W. Pierce, J. W. Mytton, and G. B. Gott (written communication, 1956) report finding solid particles in crude oil that had been filtered through a porous plate having openings 50 microns in diameter. The particles consisted of carbonized material, black pellets having resinous lustre, and brassy-colored particles thought to be metallic sulfides or arsenic-bearing minerals. The particles ranged from less than one micron to 50 microns in diameter. Crude oils, and even asphalts, may be accompanied by water carrying dissolved salts that must be removed before analysis. Samples of crude oil stratify during storage; therefore, representative splits cannot be obtained by decanting from the top of the container.

During the investigations being described, the ash obtained by combustion and ignition of most of the samples was divided into two portions; one portion was used for determination of uranium content by the fluorimetric method described by Grimaldi and others (1954); the other portion was analyzed spectrochemically; if the quantity of ash was very small, it was not divided, and the uranium content only was determined. The specific gravities of most of the samples of crude oil were determined; this was done after the samples had been filtered to remove suspended matter and washed with distilled water to remove salts.

DISTRIBUTION OF URANIUM IN PETROLEUMS AND NATURAL ASPHALTS

GENERAL DISCUSSION

Uranium is a minor trace-metal constituent of petroleums and their natural derivatives. This statement is based on analyses of 498 samples of crude oils, natural asphalts, and bitumens extracted from rock asphalts listed in tables 2 and 3. Previously published reports generally are in agreement with this statement. Unkovskaya (1940) has reported the uranium contents of several crude oils of the U.S.S.R. ranging from 2.7×10^{-7} to 8.2×10^{-6} grams per liter (roughly, from about 0.3 to 8.0 ppb). Inasmuch as Unkovskaya's data have been incorrectly referred to by several writers, they are quoted here in the following table. The entries of the first four columns are exactly as presented by Unkovskaya except that the column headings are translated into English, and a few words in the column headed "source" have also been translated. In the fifth column the uranium contents of the crude oils are indicated in grams of uranium per ton of oil, this being the form in which the information often has been incorrectly presented. In the sixth column the uranium contents of the crude oils are shown in parts per billion, in conformity with other data of this report.

Erickson and others (1954), and Breger and Deul (1955) report that the uranium content of crude oils ranges from less than 1 ppb to a few thousand ppb. Samples studied by these investigators were obtained from a variety of sources, including commercially productive oil wells, oil seeps at the earth's surface, and oil seeps within uranium mines, which is the reason for the wide range in uranium contents. Uranium also is a minor trace-metal constituent of some natural asphalts. The quantity of uranium in these substances generally is very small, and its determination is possible only by ashing the bitumens and by making quantitative determinations of uranium in the ash through the use of the fluorescence of uranium fluoride phosphors.

Ash and uranium content of some crude oils of the U.S.S.R.

[The information in the first four columns is quoted, with essential translation, from Unkovskaya (1940, p. 381). Place names are not translated]

Source	Quantity of ash (grams per liter)	Uranium content		Uranium in oils [1]	
		Percent of the ash	Grams per liter	Grams per ton	Parts per billion
Berekey, Dagestan A.S.S.R. Well 2	0.11	3.6x10⁻⁴ 3.9x10⁻⁴	4.0x10⁻⁷ 4.4x10⁻⁷	.0004 .0004	0.4 .4
Well 8	.56 .28	4.2x10⁻⁴ 2.3x10⁻⁴ 3.9x10⁻⁴	2.4x10⁻⁶ ------ 1.1x10⁻⁶	.0026 ---- .0011	2.6 ---- 1.1
Maili-Su, Kirguises	.24	1.3x10⁻³ 3.8x10⁻³	8.2x10⁻⁶	.0082	8.2
Schubar-Kudack-Kasakhstan; Well 106	.27 .20	1.0x10⁻⁴ 1.4x10⁻⁴	2.7x10⁻⁷ 2.8x10⁻⁷	.0003 .0003	.3 .3
Bibi-Eibat, Baku region; Well 118	.37 .41	2.3x10⁻⁴ 3.4x10⁻⁴	.85x10⁻⁶ 1.4x10⁻⁶	.0008 .0014	.8 1.4
Naphtalan, Baku region	.44	7.5x10⁻⁵	3.3x10⁻⁷	.0003	.3

[1] The figures in the fifth and sixth columns are approximations because the specific gravities of the crude oils are not known.

Crude oils ranging from very light, highly volatile condensates to heavy residual natural tars or asphalts have been analyzed for uranium and other trace elements, and the analytical data are presented in table 2. Facilities for determining the major organic constituents and classification of the crude oils were unavailable; therefore, some of this information has been obtained from other sources. The U.S. Bureau of Mines has reported oil classifications for crude oils from the same pools that were the source of some of the samples analyzed for trace elements. Some information concerning oil classifications and specific gravities was obtained from miscellaneous geologic reports. Such quoted information is considered to be sufficiently accurate for the following discussion.

A sample of crude oil taken from a wellhead is not representative of the bitumen in the reservoir. Nutting (1934) has shown that some of the heavier constituents of petroleum tend to cling to the pore walls of some reservoir rocks. Investigations by the U.S. Bureau of Mines (1938, p. 19) have shown the following condition.

Usually the oil produced from a certain horizon or formation becomes heavier as the field is depleted. Oil can be distilled by lowering its pressure as well as by raising its temperature; therefore, as the pressure in a producing horizon is decreased, a partial distillation takes place and the lighter fractions tend to move toward the producing well more rapidly than the heavier fractions. Thus, the oil produced from the well tends to be lighter than the oil remaining in the sand. This tendency is increased by the movement of natural gas associated with the oil, which carries the lighter fractions toward the well. With the reduction in the formation pressure, there is a decrease in the percentage of lighter fractions contained in the produced oil. This tendency of an oil to become heavier is more marked during the period of flush production than during the later life of the field.

Other investigations by the Bureau of Mines have shown that the characteristics of oil are not constant throughout a reservoir but vary with depth below a gas cap. In the Rangely field of Colorado (Cupps and others, 1951) and in the Elk Basin field of Wyoming and Montana (Espach and Fry, 1951), both the saturation pressure and the ratio of dissolved gas to oil of the original reservoir oil decreased with depth below the gas-oil contact, and the density and viscosity of the oil increased with depth below the gas-oil contact. In general, the trace-element contents of crude oils increase as specific gravities of the oils increase. Therefore, oil samples collected during different periods of the productive life of an oil field reasonably can be expected to contain different amounts of trace elements, and the greatest quantities will be present in the heavier oil recovered during the late stages of production. Samples of oil obtained from different depths below a gas-oil contact can be expected to contain different quantities of trace elements, and the amounts probably increase with depth below the contact. The uranium content of natural tars and of bitumens extracted from rock asphalts is relatively high as compared to the uranium content of crude oils, thereby indicating that the petroliferous residues left in reservoir rocks probably are more uraniferous than crude oils. The analytical data presented in this report should be considered as being representative of commercial crude oils and may not be strictly representative of the bitumen in petroleum reservoirs.

It is pointed out in the discussion of analytical techniques that the method used to obtain the data for this report was developed specifically for the determination of uranium. Determinations of other elements were obtained by a semiquantitative spectrochemical method, and because the quantities of each element cannot be determined with the same accuracy, the limitations of the analytical technique must be kept in mind. Analytical data for constituents other than uranium are presented in tables 2 and 3, but their geologic and economic significance are not discussed in this report.

URANIUM IN PARAFFIN-BASE CRUDE OILS

The light-yellow or pale-green paraffin-base crude oils generally carry less than 1 ppb of uranium. Some of the paraffin-base crude oils yielded insufficient ash for the determination of uranium even though several liters of sample were burned. The light hydrocarbons of the paraffin and olefin series, which constitute the bulk of these crude oils, apparently are incapable of holding uranium in solution, or in suspension, or as an organic complex. The amounts of uranium in these crude oils are so small that it has not been practical to

attempt to determine if the uranium is associated with any particular organic constituent.

The paraffin-base crude oils have the smallest uranium contents of any type of crude oils. A sample (No. 235037) of yellow oil recovered from sandstone in the lower part of the Green River formation of Eocene age at the Flat Mesa field, Duchesne County, Utah, had a specific gravity of 42° API and a uranium content, if any, that was too small to be determined. Light-green oils recovered from the Lance formation of Late Cretaceous age in the Powder Wash field (No. 235036) and from the Wasatch formation of Eocene age in the Hiawatha field (No. 223234), both in Moffat County, Colo., had a specific gravity of 47° API and uranium contents of 0.1 ppb. Green crude oils from the Mancos shale of Late Cretaceous age were found to have specific gravities ranging from 39° to 35° API and uranium contents of 0.3 or 0.2 ppb. Samples of these oils were obtained from the Moffat Dome field, Moffat County (No. 211047), and from the Rangely field, Rio Blanco County (No. 217873), both in Colorado. Some pale-yellow crude oils recovered from the Dakota sandstone of Early(?) and Late Cretaceous age, in the Rattle-snake field (Nos. 217869 and 217870) and the Table Mesa field (Nos. 96124 and 96126), San Juan County, N. Mex., had specific gravities ranging from 70° to 55° API and uranium contents, if any, that were too low to be determined. A green crude oil obtained from a limestone of Mississippian age at Big Flat, Grand County, Utah (No. 235028), had a specific gravity of 39° API and a uranium content of 0.1 ppb.

These samples are cited as being typical of paraffin-base crude oils. No correlation is observed between the uranium contents, the kinds of reservoir rocks, or the geologic ages of the reservoir rocks. The uranium contents of these crude oils probably are too small to permit analyses to be precise enough to show any possible correlations.

URANIUM IN ASPHALT-BASE CRUDE OILS

The asphalt-base crude oils contain the largest quantities of uranium of all the types of crude oil. These crude oils are composed predominately of aromatic constituents and asphaltenes, are heavy, and are dark brown or black. There is a rough correlation between their specific gravity and their uranium content; the heavier oils tend to contain the most uranium (table 2).

The uranium content of asphalt-base crude oils ranges from a fraction of a part per billion up to a few tens of parts per billion. Such crude oils from formations of Tertiary age in southern California have specific gravities in the range of 20° to 12° API and contain

approximately 1 to 3 ppb of uranium (table 2). A sample of asphalt-base crude oil from a limestone reservoir rock in the Hermosa formation of Pennsylvanian age at Upper Valley, Garfield County, Utah (No. 97491), had a specific gravity of approximately 17° API and contained 8 ppb of uranium. Another similar sample from a limestone reservoir rock in the Arbuckle group of Cambrian and Ordovician age, at the Solomon field, Ellis County, Kan. (No. 247608), had a specific gravity of 13.1° API and contained 31.1 ppb of uranium.

There seems to be no correlation between the uranium content of asphalt-base crude oils and the geologic age of the reservoir rocks. It is noteworthy that among the heavy asphaltic crude oils listed in table 2 those from limestone reservoir rocks tend to have the highest uranium contents; this observation may be significant and should be confirmed by analyses of more samples. The bulk of the uranium in some asphalt-base crude oils, and in some mixed-base crude oils, may be associated with asphaltenes or those constituents that are insoluble in n-pentane.

Breger and Deul (1959, p. 141) have reported analytical data for four samples of oils collected from seeps and from petroliferous sandstones taken from uranium mines at Temple Mountain, Grand County, Utah. These oils were not classified, but they probably belong to the mixed-base group. They are abnormal in that they have migrated through or been in contact with uranium ore bodies and have acquired anomalously large quantities of uranium. These data are as follows:

TABLE 1.—*Distribution of uranium in the oils from the Temple Mountain area*

[From Breger and Deul, 1959, p. 141; all data are in percent]

	AEC No. 4 mine	AEC No. 5 mine	Marsh Bank Canyon mine	AEC No. 8 mine
Original oil:				
Uranium	0.0000438	0.00445	0.0137	0.0310
Asphaltenes	22.7	16.2	22.5	27.8
Asphaltenes:				
Uranium	.000147	.0221	.0386	.0922
Ash	.34	.28	1.83	1.07
Uranium in ash	.0432	7.89	2.11	8.62
Uranium in original oil held by asphaltenes	76.2	80.5	63.4	82.6
Uranium in extracted sandstone	.00020			

The uranium contents of the original oils are 437, 44,500, 137,000, and 310,000 ppb respectively.

A mixed-base crude oil from Masterson J-1 well, sec. 59, block 018, D&P Survey, Moore County, Tex., sampled by A. W. Pierce, U.S. Geological Survey, was fractionated by passage through a thermal diffusion column, and the fractions were analyzed for uranium content (analytical work by C. A. Horr, U.S. Geologi-

cal Survey). Data for the original oil and for each of four fractions are as follows:

Fractionation of a mixed-base crude oil

[Data from A. W. Pierce, J. W. Mytton, and G. B. Gott (written communication 1956)]

Serial No.		Ash (percent)	Uranium	
			In ash (percent)	In oil (ppb)
237425	Crude oil 1_____	0.087	0.0150	130.5
237430	Fraction 1_____	.011	.0051	5.6
237431	Fraction 2_____	.035	.0102	35.7
237432	Fraction 3_____	.105	.0052	54.6
237433	Fraction 4_____	.092	.0230	211.6

These data indicate that uranium, heavy hydrocarbons, and asphaltenes were concentrated in the heaviest fractions. The quantities of asphaltenes and hydrocarbons in the different fractions were not determined.

An attempt was made to determine whether a correlation exists between the uranium and asphalt contents of crude oils by plotting uranium contents, as determined for samples collected by the Geological Survey, versus asphalt contents of oil samples from the same reservoirs, as calculated from data reported by the U.S. Bureau of Mines. This asphalt is the residue that remains after the volatile constituents have been distilled from crude oil, and consists of a complex mixture of heavy organic compounds, including hydrocarbons, oxhydrocarbons, asphaltenes, resins, and other substances. The uranium and asphalt determinations are for different samples, and some of the samples were collected several years apart and not from the same wells. Percent asphalt in the crude oil was calculated by multiplying percent carbon residue in the crude oil, as reported in Bureau of Mines modified Hempel analyses, by 4.9. This calculation furnishes a close estimate of the amount of 100-penetration asphalt in the crude oil (Stanfield and Hubbard, 1949; Smith and others, 1950). The Bureau of Mines data are listed in table 2. The figures thus obtained are admittedly not precise, but they are thought to be sufficiently accurate to demonstrate any correlation or lack of correlation between the content of uranium and that of asphalt in crude oils. No correlation was indicated by the plotted data, and, because the points showed a random distribution, the chart is not reproduced. The absence of a discernible correlation is attributed mainly to the variability in composition of crude oils and to a much lesser degree to the relatively large probable errors inherent in determining minute quantities of uranium and to the calculation of asphalt content by an empirical method.

URANIUM IN MIXED-BASE CRUDE OILS

The uranium content of mixed-base crude oils ranges from a fraction of a part per billion to a few tens of parts per billion. These oils are composed of substantial amounts of paraffinic and aromatic constituents and may include variable amounts of members of other hydrocarbon series. They show a variety of colors of which black and dark shades of green or brown are most common.

Among the mixed-base crude oils there is a rough correlation between specific gravity and uranium content. A crude oil from the Second Wall Creek sand (local usage) of Late Cretaceous age in the Salt Creek field, Natrona County, Wyo. (Nos. 227737 and 227738), had a specific gravity of 38° API and contained 0.07 ppb of uranium. Another crude oil from the Weber sandstone of Pennsylvanian age in the Rangely field, Rio Blanco County, Colo. (No. 217875), had a specific gravity of 30° API and contained 0.5 ppb of uranium. A crude oil from the Marchand sand (local usage) of Pennsylvanian age in the Cement field, Caddo County, Okla. (No. 86637), had a specific gravity of 19° API and contained 1.9 ppb of uranium. These examples are cited to illustrate the general trend of uranium content as related to specific gravity. Many exceptions to this trend exist, and deviations from a strict correlation of uranium content with specific gravity are attributed to variations in proportions of organic constituents and to the migration histories of the petroleums.

No correlation between the uranium content of mixed-base crude oils and the geological age or type of reservoir rock is apparent.

URANIUM IN CRUDE OILS EXTRACTED BY SECONDARY-RECOVERY PROCESSES

Samples of crude oils extracted by secondary-recovery processes from the Bartlesville sand (local usage) of Pennsylvanian age at the Nowata field, Nowata and Rogers Counties, Okla., contained above-average quantities of uranium. The uranium content of these samples ranged from 2 to 28 ppb and the average was about 12 ppb. The specific gravities of these oils as received in the laboratory were about 35° API. These uranium contents are considerably higher than the average uranium content of crude oils of this specific gravity and are higher than those of crude oils recovered elsewhere from the same sand by primary-recovery processes. A variety of detergents is used in secondary-recovery processes, but as of 1957 no reports concerning their ability to leach metals and petroliferous residues from reservoir rocks had been published. Secondary-recovery processes undoubtedly remove some of the heavy residue which clings to pore walls after the primary

recovery process has removed the readily available oil. The residues may contain substantial amounts of asphaltenes and heavy hydrocarbons or other heavy organic compounds and therefore a higher metal content than the more fluid crude oil. No analyses have been made by the Geological Survey to determine whether or not secondarily recovered crude oil carries anomalous quantities of asphaltenes and other heavy organic compounds.

URANIUM IN THE BITUMENS OF ROCK ASPHALTS

The bitumens of asphaltic sandstones and limestones contain uranium in quantities ranging from a few tens of parts per billion to a few tens of thousands of parts per billion (table 3). The average uranium content of all these bitumens is approximately 1,000 ppb, about a thousand times greater than that of crude oils. The bitumens of asphaltic sandstones and tuffaceous and phosphatic rocks commonly contain more uranium than those of asphaltic limestones and dolomites. The uranium contents of the host rocks, determined after the complete removal of the bitumens, are in the normal ranges for sedimentary rocks. (Erickson and others, table 6, 1954.)

SIGNIFICANCE OF URANIUM CONTENT OF PETROLIFEROUS SUBSTANCES

The analytical data presented in table 2 show conclusively that uranium is a minor metallic constitutent of petroleums. It is believed that the listed crude oil samples adequately represent the various types of crude oils and the different kinds and ages of reservoir rocks. Because the samples represent a large number of oil pools that differ greatly in size, and because there is a much greater number of unsampled pools, it is impossible to derive a precise figure for an average uranium content of all petroleum. A reasonable estimate for the average content seems to be 1 ppb, or roughly 0.001 gram of uranium per short ton of crude oil, or 0.0001 gram of uranium per barrel of crude oil.

The analytical data presented in table 3 show that uranium is also a minor metallic constituent of the bitumen of rock asphalts. Again it is impossible to state a precise figure for the average uranium content of these bitumens, but an estimate of 1,000 ppb, or 1 gram uranium per short ton of bitumen seems to be reasonable.

The uranium contents of crude oils generally range from possibly none to a few tens of parts per billion. The major factors affecting the concentration of uranium seem to be the composition and proportions of organic constituents. The migration history of crude oil and the uranium contents of reservoir or host rocks

generally are minor factors, but some outstanding exceptions have been found.

Uranium is preferentially concentrated in petroleums having high contents of aromatic constituents and asphaltenes. Condensates and light crude oils having specific gravities ranging from about 40° API to about 65° API contain no, or essentially no, uranium; these light crude oils, which are relatively scarce, are predominantly paraffinic. Most of the paraffin-base crude oils are within the specific gravity range of 40°–30° API and contain only traces of uranium. Although heavy aromatic constituents and asphaltenes are present in some crude oils of specific gravity about 40° API, they generally reach significant proportions in 30° API crude oils, and predominate in 20° API or heavier crude oils, that is, those that are most likely to be classified as asphalt-base. The highest uranium contents have been found in asphalt-base crude oils. What part, if any, that olefins, naphthenes, and other less abundant constituents of petroleums and crude oils may play in holding trace amounts of uranium has not been determined. It is possible that the uranium content of petroleums and crude oils is held by minor organic constitutents.

Some evidence has been collected which suggests that crude oils extract at least part of their uranium content from rocks through which they migrate or from reservoir rocks. The analytical data reported by Breger and Deul (1959, table 3) that pertain to four samples of crude oil that had migrated through the uranium deposits at Temple Mountain, Utah, (table 1) show uranium contents of 438; 44,500; 137,000; and 310,000 ppb. Erickson and others, (1954) reported uranium contents of 32,000; 30,000; 50,000; and 67,000 ppb for samples of crude oil extracted from sandstones in the same locality. These are abnormal concentrations of uranium. Unfortunately there are no oil wells in the immediate vicinity of Temple Mountain from which samples can be obtained for comparison. It is possible that the petroleum at Temple Mountain migrated upward along faults from source beds in Paleozoic formations, or from source beds in the Moenkopi formation of Early and Middle(?) Triassic age, and through sandstones of Triassic age in which the uranium deposits are located. Crude oil samples obtained from Paleozoic and Mesozoic reservoir rocks in Utah showed uranium contents ranging from a fraction of a part per billion to a maximum of 39 ppb (table 2).

Erickson and others (1954) also reported uranium contents ranging from 2,100 to 50,000 ppb for samples taken from oil seeps near the contact of sedimentary rocks with Precambrian igneous rocks in the vicinity of Morrison and Golden, Jefferson County, Colo. Sev-

eral uranium deposits have been found in both sedimentary and igneous rocks in these localities.

It is significant that the only uranium contents exceeding 500 ppb have been found in samples of crude oil collected from seeps alongside or very near uranium deposits.

From data now available, no direct correlation can be made between the uranium contents of source rocks, reservoir rocks, and crude oils, but on the basis of the generally very low uranium contents of crude oils in general and of the anomalously high contents of crude oils from seeps in the vicinity of uranium deposits, it is concluded that the latter crude oils have extracted uranium from deposits in the immediate vicinity.

The average uranium content of bitumens in rock asphalts is estimated to be roughly a thousand times greater than that of crude oils. If it is assumed that these bitumens are the residues of petroleums left after loss of some of the more volatile constituents, then a part of the uranium content can be attributed to concentration by reduction in volume. Reduction in volume probably does not bring about more than a hundred-fold increase in uranium content of the bitumens. The bitumens in rock asphalts probably retain all the uranium that was present in the parent petroleums. Crude oils do not retain all of this uranium; some of it remains with petroliferous residues in the reservoir rocks although it is not known how much. Even if it is assumed that the bulk of the uranium remains behind as the crude oil is extracted, then the major part of the increase in the uranium content of the bitumens in some rock asphalts still is unexplained.

The uranium content of the bitumen in a rock asphalt commonly differs abruptly from one stratum to another within the deposit; in some places it differs by a factor of a hundred or more. It has been pointed out by Hail and others (1956) that the concentration of uranium in these materials bears no consistent relationship to age of the host rock or to the age of the parent petroleum. The fact that some deposits are relatively high in uranium with respect to others and that considerable variation may occur within a deposit is believed due to the migration history of the bitumen and to the availability of uranium in the host rocks. No thorough study has been made to determine to what extent a correlation exists between the uranium content of the bitumen, and the type of host rock and its uranium content.

The bitumens in the rock asphalts of the Mid-Continent region and of Texas contain, on the average, less uranium than those in the rock asphalts of Utah and California (table 3). This condition may be explained, in part, by the general difference in types of host rocks.

The host rocks of the mid-continent and Texas deposits are predominantly marine limestones, dolomites, and sandstones of Paleozoic age that contain no appreciable amounts of uranium. The host rocks of the major Utah deposits are fluviatile, deltaic, and lacustrine sandstones of Lower Tertiary age that locally contain substantial amounts of volcanic detritus. The uranium content of these sandstones is variable. Large amounts of the sandstone contain 0.003–0.005 percent of uranium, and small deposits of ore-grade material (0.1 percent or more) have been found in them. The host rocks of the California deposits are sandstones of Miocene and Pliocene age that locally contain arkose, volcanic detritus, or phosphatic nodules. The latter materials locally contain a few thousandths of a percent of uranium.

The bitumens in rock asphalts in limestone or dolomite host rocks contain less uranium than those in sandstones. The deposits in Uvalde County, Tex., are in such rocks and are the least uraniferous of all the deposits listed in table 3. This condition is interpreted as a reflection of the fact that marine limestones and dolomites are among the least uraniferous of all rocks.

The bitumens in rock asphalts in the Tertiary formations of central and southern California contain higher-than-average quantities of uranium (table 3). Source beds of the bitumens are believed to be the argillaceous strata rich in organic matter within the Monterey shale. The bitumens have migrated into sandstone strata within the Monterey and into younger sandstones. Samples of crude oils recovered from the Monterey in the Santa Maria field (No. 91420), Santa Barbara County, and the Edna field (No. 235033), San Luis Obispo County, contained 3.1 and 1.6 ppb of uranium, respectively. Bitumens in rock asphalts of the area contain more than a thousand times this amount of uranium.

The rock-asphalt deposits in the vicinity of Edna are the most uraniferous of those listed in table 3. The bitumen in these deposits is unquestionably the residue of petroleum from the Edna pool. Some of this petroleum migrated upwards along permeable strata in the steeply dipping Monterey shale; partial loss of its volatile constituents near the surface caused it to form an asphalt seal at the outcrop of the Monterey and in remnants of the Pismo formation that lies unconformably upon the Monterey. A heavy, asphalt-base crude oil is produced from the pool under the asphalt cap. A sample of this crude oil (No. 235033) contained 1.6 ppb of uranium. The average uranium content in the bitumen of seven samples of the rock asphalt was 21,000 ppb (Hail, 1956; see also table 3). The urani-

um contents of samples taken from different strata range from 700 to 70,300 ppb. This variation is attributed to availability of uranium from sediments in different strata; the bitumen probably has extracted most of its uranium from these sediments. The Monterey shale, particularly the lower parts, includes phosphatic shale and layers of phosphatic nodules (Woodring and Bramlette, 1950, p. 18). Gamma-ray logs of oil wells show that the phosphatic strata are significantly more radioactive than other strata of the formation, presumably because of a higher uranium content. In the Edna locality the Monterey includes a basal volcanic member, and the Pismo formation includes an abundance of arkosic materials (Page and others, 1944). The rocks of the locality are kinds that generally contain above-average quantities of uranium. It seems that there is ample opportunity for the bitumen to extract uranium from the rocks through which it migrates, or from the present host rocks, either directly or with the aid of aqueous solutions. The bitumen probably acquired the bulk of its uranium content after becoming immobilized as a constituent of the rock asphalt, and the differences in distribution of its uranium content may reflect similar differences in distribution of uranium in the host rock.

The bitumens in rock-asphalt deposits at Vernal, Uintah County, Utah, and Sunnyside, Carbon County, Utah, contain, on the average, about 2,000 ppb uranium. That in the deposit at PR Springs, Uintah County, contains about 1,000 ppb uranium. In each of these deposits the uranium content differs considerably from one place to another. The deposits are in sandstones of the Green River and Uinta formations of Eocene age. These formations locally include large amounts of volcanic detritus, and their uranium contents are, in many places, substantially above the average for sandstones. Probable sources of the bitumens are the petroleums in the lower part of the Green River formation. Crude oil samples obtained from the Green River formation contained less than 1 ppb of uranium (table 2). Again, it is probable that the bitumen acquired much of its uranium from the host rock.

An approximate comparison of the distribution of 20 metals in the ashes of the crude oils and rock-asphalt bitumens listed in tables 2 and 3 is shown by the histograms of figure 22. These histograms do not show a precise comparison between the metallic constituents of crude oils and rock-asphalt bitumens in general, mainly because it was impossible to collect a large number of paired samples of crude oils and their associated residual rock asphalts, and therefore, the available materials were considered collectively; furthermore, the analytical data, with the exception of those for uranium, were obtained by semiquantitative spectrochemical methods. Distributions of the metals are shown as percentages of the total number of determinations of each metal falling within each order of magnitude. Three distinct differences in the distribution of various metallic constituents are indicated. The uranium content of the ashes of rock-asphalt bitumens is significantly greater than that of the ashes of crude oils. The contents of nickel and vanadium in the ashes of rock-asphalt bitumens are less than those in the ashes of crude oils. Conversely, the amounts of the common rock-forming elements, iron, aluminum, calcium, and magnesium, are greater in the ashes of rock-asphalt bitumens than those in the ashes of crude oils. No attempt is being made to explain these distributions. A rich field for geochemical research is indicated.

In summary, it has been found that the bitumens of rock asphalts apparently contain more uranium than reasonably can be accounted for in petroleums from which they might have been derived. Limited data indicate a possible correlation between the uranium content of the bitumen and that of the host rock, and little, if any, correlation with the uranium content of the possible parent petroleum. The bitumens of rock asphalts probably contain some adventitious uranium that has been extracted from the host rocks or from aqueous solutions that have passed by or through the bituminous deposits.

SOURCE OF URANIUM

The quantity of uranium contained in petroleums and their natural derivatives is so small that it has been impossible to establish definitely its source. The uranium may be syngenetic with the organic source materials of the bitumens, may be extracted from connate or other waters, may be extracted from rocks or unconsolidated sediments, or may be derived from any combination of these sources.

Many plants and organisms contain trace amounts of uranium, possibly held in organic complexes which ultimately may become incorporated in petroleum. Results of investigations by Daniel R. Norton (written communication concerning his unpublished paper "Inorganic Constituents of Marine Plankton") indicate that the ratio of concentration of uranium in dried marine plankton to its concentration in sea water ranges from 28 to 1,600, depending upon the source of sample and organisms included in it. The plankton were washed free of water-soluble salts prior to determination of uranium. Hoffmann (1941) has reported that algae growing in fresh water concentrate uranium and the algal ash contains as much as 9.1×10^{-4} per-

cent uranium (9,100 ppb). The fresh water contains 10^{-6} grams of uranium per liter (1 ppb). A. P. Pierce (written communication) reports the following concentrations of uranium (in parts per billion) in the ash of marine algae from the coast of Japan: *Porphyra* sp., 1,700; *Laminaria* sp., 800; *Undalaria* sp., 3,000.

The uranium content of ocean water varies slightly with salinity, depth, and position with respect to shoreline. Contents ranging from 0.37 to 3.5 ppb for ocean water from various localities have been presented by different authors (Hernegger and Karlick, 1935;

Föyn and others, 1939; Koczy, 1950; Nakanishi, 1952; Rona and Urry, 1952; Stewart and Bentley, 1954; Rona and others, 1956).

Very few sediments and sedimentary rocks contain less than 1 ppm of uranium. Limestones and dolomites as a group are among the least uraniferous of all the sedimentary rocks, but their uranium probably is the most readily extracted in nature. Sandstones, on the average, contain a few parts per million of uranium, a large part of which may not be readily extractable because it may be a constituent of heavy refractory min-
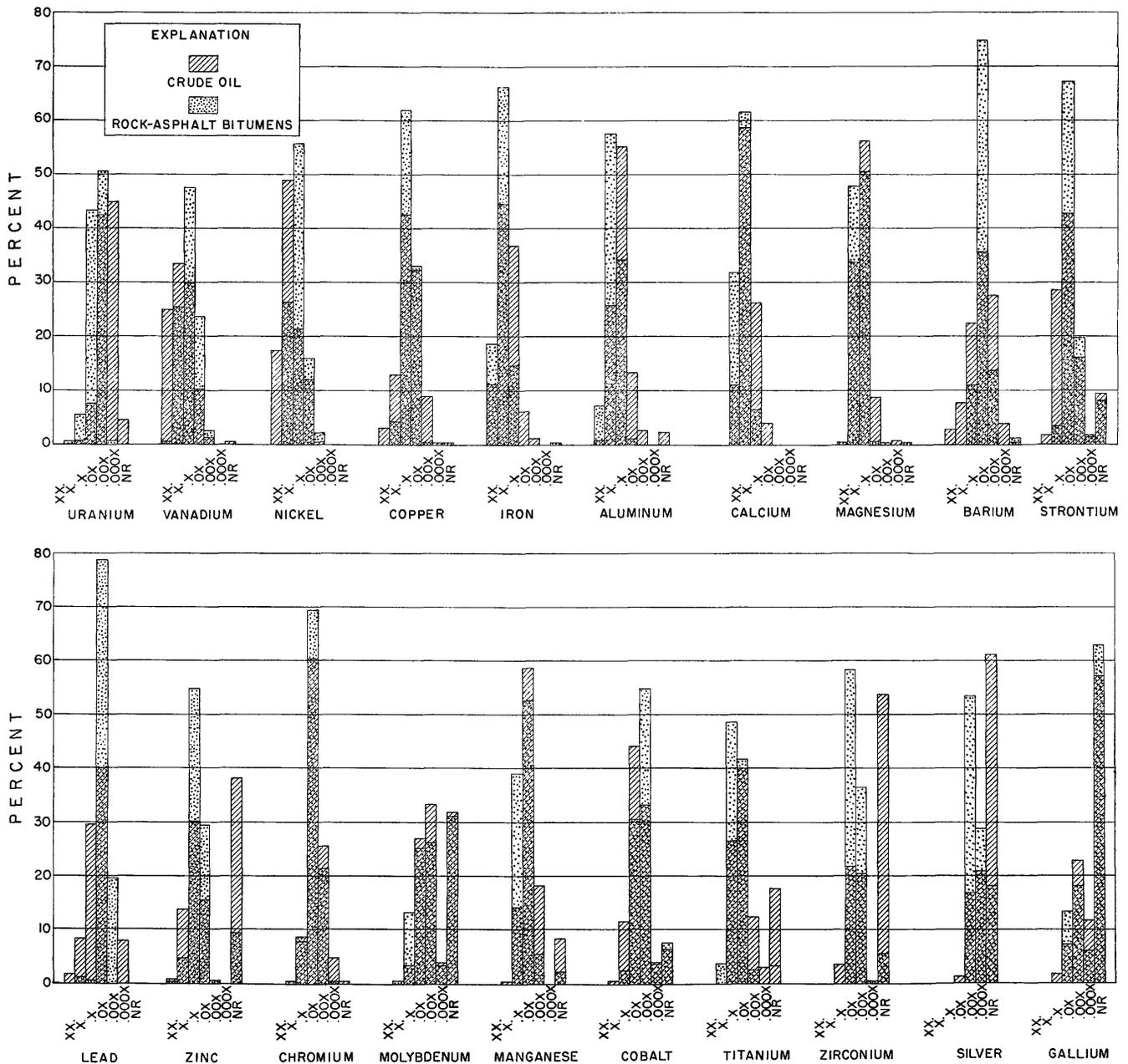
FIGURE 22.—Distribution of trace metals in the ash of crude oils and rock-asphalt bitumens; distribution indicated by percent of determinations falling within each order of magnitude or not reported.

erals, such as zircon. The uranium contents of shales, phosphatic sediments, tuffs, and arkoses commonly range from a few parts to a few tens of parts per million.

All materials with which a petroleum may be in contact, from its origin in source beds to its accumulation in reservoir and host rocks except possibly some nonsaline ground waters, contain as much or more uranium that the petroleum itself. Those petroleums and asphalts that contain relatively large amounts of uranium apparently extract uranium from host rocks and from rocks through which they migrate or from aqueous solutions with which they come in contact.

MODE OF OCCURRENCE OF URANIUM

The problem of how uranium is held in petroleums and other bitumens has not been fully investigated. As no specific organo-uranium complexes have been identified in petroleums, it cannot be stated positively that uranium is held in such complexes. Work by I. A. Breger and M. Deul (1959) and by A. W. Pierce, J. W. Mytton, and G. B. Gott (written communication) has shown that a major part of the uranium in some crude oils is associated with asphaltenes and heavy hydrocarbons or other heavy organic constituents. Highly paraffinic crude oils carry little or no uranium, as is indicated by available data (table 2). Many, if not all, crude oils and liquid asphalts carry finely divided mineral matter in suspension. Such matter varies from colloidal to sand size particles and commonly is very difficult to remove completely, either by centrifuging or filtering. It may include clay and other finely divided detritus taken from rocks through which the oil has moved or from the reservoir rock. Metallic sulfides and possibly other minerals may form in the crude oil and be carried in suspension. Uranium may be sorbed by some of this mineral matter.

Uraninite has been shown to be dispersed in many native solid bitumens and pyrobitumens, variously called asphaltite, carbon, anthraxolite, or thucholite (Davidson and Bowie, 1951; Rosenzweig and others, 1952; Liebenberg, 1955; A. W. Pierce, J. W. Mytton, and G. B. Gott, written communication 1958), but it is not known whether the uranium originally existed in the organic substances in this form. These substances also commonly contain dispersed metallic sulfides, indicating that reducing sulfide environments existed as they were formed. Gruner (1956) has demonstrated that hydrogen sulfide is a precipitant of uranium under some conditions, and the solid substance that forms generally is uraninite. Hydrogen sulfide occurs in most petroleum reservoirs, and it is likely to precipitate as uraninite any uranium ions that might

enter or be formed in the area. There is no evidence that uranium is carried in solution by liquid hydrocarbons.

Some, if not all, of the uranium in petroleums and asphalts probably is held by organic compounds that consist in part of radicals containing oxygen, nitrogen, sulfur, or combinations of these elements. Some resins are effective collectors of uranium and are used in ore-treatment processes. Research on the flotation of uranium minerals by Butler and Morris (1956) indicates that some aliphatic compounds with nitrogen loadings are effective collectors of secondary minerals of uranium and that aliphatic compounds are better collectors than aromatic compounds. Aliphatic compounds may be minor constituents of petroleums and asphalts.

How trace amounts of uranium are held by petroleums, liquid asphalts, and some solid bitumens and pyrobitumens is a problem still to be solved.

HYPOTHETICAL ROLE OF PETROLEUMS IN THE GENESIS OF URANIUM DEPOSITS IN SEDIMENTARY ROCKS

The common occurrence of uranium deposits and petroleum reservoirs in the same localities and even short distances apart within the same sedimentary formations and the frequent usage of the terms "asphaltite" and "uraniferous asphaltite" to designate various kinds of highly uraniferous native organic substances have led some geologists and geochemists to postulate that uranium minerals may be deposited from oilfield waters. Some of these hypotheses have received considerable publicity. Tomkeieff (1946) has supported the hypothesis that petroleum has a direct role in the genesis of some uranium deposits. Erickson and others (1954) suggested that the so-called uraniferous asphaltite of Temple Mountain, Utah, was formed from petroleum. They further suggested that slightly acid ground waters might leach metals, including uranium, from petroleum-stained reservoir rock and deposit them elsewhere. Gott and Hill (1953) suggested that uranium may be flushed from subsurface rocks by petroleum. Many geologists engaged in the search for and development of uranium deposits apparently have accepted these ideas as facts rather than as the hypotheses as they were intended to be by the authors, and as a result considerable confusion exists concerning what role, if any, petroleum may play in the genesis of these deposits.

The type locality for an association of minable uranium deposits and petroliferous materials is Temple Mountain, Utah. In this locality petroleum saturates parts of the ore-bearing sandstones and seeps from

mine faces and outcrops. In the Yellow Cat district, Grand County, Utah, uranium is being mined from lenticular sandstone strata of the Morrison formation that crop out in the district and dip gently northward. A few miles to the north, crude oil is being produced from lenticular sandstone strata of the same formation in the Cisco, Seiber, and Crescent Junction fields. Oil seeps have formed within mines in the Big Indian Wash-Lisbon Valley and Elk Ridge districts, San Juan County, Utah. The Big Flat, Cane Creek, Desert Creek, Boundary Butte, Aneth, and San Juan oil fields of Utah, the Rattlesnake field of New Mexico, the Mancos Creek and Dove Creek fields of Colorado, the Crooks Gap field of Wyoming, and many others are located near uranium-mining districts. Noncommercial uranium deposits have been found near oil fields and seeps in the vicinity of McKittrick, Calif., and Cement, Okla. The apparent close association of uranium deposits and petroleum fluids in sedimentary rocks has provided opportunity for much speculation.

There is no indication that crude oils from one region contain substantially more uranium than those from any other region unless variations of 1 or 2 parts per billion caused by predominance of paraffinic, aromatic, or asphaltic constituents are considered significant. If petroleums play a direct role in the genesis of some uranium deposits, it would be reasonable to expect to find crude oils carrying anomalously high quantities of uranium in the Colorado Plateau region. Except for seeps issuing within mines or from mineralized ground, uraniferous crude oils have not been found. The predominately paraffin-base crude oils produced from Pennsylvanian and Mississippian formations in the Colorado Plateau area contain small fractions of a part per billion of uranium. Mixed-base crude oils produced from younger formations in the same area seem, on the average, to contain no more uranium than do the paraffin-base oils, although one sample from the Boundary Butte field (No. 235027), San Juan County, Utah, was found to contain 4 ppb and one sample from the Crescent field (No. 235031), Grand County, Utah, 3 ppb. Paraffin-base crude oils produced from the Cretaceous and Tertiary formations of the Uinta Basin, Utah, and northwestern Colorado, contain fractions of a part per billion of uranium. Two samples of weathered asphaltic crude oils recovered from the upper part of the Kaibab limestone of Permian age at John's Valley (No. 240697) and from a limestone in the Hermosa formation of Pennsylvanian age at Upper Valley (No. 97491), both in Garfield County, Utah, contained 39 and 8 ppb of uranium, respectively. These two crude oils apparently consist of asphaltic residues that remained after the bulk of

the original petroleum escaped by volatilization. Although the oil fields of the Colorado Plateau region are located in one of the great uranium provinces of the world and in the midst of the largest known uranium deposits of the United States, this situation is not reflected in the uranium contents of the crude oils. In fact, the average quantities of uranium in crude oils of the Colorado Plateau region are less than those in crude oils from other regions, probably because of the preponderance of paraffinic types. The mixed-base and asphalt-base crude oils from Tertiary formations of central and southern California contain greater quantities of uranium, possibly averaging about 2 ppb, probably because their content of asphaltenes and aromatic constituents is greater. No significant deposits of uranium have yet been found in this area.

Crude oils from Wyoming and Montana, where significant uranium deposits have been found, range from light paraffinic to heavy asphaltic types and generally contain about 1 ppb of uranium. There are no anomalous quantities of uranium in the crude oils from the Riverton Dome, Beaver Creek, and Sand Draw fields, which are situated 6 to 25 miles from uranium mines in the Gas Hills and Conant Creek districts in Wyoming, nor in the crude oils from the Crooks Gap, Sheep Creek, and Happy Springs fields, situated within 6 miles of the Crooks Gap uranium district in Wyoming. The crude oils from all these fields, except the Sheep Creek field, are predominately paraffin- or light mixed-base oils, are light green to brownish green, and are produced from several stratigraphic units ranging in age from Pennsylvanian to Cretaceous. The highest uranium concentration found was 2.7 ppb in a sample of black, asphaltic oil from the Sheep Creek field (No. 244958).

Crude oils are produced from the Madison limestone of Mississippian age and from the Tensleep sandstone of Pennsylvanian and Permian age in the Frannie and Sage Creek fields in the northern part of the Big Horn Basin, Wyo. These fields are approximately 6 miles from uranium deposits in the Madison limestone on Big Pryor Mountain. The crude oil from the Tensleep sandstone is mixed-base oil and contains less than 1 ppb of uranium. The crude oil from the Madison limestone is a heavy, black, asphaltic oil; a sample from the Sage Creek field contained less than 2 ppb of uranium, whereas another from the Frannie field contained 476 ppb. The anomalous quantity of uranium in the Frannie sample cannot readily be explained. It is possible that uranium deposits exist in the Madison limestone here, as on Big Pryor Mountain, and the crude oil acquired its uranium from a local source.

An anomalous quantity of uranium (248 ppb) was

found in a sample of heavy, black asphaltic crude oil (No. 86636) produced from the Marchand sand at a depth of approximately 7,000 feet in the Cement field, Caddo County, Okla. Within the oil field, small deposits of uranium have been found within a few feet of the surface of the ground. No relationship between the deep petroleum and the shallow uranium deposits has been found.

No correlation can be established on a regional basis between uranium contents of crude oils and their proximity to or other possible association with uranium deposits. For example, crude oils from the Mid-Continent region, where no significant uranium deposits have been found, are indistinguishable from those of the Rocky Mountain region, where substantial uranium deposits exist, so far as uranium contents are concerned. The occasional anomalous uranium concentrations found in crude oils seem to be strictly local conditions.

Many thousands of gamma-ray logs have been made of oil wells. There is no log known to the author that shows anomalous radioactivity that can be attributed to a concentration of uranium and its daughter products in petroleum. Likewise, no example of a uraniferous deposit within a petroleum reservoir is known to the author.

There is no evidence indicating that uranium associated with heavy hydrocarbons, asphaltenes, or other organic constituents of petroleums is subsequently released under conditions that would permit substantial deposits to be formed in sedimentary rocks. It is apparent that uranium is tenaciously held and is released only when the petroleums are destroyed; such action may result from oxidation, nuclear irradiation, or leaching by certain acid or alkaline solutions; also, at the surface of the earth, petroleums may be destroyed by certain bacteria, yeasts, and molds (ZoBell, 1946). Asphaltenes are among the most resistant major constituents of petroleums and form the bulk of residues in tar seeps, rock-asphalts, and natural-asphalt deposits. It seems unlikely that there has been any loss of uranium from the bitumen; instead it is more probable that additional uranium extracted from the host rocks or from aqueous solutions has been added.

Many of the known uranium deposits of the Colorado Plateau region are located along the flanks of anticlinal structures or near the crests of monoclinal folds. Some of these structures have been breached, and the principal uranium-bearing formations are exposed on inward-facing cliffs surrounding denuded crests. The surface drainage has deeply dissected the area, forming canyons along the flanks of the structures. The excellent exposures on the cliffs and rims logically were the first parts of the uranium-bearing formations

to be prospected. Inasmuch as the less favorably situated parts of the formations have not been prospected as thoroughly, the distribution of uranium deposits around the flanks of anticlinal structures may be more apparent than real.

The principal uranium-bearing formations of the Colorado Plateau region, the Morrison formation of Jurassic age and the Chinle formation of Triassic age, form reservoirs for petroleum in unbreached structures and stratigraphic traps in the plateau region and at several localities around its borders. Recently, in the plateau region, several oil pools have been discovered in the Kaibab limestone of Permian age, in the Paradox member of the Hermosa formation of Pennsylvanian age, and in limestones of Mississippian age, all of which lie on unbreached anticlinal structures; other pools have been discovered in dolomite reefs in the Hermosa formation.

Even though uranium deposits and petroleum exist in different parts of the same sedimentary formations there is little likelihood that petroleum ever acts as an ore-forming fluid for uranium. A simple computation of the quantities of materials required to form a single small ore body suffices to emphasize this point. A 100,000-ton ore body having an average grade of 0.25 percent uranium contains 250 tons of that metal. As a first estimate, it is assumed that a hypothetical petroleum ore-forming fluid contains 1 ppb of uranium, this being the average uranium content of crude oils. Assuming 100 percent deposition of uranium, which would be an unlikely event, a minimum quantity of 250 billion tons, or 1,500 billion barrels, of petroleum is required. This minimum amount of petroleum required for the deposition of one rather small ore body is approximately 50 times greater than the total reserves of the United States. Because crude oil probably contains somewhat less uranium than petroleum in the ground, the problem is recomputed on the assumption that the bitumen of a rock asphalt acts as an ore-forming fluid. It is assumed that this bitumen is a petroliferous residue containing all of the metals that were present in the original petroleum. The uranium content of the bitumen is taken to be 1 ppm, this being approximately the average uranium content of the bitumens in rock asphalts of the western United States. A minimum quantity of 250 million tons, or 1,500 million barrels, of bitumen is required to deposit the ore body. It is readily seen that any reasonable assumption concerning the uranium content of a hypothetical petroleum ore-forming fluid necessitates a tremendous volume of fluid. Petroleum does not exist in unlimited quantities. Compared to water, its availability is small. Petroleum is not likely to be recirculated, and its pas-

sage through a certain stratum generally is a one-way trip. Billion-barrel petroleum reservoirs are uncommon, whereas 100,000-ton uranium ore bodies are relatively abundant. Also, uranium ore bodies, some larger and some smaller, within a district are considerably more abundant than petroleum reservoirs. When the total amount of uranium within mining districts is considered, any assertion that petroleum could have been the ore-forming fluid becomes ridiculous. Petroleum could have been the ore-forming fluid only for some very small deposits, and even this possibility is unlikely.

Because no evidence has been found to support the hypothesis that petroleum can be an ore-forming fluid for uranium, it must be assumed that petroleum, uraniferous solutions, and other fluids simply have migrated, at one time or another, through the permeable strata. Undoubtedly many migrations of various fluids through some strata have occurred and are continuing today. The uranium minerals and petroleum are genetically unrelated except that structural and stratigraphic features have controlled their movement and accumulation.

Some interesting deposits of uranium and rock asphalt are located on the west flank of the Conant Creek anticline in SW¼SE¼ sec. 3, T. 32 N., R. 94 W., Fremont County, Wyo. A pit approximately 250 feet long, 175 feet wide, and 30 feet deep has been dug in sandstones of the lower (Eocene or Oligocene) part of the White River formation of Granger (Van Houten, 1954), and a small amount of uranium ore has been recovered during the operation. The sandstone strata range from about an inch to about five feet in thickness. Except for variable amounts of clay, each stratum consists of fairly well sorted material that may be silt or sand. Some strata are thoroughly saturated with asphaltic bitumen, other strata are lightly stained with the bitumen or contain it in a spotty distribution, and some strata seem to contain no bitumen at all. It is evident that the bitumen is a petroliferous residue. Several oil fields are located within distances of 5 to 14 miles to the west and northwest. Petroleum probably has ascended along some of the faults in the area and has penetrated those near-surface strata that have favorable permeabilities. Most of the uranium is in oxidized minerals in the nonbituminous-sandstone strata. A thorough survey of the pit with a Geiger-Mueller counter revealed that the bitumen-saturated sandstone strata are the least radioactive of all those exposed. Nonbituminous sandstone containing visible uranium minerals (mostly carnotite) is the most radioactive. The bitumen contains an anomalously large amount of uranium, as compared to the average for

bitumens of rock asphalts, in general. One sample (No. 244376) from a bitumen-saturated stratum contained 7.78 percent bitumen of which ash was 0.035 percent, and the uranium content of the bitumen ash was 5.72 percent, this being 20 ppm uranium (0.002 percent) in the bitumen. After extraction of the bitumen, the sandstone residue contained 0.004 percent uranium (40 ppm). Two samples (Nos. 250515 and 250516) were taken from opposite sides of the contact of a bitumen-saturated stratum with a nonbituminous stratum. The uranium content of the sample from the bituminous stratum was 0.007 percent (70 ppm), and that of the sample from the nonbituminous stratum was 0.10 percent (1,000 ppm). The nonbituminous ore-bearing strata were not thoroughly sampled, but it would be possible to select samples containing several tenths of a percent of uranium. The rock asphalt exposed in the pit is abnormally uraniferous, but it contains considerably less uranium than adjacent nonbituminous sandstone. The sequence of events seems to have been: first, introduction of the bitumen, which selectively followed strata of favorable permeability; second, uranium mineralization of some nonbituminous-sandstone strata, possibly aided by diffusion of hydrogen sulfide from the bitumen; and third, possible oxidation of a primary uranium mineral. Uraniferous solutions undoubtedly penetrated the bituminous sandstone during the second and third stages, and a small amount of uranium was precipitated. This deposit is the only known occurrence wherein a substantial quantity of rock asphalt and uraniferous sandstone are in juxtaposition.

It is possible that petroleums may play an indirect role in the genesis of some uranium deposits. Petroleums generally contain small amounts of water-soluble naphthenic acids, phenols, and other organic acids, bases, and salts (Lochte, 1952). It is not known precisely how most of these substances react with uranium in the kind of environment in which the uranium-mineral deposits supposedly were formed. If they are extracted from petroleums by water and attain sufficient concentrations under reducing conditions in the edge waters surrounding petroleum reservoirs, an environment may be formed in which uranium could be precipitated. The uranium would have to be introduced by ground waters or hydrothermal solutions and might be expected to be precipitated along interfaces of the two solutions. Most petroleums contain hydrogen sulfide, commonly in immense quantities. Inasmuch as hydrogen sulfide is highly soluble in water, the edge water in contact with a petroleum can become sulfurous, and a reducing environment can be formed. Hydrogen sulfide, under some conditions, is an effective

reducing agent and precipitant of uranium (Gruner, 1956). If uraniferous ground waters or hydrothermal solutions meet sulfurous edge waters, precipitation of uranium might be expected at the interfaces. If water-soluble organic compounds or hydrogen sulfide in edge waters are effective precipitants for uranium, it is reasonable to expect to find uranium deposits around the peripheries of petroleum-bearing structures.

If petroleums play a significant role in the genesis of some uranium deposits, either directly or indirectly, then the peripheries of oil fields should be favorable areas for prospecting. Many thousands of gamma-ray logs have been made of holes drilled to develop oil fields and to explore for petroleum. None of these gamma-ray logs that have been examined to date indicates the presence of a uranium deposit. The only parts of the United States where major accumulations of both uranium and petroleum are known are the Rocky Mountain region, the Colorado Plateau region, and the southeast Texas coastal plain, and in these areas no relation between the two types of accumulations has been established. Because the Rocky Mountain and Colorado Plateau regions are parts of a major uranium province, it is possible that uraniferous solutions have been available to react with edge waters, whereas uraniferous solutions have been lacking in some other petroliferous regions.

The total amount of uranium contained in the petroleum of the United States seems to be very small compared to that in mineral deposits in sedimentary rocks. If the average uranium content of crude oil is considered to be 1 ppb, then the total uranium in the crude oil reserves of the United States (30 billion barrels at end of 1956; World Oil, 1957) is less than 5 tons. Possibly petroliferous residues left in reservoir rocks contain considerably more uranium than the extracted crude oil. No data are available that permit an estimate of this amount of uranium. Even if it is assumed that only a small part of the uranium in petroleum leaves the reservoirs with commercially produced crude oil, it is probable that the original amount is small compared to that in sedimentary rocks.

It has been suggested by Erickson and others (1954) that over a long period of time slightly acid ground waters might leach metals from a petroleum-stained reservoir rock and ultimately deposit them elsewhere under conditions favorable for precipitation. This action undoubtedly occurs, but whether or not enough uranium can be leached and subsequently be redeposited to form deposits such as those of the Colorado Plateau region is problematical. Present knowledge limits this idea to the realm of speculation.

In summary, it can be stated that there is no evidence to support a hypothesis that the origin of some uranium deposits has been deposition from petroliferous fluids. Petroleums contain too little uranium to be ore-forming fluids. There is no significant pattern in the distribution of uranium in petroleum from one region to another, nor from one stratigraphic unit to another. In general, it can be stated that petroleums from one region are no more uraniferous than those from any other region, and such systematic minor differences as exist from one area to another are related directly to the composition of the petroleums, that is to a preponderance of paraffinic, naphthenic, or aromatic constituents, and to the asphaltene content. The amount of uranium contained in petroleums is small compared to that in most common sedimentary rocks. The bulk of uranium in petroleums is contained in mixed-base and asphalt-base oils and is not readily released. Hydrogen sulfide or water-soluble organic compounds in edge waters peripheral to petroleum reservoirs produce a reducing environment that may cause precipitation of uranium at interfaces with uraniferous ground waters or hydrothermal solutions. It is only in the uranium province of the Rocky Mountain and Colorado Plateau regions that uranium deposits are known that might have been formed in this manner, and even here the relationship is hypothetical.

URANIFEROUS ORGANIC SUBSTANCES CALLED "ASPHALTITE"

It has become a rather common practice to apply the term "asphaltite" to some native black organic substances that cannot readily be identified as specific substances. Some of these substances form commercially valuable ores of uranium, as in the San Rafael Swell area of Grand and Emery Counties, Utah. Others such as the nodules and pellets in the Azotea tongue of the Seven Rivers formation of Permian age in southeastern New Mexico may contain substantial amounts of uranium but are too sparsely distributed in the host rocks to be uranium ores. Many of these uraniferous organic substances are included in the term "uraniferous asphaltite."

The so-called "uraniferous asphaltites" generally are not bitumens. Their present compositions, solubilities in organic solvents, and physical properties require that they be classified as pyrobitumens. Their origins are controversial subjects that are far from being settled at present. Speculations concerning the genesis of various deposits include hypothetical origins from petroleum, from mouldering plant debris or from organic materials released during coalification, and from kerogen. Different deposits of "uraniferous asphaltite" probably have formed from different source

materials. Some of them possibly have formed from bitumens.

The so-called "uraniferous asphaltites" are not discussed further in this report because they cannot definitely be classified as petroleum derivatives.

PETROLEUMS AND ROCK ASPHALTS AS SOURCE MATERIALS FOR URANIUM

In common with most other naturally occurring substances, petroleums and their natural derivatives have been examined to determine their value as source materials for uranium. Although it is generally conceded that their uranium content is very small and that the amount of uranium that might be recovered would be small, some over-optimistic estimates have been made concerning their value as potential source materials. Any uranium recovered from crude oils and rock asphalts would have to be a byproduct extracted from refinery residues or from combustion residues.

The published estimate of the crude-oil reserves of the United States as of 1956 is 30 billion barrels (World Oil, 1957). On the basis of an average uranium content of 1 ppb, the total uranium content of the reserves is less than 5 tons. If it is assumed that secondary-recovery processes and improved methods of extraction ultimately may result in a recovery of twice as much crude oil from presently known reservoirs, a possible potential source of 10 to 15 tons of uranium is indicated. An allowance for a somewhat higher uranium content in secondarily recovered crude oil is included in the latter estimate.

A tarry or an asphaltic residue adheres to pore walls of some reservoir rocks (Nutting, 1934) and may remain after recoverable crude oil has been extracted. The compositions of these residues are such that they can be expected to contain greater percentages of trace metals than the recoverable crude oil. No data are available to indicate what their metallic contents might be, but contents of several or even a few tens of parts per billion of uranium are possible. How this uranium could be recovered poses a difficult problem.

The bituminous constituents of rock asphalts contain, on the average, about a thousand times as much uranium as does the average crude oil. Because of the great tonnages of rock that would have to be processed and the low uranium content of the bitumens, averaging about 1 ppm, rock asphalts are not practical source materials for the recovery of uranium. This condition is indicated by the following facts pertaining to three of the major rock-asphalt deposits of the United States.

The rock-asphalt deposits in the vicinity of Edna, San Luis Obispo County, Calif., have the highest content of uranium of all the deposits sampled (table 3). Measured, indicated, and inferred reserves of the deposits are estimated to be 282,880,000 short tons of rock containing 11.0 percent bitumen by weight (Page and others, 1944). Analyses of 7 spot samples show an average of 0.55 percent ash in the bitumen and 0.376 percent uranium in the ash (Hail and others, 1956). The bitumen therefore contains about 21 ppm of uranium. Inasmuch as sampling of this large deposit is sparse, only a rough estimate of the uranium potential can be made. The quoted figures indicate that there are approximately 650 tons of uranium in the deposit. Assuming that complete recovery could be attained, it would be necessary to process about 215 tons of rock, extracting all the bitumen from it, and then removing all the uranium from the bitumen, to obtain one pound of uranium. One sample (No. 99135), taken from a relatively thin bed, showed an abnormally high content of uranium, thereby heavily weighting the average. If this sample is disregarded, an average of 0.6 percent ash in the bitumen and 0.122 percent uranium in the ash is indicated. The bitumen therefore would contain about 7 ppm of uranium. These figures indicate that there are approximately 220 tons of uranium in the deposit. About 630 tons of rock would have to be processed to obtain one pound of uranium, assuming complete recovery.

The rock asphalt deposits near Sunnyside, Carbon County, Utah, probably are the largest in the United States. Reserves of bituminous sandstone are estimated to be 1,600 million cubic yards, of which one-half is assumed to contain at least 9 percent bitumen by weight (Holmes and others, 1948). Analyses of 11 spot samples showed 1.10 percent ash in the bitumen and 0.021 percent uranium in the ash (Hail and others, 1956). The bitumen contains approximately 2 ppm of uranium. There are indicated to be about 295 tons of uranium in the half of the reserves containing 9 percent bitumen. Assuming complete recovery, approximately 2,400 tons of rock would have to be processed to provide one pound of uranium.

There are large deposits of asphalt-bearing limestone near Blewett, Uvalde County, Tex. Total reserves of minable rock are 340 million tons (Gorman and Robeck, 1945). Analyses of 11 spot samples showed 8.5 percent bitumen in the rock, 0.43 percent ash in the bitumen, and 0.002 percent uranium in the ash (Hail and others, 1956); the bitumen contains approximately 0.08 ppm of uranium. There are about 2.5 tons of uranium in the estimated reserves of the deposit. Approximately 68,500 tons of rock would have to be processed to provide one pound of uranium, assuming complete recovery.

Data pertaining to these three rock-asphalt deposits are summarized in the following table.

Bitumen and uranium content of some rock ashpalt deposits

[Sources: Gorman and Robeck, 1945; Hail and others, 1956; Holmes and others, 1948; Page and others, 1944]

	Edna, Calif.		Sunnyside, Utah	Uvalde County, Tex.
Rock asphalt_____tons__	282,880,000		1,416,000,000	340,000,000
Bitumen_____percent__	11.0		9.0	8.5
Do_____tons__	31,116,800		127,520,000	28,900,000
	Average			
	(1) 7 samples	(2) 6 samples[1]		
Ash in bitumen_____percent__	0.55	0.6	1.10	0.4
Do_____tons__	174,000	183,600	1,402,720	124,270
Uranium in ash_____percent__	0.376	0.122	0.021	0.002
Uranium in deposit_____tons__	650	220	295	2.5
Uranium in bitumen_____ppm__	21	7	2	0.08
Tons of rock asphalt per pound of uranium_____	215	630	2,400	68,500

[1] Average of 6 of 7 samples, excluding 1 sample containing an anomalously high uranium content.

There may be several hundred tons of uranium contained in the bitumens of rock-asphalt deposits of the United States. The concentration of uranium in the bitumens is very low, only a few parts per million at best, and the bitumens in turn are dispersed in several billion tons of rock. Inasmuch as a few hundred to several thousand tons of rock would have to be processed for each pound of uranium recovered, use of rock asphalts as source materials of uranium seems to be impractical even if the uranium should be recovered as a byproduct of bitumen production.

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