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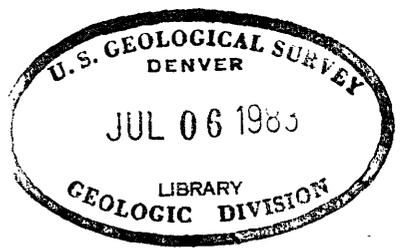
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

URANIUM IN PETROLEUM AND ROCK ASPHALT*

By

Kenneth G. Bell

September 1957



Trace Elements Investigations Report 697

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.



USGS - TEI-697

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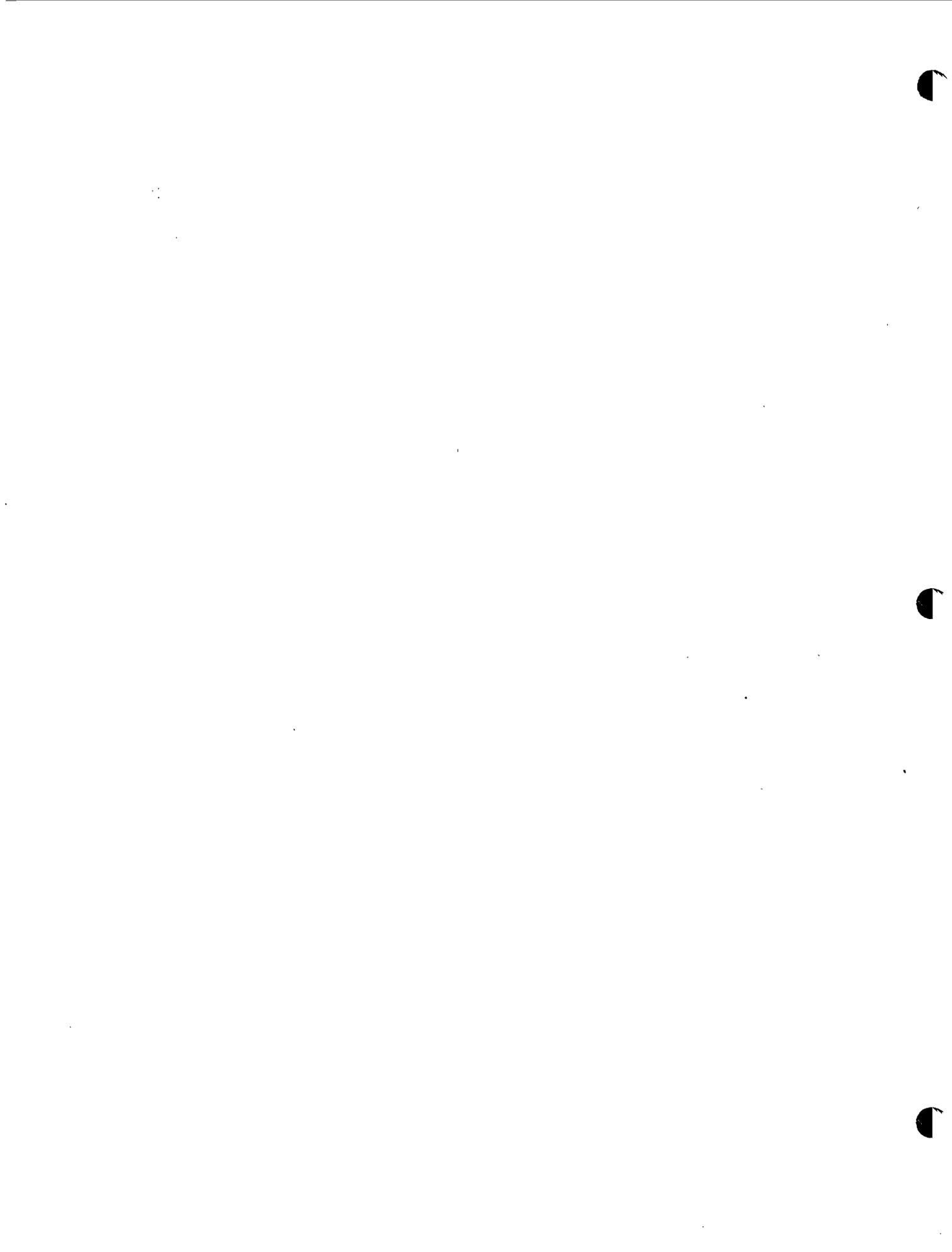
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* See letter of transmittal.



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ABSTRACT

Uranium is a minor trace element constituent of petroleum and its natural derivatives. The amounts of uranium present in crude oils produced by primary recovery processes range from nil to a few tens of parts per billion. An average uranium content for all crude oil is estimated to be about one part per billion, or about one third of the average content of sea water. Paraffin-base crude oils contain the smallest quantities of uranium which, if detectable, are a fraction of one part per billion. Mixed-base and asphalt-base crude oils, which in general contain a slightly greater amount of uranium, show a rough positive correlation between specific gravity and uranium content. There is no correlation between uranium contents of crude oils and their geologic ages. Crude oils from one region are no more uraniferous than those from any other region 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, which are uraniferous provinces, carry less-than-average quantities of uranium, a condition which is attributed to predominance of paraffinic constituents. Crude oils produced by secondary recovery processes utilizing water flooding and detergents apparently carry above-average quantities of uranium, possibly because asphaltic residues are removed from pore walls of reservoir rocks. The state of uranium in petroliferous materials and its source have not been determined.

The bituminous constituent of rock asphalts carries up to a few thousands of parts per billion uranium with the average being about 1,000 parts per billion. This concentration 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 bitumen extracts uranium from the host rock under near-surface conditions. There appears to be a positive correlation between uranium contents of the bitumens and of the host rocks.

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

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. There are several hundred tons of uranium in the bitumen of rock asphalt deposits of the United States. Because this bitumen is dispersed in several billion tons of rock, it does not represent a practical source material for uranium.

INTRODUCTION

Petroleums, natural asphalts, and rock asphalts carry many metallic elements in trace amounts. The trace metal content of crude oils has been a subject of considerable research because of possible clues that it might furnish concerning the origin and migration of petroleum and because of the deleterious effects that some metals have upon catalytic cracking processes and upon refinery and combustion equipment. The suite of metals 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-earths, uranium and other elements are sporadic constituents. Although the suite of metals is quite consistent, the amounts of individual metals vary 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 which bring about associations of other metals in petroleum have been subjects of but little investigation.

Considerable data concerning the quantities of vanadium, nickel, and copper present in petroleums 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 up to about 0.1 percent of the fluid or about 75 percent of the ash. Nickel generally occurs in lesser quantities and amounts to as much as 10 percent of the ash. Nickel appears 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, but some crude oils contain several parts per million copper amounting to as much as 10 percent of the ash. It has been established by Treibs (1934), Uspenskii and Gorskaya (1938), Skinner (1952), and others that some of the vanadium in crude oils is held as porphyrin complexes; Gleboskaya and Vol'kenshtein (1948) claim to have extracted and identified nickel-porphyrin complexes from crude oil; 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 appear 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 constituents of petroleum and other natural bitumens; because, in common with other metals, they have deleterious effects on catalytic cracking agents; and, in the case of vanadium, because the oxide formed during combustion of fuel oils has deleterious effects on silica-brick furnace linings, turbine blades, and other equipment; and furthermore in the case of vanadium because some bitumens are source materials for this metal.

Some recent investigations have dealt with the varying contents of trace metals in crude oils and the geologic interpretations that can be deduced from them. Attempts have been made to use trace metals as an aid in correlating petroleum from different pools within a formation, to correlate petroleum 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 oil field waters (Burton, 1904; Engler, 1907; Bohn, 1930; Nikitin and Komleff, 1930; Hahn and Born, 1935; Bell and others, 1940; Tiratsco, 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 petroleum and its natural derivatives, and the possible role of petroleum 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 also are generally equally good reservoir rocks for petroleum. In the Rocky Mountain region and the Colorado Plateau region petroleum reservoirs and uraniferous mineral deposits are distributed throughout a stratigraphic sequence 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, California, where small non-commercial uranium deposits are known. Some oil shales are uraniferous. These common occurrences of petroliferous substances and deposits of uranium minerals in the same localities and formations have posed some intriguing problems.

Some naturally occurring solid carbonaceous minerals and organic substances are highly uraniferous, but their compositions and origins are not 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 petroleum and asphalts and to present analytical data compiled during the course of investigations by the U. S. Geological Survey on behalf of the Division of Raw Materials, U. S. Atomic Energy Commission. All samples of petroleum and crude oil were collected from localities west of the Mississippi River. A few samples of rock asphalt were collected in northern Alabama; the remainder of the rock asphalts were collected in localities west of the Mississippi River.

This report is concerned principally with uranium and petroleum and natural asphalts. The association of other metals with petroleum and natural asphalts is not discussed in the text, but analytical data accumulated during the course of the investigations are presented in tabular form.

DEFINITIONS

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

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

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-insoluble sulfonation products.

Scope. This definition includes petroleums, native asphalts, native mineral waxes and asphaltites."

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, anthracite coal) and their respective shales."

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."

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).

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

Asphalt and rock asphalt: "A term applied 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.

This definition is applied to native asphalts and pyrogenous 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."

Native asphalts associated naturally with sandstone, limestone, etc., 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," (Fay in Rice, 1953). "That portion of asphalt which is insoluble in ethyl ether," (Abraham, 1945), (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 difficultly fusible, and largely soluble in carbon-disulfide, yielding water-insoluble sulfination products.

Scope. This definition includes gilsonite, glance pitch, and grahamite."

Kerogen: There appear 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." (The author).

SOURCES OF SAMPLES AND SAMPLING METHODS

Most of the samples for which analytical data are listed in tables V and VI were collected during the course of several Geological Survey investigations concerning possible associations of uranium with naturally occurring carbonaceous 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 492 samples of crude oil 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 39 samples were collected by other individuals. Credit is given to collectors in footnotes to the tables. All analytical work was done in the Geological Survey laboratories at Denver, Colorado under the direction of A. T. Myers and C. A. Horr.

The crude oils listed provide a representative sampling of paraffinic-, mixed-, and asphaltic-base oils. Also, the samples represent pools distributed in rocks ranging in age from Cambrian through Miocene and which occur in all types of reservoir rocks. 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 well head, 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 of new wells. When fluid was taken from a well head, it was allowed to stand for a short time while gas and water separated from the oil, and the oil was then 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, otherwise 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 sampling was very sparsely distributed considering the abundance of sources from which material can be collected. It is thought that the sampling is 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 commonly used methods of identifying metallic constituents of carbonaceous substances involve burning off the organic constituents and analyzing the ash. During the past decade spectroscopy has come into common usage for making qualitative and semiquantitative determinations of a large number of elements which may be present 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 A.S.T.M designation D482-46. Wet ashing techniques consist of heating the sample in an excess of concentrated sulfuric acid, strong oxidizing acids such as nitric or perchloric, or in mixtures of these acids, until organic constituents are broken down to a carbon residue or eliminated, then evaporating to dryness and igniting 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 procedures 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 carbonaceous substances that occur in the greatest quantities were investigated thoroughly.

The development of analytical procedures for quantitative determinations of trace metals in crude oils and petroleum products has been the subject of much recent research. The accuracy of wet vs. dry ashing techniques as concerns various metals 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 uranium in bitumens and other carbonaceous substances. The organic constituents are eliminated by a dry ashing technique, and uranium is determined by the fluorimetric method described by Grimaldi and others (1954). The accuracy of currently used techniques for other metals has not yet been discussed in published reports.

Spectrochemical analysis of ashes of carbonaceous 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, and secondly, an element must be present in the ash sample in such quantity as permits 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 differing probable errors.

There are many factors that contribute to incomplete analyses and large probable errors while determining the trace-metal 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). Mercury and germanium are other metals subject to losses through volatilization (Ahrens, 1950). 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. Other volatile elements such as cadmium may be determined as less than the actual amounts because of early volatilization in the arc of the spectrometer.

Inadvertent contamination during analysis may result in high determinations of some elements. As examples, trace amounts of metals have been extracted from non-metallic laboratory apparatus (A. T. Myers, personal communication) and from porous silica boiling chips (Southwick, 1951) during wet ashing of bitumens. Glassware cleaned with chromic acid may cause chromium contamination of samples treated in it (A. T. Myers, personal communication). Improper preparation of samples may leave foreign material in the split analyzed. Some crude oils and other native bitumens carry varying amounts of 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) 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 pitch-like pellets, and brassy-colored particles thought to be metallic sulfides or possibly 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 which must be removed before analysis. Crude oil samples stratify during storage; therefore, representative splits cannot be obtained by decanting from the top of the container.

The primary objectives of the investigations described in this report were to determine the uranium contents of crude oils, petroleums, and natural asphalts and to survey the role, if any, that petroleum may play in the origin of uranium deposits. The analytical procedure used is one developed specifically for determination of low-level quantities of uranium with a small probable error.

Combustible material was eliminated by a dry ashing technique. The ash was reduced to constant weight by ignition and, if a sufficient amount was obtained, was divided into two portions. One portion was dissolved in hydrofluoric and nitric acids and uranium determined by the fluorimetric method described by Grimaldi and others (1954). The second portion was analyzed spectrochemically.

Specific gravity determinations were performed on most of the crude oil samples submitted for analysis. The specific gravity was determined after the sample had been filtered to remove suspended matter and washed with distilled water to remove salts.

DISCUSSION

Introduction

Uranium is a minor trace-metal constituent of petroleum and its natural derivatives. This statement is based on analyses of 492 samples of crude oils, natural asphalts, and bitumens extracted from rock asphalts listed in tables V and VI. Previously published reports generally are in agreement with this statement. Unkovskaya (1940) has reported uranium contents for several crude oils of the USSR ranging from 2.7×10^{-7} to 8.2×10^{-6} grams per liter (roughly from about 0.3 to 8.0 parts per billion). Inasmuch as these data have been quoted incorrectly by several writers they are quoted here in table I. The data of columns 1 through 4 are in the form presented by Unkovskaya. In column 5 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 has been misquoted. In column 6 the uranium contents of the crude oils are shown in parts per billion in conformity with other data of this report.

Table I. --Ash and uranium content of some Russian crude oils.

(1) <u>Source</u>	(2) Ash <u>grams/liter</u>	(3) <u>Uranium contents</u> % of ash	(4) <u>grams/liter</u>	(5)* Uranium in oil, <u>grams/ton</u>	(6)* Uranium in oil, <u>ppb</u>
Berekey, ASSR of Dagestan; Well No. 2	0.11	$\left\{ \begin{array}{l} 3.6 \times 10^{-4} \\ 3.9 \times 10^{-4} \end{array} \right.$	4.0×10^{-7} 4.4×10^{-7}	0.0004 0.0004	0.4 0.4
Berekey, ASSR of Dagestan; Well No. 8	0.56 0.28		4.2×10^{-4} $\left\{ \begin{array}{l} 2.3 \times 10^{-4} \\ 3.9 \times 10^{-4} \end{array} \right.$	2.4×10^{-6} 1.1×10^{-6}	0.0026 0.0011
Maili-Su, Kirguises	0.24	$\left\{ \begin{array}{l} 1.3 \times 10^{-3} \\ 3.8 \times 10^{-3} \end{array} \right.$	8.2×10^{-6} .	0.0082	8.2
Schubar-Kudack, Kasakhstan; Well No. 106	0.27 0.20		1.0×10^{-4} 1.4×10^{-4}	2.7×10^{-7} 2.8×10^{-7}	0.0003 0.0003
Bibi-Eibat (Baku Region); Well No. 118	0.37 0.41	2.3×10^{-4} 3.4×10^{-4}	0.85×10^{-6} 1.4×10^{-6}	0.0085 0.0014	8.5 1.4
Naphtalan Baku Region	0.44	7.5×10^{-5}	3.3×10^{-7}	0.0003	0.3

*Note: The figures in columns 5 and 6 are approximations for the reason that the specific gravities of the crude oils are unknown. Columns 1-4 are quoted from Unkovskaya (1940).

Erickson and others (1954), and Breger and Deul (1955) report that the uranium content of crude oils ranges from a fraction of a part per billion to a few thousand parts per billion. Samples studied by these men were obtained from a variety of sources which included commercially productive oil wells, oil seeps at the earth's surface, and oil seeps within uranium mines, thereby accounting for the wide range of uranium contents. Uranium also is a minor trace-metal constituent of some natural asphalts. The quantities of uranium present in these substances generally are very small, and only ashing the bitumens and making quantitative determinations of uranium in the ash by utilizing the fluorescence of uranium fluoride phosphors permits its determination at all.

Crude oils ranging from very light, highly volatile condensates to heavy residual natural tars or asphalts have been analyzed for uranium and other trace metal content, and the analytical data are presented in table V. 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 recovered from the same pools from which many of the samples were obtained for trace metal analysis. Some information concerning oil classifications and specific gravities has been gleaned from miscellaneous geologic reports. Such quoted information is considered to be sufficiently accurate for the following discussion.

It is granted that a sample of crude oil taken from a well head is not representative of the bitumen in the reservoir. It is known that some of the heavier constituents of petroleum tend to cling to the pore walls of some reservoir rocks (Nutting, 1934). Investigations by the U. S. Bureau of Mines (1938) have shown that, "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, Colorado (Cupps and others, 1951), and the Elk Basin field, Wyoming and Montana (Espach and Fry, 1951), it was found that the saturation pressure and solution gas:oil ratio of the original reservoir oil decreased with depth below the gas-oil contact, and the density and viscosity increased with depth below the gas-oil contact. In general, the trace-metal contents of crude oils increase as specific gravities of the oils increase.

Therefore, oil samples collected during different periods of the life of an oil field reasonably can be expected to contain different amounts of trace metals, and the greatest quantities will be present in the heavier oil recovered during late stages of production. Likewise, oil samples obtained from different depths below a gas-oil contact can be expected to contain different quantities of trace metals, and the amounts probably increase with depth below the contact. The relatively high uranium contents of natural tars and of bitumens extracted from rock asphalts as compared to uranium contents of crude oils indicate petroliferous residues left in reservoir rocks probably are more uraniumiferous than recoverable crude oil. The analytical data presented in this report should be considered as representative of commercial crude oils and may not be strictly representative of the total bitumen in petroleum reservoirs.

It is pointed out in the discussion of analytical procedures that the method used to obtain the data for this report was developed specifically for the determination of uranium. Data pertaining to other metals were obtained by a semiquantitative spectrochemical method. Inasmuch as the quantities of each metal cannot be determined with the same accuracy, limitations imposed by the analytical procedure must be kept in mind. Analytical data for constituents other than uranium are presented in tables V and VI, 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 one part per billion 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 carrying uranium either in solution or in suspension, or as an organic complex. The amounts of uranium present 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 lowest uranium contents of any class of crude oils. A sample (No. 235037) of yellow oil recovered from sandstone in the lower part of the Eocene Green River formation at the Flat Mesa field, Duchesne County, Utah, had a specific gravity of 42° API and a uranium content, if any, too low to be determined. Light green oils recovered from the Upper Cretaceous Lance formation in the Powder Wash field (No. 235036) and from the Eocene Wasatch formation in the Hiawatha field (No. 223234), both in Moffat County, Colorado, had specific gravities of 47° API and uranium contents of 0.1 part per billion. 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 part per billion. 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 Late Cretaceous age, in the Rattlesnake field (Nos. 217869 and 217870) and the Table Mesa field (Nos. 96124 and 96126), San Juan County, New Mexico, had specific gravities ranging from 70° to 55° API and uranium contents, if any, 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 part per billion.

These samples are cited as being typical paraffin-base crude oils. No correlation is observed between uranium content, kind of reservoir rock, or age of reservoir rock. It is probable that the amounts of uranium present in these crude oils are too small to permit analyses to be made with enough precision to show whether or not any correlations do exist.

Uranium in asphalt-base crude oils

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

Asphalt-base crude oils carry from a fraction of a part per billion up to a few tens of parts per billion of uranium. Such crude oils from the Tertiary formations of southern California have specific gravities in the range of 20° to 12° API and carry approximately 1 to 3 parts per billion of uranium (table V). A sample of crude oil from a limestone in the Hermosa formation of Pennsylvanian age, Upper Valley, Garfield County, Utah (No. 97491), had a specific gravity of approximately 17° API and 8 parts per billion of uranium. Another sample from the Arbuckle limestone of Cambrian and Ordovician age, Solomon field, Ellis County, Kansas (No. 247608), had a specific gravity of 13.1° API and 31.1 parts per billion of uranium.

There appears to be no correlation between the uranium contents of asphalt-base crude oils and the ages of the reservoir rocks. It is noted that among the heavy asphaltic crude oils listed in table V those from limestone reservoir rocks tend to have the higher 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, as well as some mixed-base crude oils, may be associated with asphaltenes or those constituents that are insoluble in n-pentane.

Breger and Deul (table II) 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. The classifications of these oils were not determined, but it is probable that they belong to the mixed-base group. These oils are abnormal in that they have migrated through or made contact with uranium ore bodies and have picked up anomalously large quantities of uranium. These data are as follows:

Table II.*-- Distribution of uranium in the oils from the Temple Mountain area.

	<u>AEC No. 4</u> <u>mine</u>	<u>AEC No. 5</u> <u>mine</u>	<u>Marsh Bank</u> <u>Canyon mine</u>	<u>AEC No. 8</u> <u>mine</u>
Original oil;				
Uranium, percent **	0.0000438	0.000445	0.0137	0.0310
Asphaltenes, percent	22.7	16.2	22.5	27.8
Asphaltenes;				
Uranium, percent	0.000147	0.0221	0.0386	0.0922
Ash, percent	0.34	0.28	1.83	1.07
Uranium in ash, percent	0.0432	7.89	2.11	8.62
Percent of uranium in original oil				
held by asphaltenes	76.2	80.5	63.4	82.6
Uranium in extracted sandstone, percent				
	0.00020	---	---	---

*Reproduced from Breger, I. A., and Deul, Maurice, The association of uranium with carbonaceous materials on the Colorado Plateau with special reference to the Temple Mountain region: in Garrels, R. M., and others, Geochemistry and mineralogy of Colorado Plateau uranium ores: U. S. Geol. Survey Prof. Paper 320 (in preparation).

**The uranium content of the original oils are 437; 44,500; 137,000; and 310,000 parts per billion, respectively.

A mixed-base crude oil from Masterson J-1 well, sec. 59, block 018, D&P Survey, Moore County, Texas, 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. Geological Survey). Data for the original oil and for each of four fractions are as follows:

Table III.*--Fractionation of a mixed-base crude oil.

<u>Serial no.</u>	<u>Percent ash</u>	<u>Percent U in ash</u>	<u>U in oil, ppb</u>
237425 (Original)	0.087	0.0150	130.5
237430 (Fraction)	0.011	0.0051	5.6
237431 Do.	0.035	0.0102	35.7
237432 Do.	0.105	0.0052	54.6
237433 Do.	0.092	0.0230	211.6

*A. W. Pierce, J. W. Mytton, and G. B. Gott, written communication

These data indicate that uranium, heavy hydrocarbons, and asphaltenes were concentrated at the bottom of the column. Asphaltenes were not separated from the hydrocarbons. Complete data that would permit a material balance to be made were not obtained.

An attempt was made to determine if 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 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 a crude oil. It consists of a complex mixture of heavy organic compounds including hydrocarbons, oxyhydrocarbons, asphaltenes, resins, and others. The uranium and asphalt determinations were made on different samples, some of which were collected several years apart and not from the same wells. Percent asphalt in the crude oil was obtained 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 V. The figures thus obtained are admittedly not precise, but they are thought to be sufficiently accurate to demonstrate any habitual correlation or non-correlation between uranium and asphalts 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, not to the imprecision of the data, but to the variable compositions of crude oils and to the relatively large probable errors inherent in the determination of minute quantities of uranium and to the determination of asphalt by an empirical method.

Uranium in mixed-base crude oils

The uranium contents of mixed-base crude oils range 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 dark shades of green or brown and black 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 of Late Cretaceous age in the Salt Creek field, Natrona County, Wyoming (Nos. 227737 and 227738), had a specific gravity of 38° API and 0.07 part per billion of uranium. Another crude oil from the Weber quartzite of Pennsylvanian age in the Rangely field, Rio Blanco County, Colorado (No. 217875), had a specific gravity of 30° API and 0.5 part per billion of uranium. A crude oil from the Marchand sand of Pennsylvanian age in the Cement field, Caddo County, Oklahoma (No. 86637), had a specific gravity of 19° API and 1.9 parts per billion of uranium. These crude oils are cited to illustrate the trend of uranium content as related to specific gravity. Numerous exceptions to this trend exist. Deviations from a strict correlation of uranium content with specific gravity are attributed to variations in proportions of organic constituents and to migration histories of the crude oils.

No correlation between uranium contents of mixed-base crude oils and age or kind 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 Nowata field, Nowata and Rogers Counties, Oklahoma, were found to contain above-average amounts of uranium. The uranium content of these samples ranged from 2 to 28 parts per billion, and the average was about 12 parts per billion. The specific gravities of these oils as received in the laboratory were about 35° API. These uranium contents are considerably higher than the average content of crude oils of this specific gravity and are higher than those of crude oils recovered elsewhere from the same formation by primary recovery processes. A variety of detergents is used in secondary recovery processes, but in 1957 no reports concerning their ability to leach metals and petroliferous residua from reservoir rocks had been published. Secondary recovery processes undoubtedly remove some heavy residium which clings to pore walls after primary recovery has removed readily available oil. The heavy residium may carry substantial amounts of asphaltenes and heavy hydrocarbons or other 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 bitumen of rock asphalts

The bitumen of asphaltic sandstones and limestones carries uranium in amounts ranging from a few tens of parts per billion up to a few tens of thousands of parts per billion (table VI). The average uranium content of all these bitumens is approximately 1000 parts per billion or about a thousand times greater than that of commercial crude oils. The bitumen of asphaltic sandstones and tuffaceous and phosphatic rocks commonly carries more uranium than that of asphaltic limestones. The uranium contents of the host rocks, determined after the complete removal of the bitumen, are in the normal ranges for sedimentary rocks. (Erickson and others, table VI, 1954).

SIGNIFICANCE OF URANIUM CONTENT OF PETROLIFEROUS SUBSTANCES

The analytical data presented in table V show conclusively that uranium is a minor metallic constituent of petroleum. It is believed that the listed crude oil samples adequately represent the various classifications and the different kinds and ages of reservoir rocks. Because of the large number of oil pools of greatly varying sizes represented by the samples, and the much greater number of unsampled pools for which reserve data were not compiled, it is impossible to derive a precise figure for an average uranium content of all petroleum. A reasonable estimate for the average content appears to be 1 part per billion, or roughly 0.001 gram uranium per short ton of crude oil, or 0.0001 gram uranium per barrel of crude oil.

The analytical data presented in table VI 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 parts per billion, or 1 gram uranium per short ton of bitumen appears to be reasonable.

The uranium contents of crude oils generally range from nil to a few tens of parts per billion. The major factors affecting the uranium concentration appear 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 petroleum having high contents of aromatic constituents and asphaltenes. Condensates and light crude oils of specific gravity 40° API or lighter carry no, or essentially no, uranium. These crude oils which are rather scarce, are predominantly paraffinic. Most of the paraffin-base crude oils fall into the specific gravity range of 40° - 30° API and carry 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 crude oil may play in holding trace amounts of uranium has not been determined. It is possible that the uranium content of petroleum and crude oils is held by minor organic constituents.

Some evidence has been collected suggesting 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 (table II) that pertains to four samples of crude oil that had migrated through the uranium deposits at Temple Mountain, Utah, (table II) show uranium contents of 438; 44,500; 137,000; and 310,000 parts per billion. Erickson and others (1954) reported uranium contents of 32,000; 30,000; 50,000; and 67,000 parts per billion for 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 Lower Triassic Moenkopi formation, and through Triassic sandstones 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 parts per billion (table V).

Erickson and others (1954) also reported uranium contents ranging from 2,100 to 50,000 parts per billion 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, Colorado. Several uranium deposits have been found in both sedimentary and igneous rocks in these localities. It is significant that the only uranium contents exceeding 500 parts per billion have been found in samples of crude oil collected from seeps alongside or very close to uranium deposits.

From data now available, no direct correlation can be made between uranium content of source rocks, reservoir rocks, and crude oils, but in consideration of their generally very low uranium contents, 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 the bitumen of rock asphalts is estimated to be roughly a thousand times greater than that of crude oils. If it is assumed that this bitumen is the residuum of petroleum 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 bitumen. It is probable that the bitumens of rock asphalts retain all of the uranium that was present in the original petroleum. Crude oils do not carry all of this uranium; some remains with petroliferous residua in reservoir rocks. It is not known what percentage of uranium remains with petroliferous residua in reservoir rocks, but even, if it is assumed that the bulk of uranium remains behind as crude oil is extracted, then the major part of the increase in the uranium content of bitumens in some rock asphalts still is unexplained.

The uranium content of the bitumen of rock asphalts varies sharply from one stratum to another within the same deposit, in some places 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 original oil. 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 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 kind of host rock and its uranium content.

The bitumens of the rock asphalts in the Mid-Continent region and in Texas carry, on the average, less uranium than those of rock asphalts in Utah and California (table VI). This condition may be explained in part by the general difference in rock types containing the asphalts. The host rocks of the Mid-Continental and Texas deposits are predominantly Paleozoic marine limestones, dolomites, and sandstones with no appreciable amounts of uranium. The host rocks of the major Utah deposits are lower Tertiary fluviatile, deltaic, and lacustrine sandstones that locally carry substantial amounts of volcanic detritus. The uranium contents of these sandstones are 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 Miocene and Pliocene sandstones that locally contain arkose, volcanic detritus, or phosphatic nodules. The latter materials locally contain a few thousandths of a percent of uranium.

The bitumens of rock asphalts in limestone or dolomite host rocks carry less uranium than those in sandstones. The deposits in Vernon County, Missouri, and in Uvalde County, Texas, are the least uraniferous of all the deposits listed in table VI. This condition is interpreted as a reflection of the uranium contents of marine limestones and dolomites which are among the least uraniferous of all rocks.

The bitumens of rock asphalts in the Tertiary formations of central and southern California carry higher-than-average quantities of uranium (table VI). Source beds of the bitumen are believed to be the argillaceous strata rich in organic matter within the Monterey shale. The bitumen has 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 parts per billion 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 VI. The bitumen in these deposits is unquestionably the residuum of petroleum from the Edna pool, some of which migrated upwards along permeable strata in steeply dipping Monterey shale. Loss of volatile constituents near the surface resulted in the formation of an asphalt seal at the outcrop of the Monterey and in nearly horizontal 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 parts per billion of uranium. The average uranium content in the bitumen of seven samples of the rock asphalt was 21,000 parts per billion (Hail, 1956; also table VI). It appears probable that the bitumen has extracted uranium from the host rock. The uranium contents of the samples, taken from different strata, range from 700 to 70,300 parts per billion. This variation is attributed to availability of uranium in different strata. The Monterey shale, particularly the lower parts, includes phosphatic shale and layers of phosphatic nodules (Woodring and Bramlette, 1950). 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 more-than-average amounts of uranium. It appears that there is ample opportunity for the bitumen to extract uranium from 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 rock asphalt, and the variable distribution may be a reflection of uranium availability in the host rock.

The bitumens in rock asphalt deposits at Vernal, Uintah County, Utah, and Sunnyside, Carbon County, Utah, carry, on the average, about 2,000 parts per billion of uranium. That in the deposit at PR Springs, Uintah County, carries about 1,000 parts per billion of 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. Parts of these formations include large amounts of volcanic detritus, and their uranium contents are, in many places, substantially above average for sandstones. Probable sources of the bitumen are the petroleum in the lower part of the Green River formation and kerogen in the oil shales of the formation. Crude oils obtained from the Green River formation carry less than a part per billion of uranium. Again it is probable that the bitumen acquired much of its uranium from the host rock.

An approximate comparison of the distribution of twenty metals in the ashes of the crude oils and rock asphalt bitumens listed in tables V and VI is shown by the histograms of figure 1. These histograms do not show a precise comparison between the metallic constituents of crude oils and rock asphalts in general, mainly because it was impossible to collect a large number of paired crude oils and their residual rock asphalts, therefore, the available materials were lumped, and secondly, the analytical data, with the exception of uranium determinations, 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 percentages of nickel and vanadium in the ashes of rock asphalt bitumens are less than those in the ashes of crude oils. The percentages 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 carry more uranium than reasonably can be accounted for in petroleums from which they might have been derived. Limited data indicate a possible correlation between uranium content of the bitumen and that of the host rock, and little, if any, correlation with uranium content of possible parent petroleum. It is probable that the bitumens of rock asphalts 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 carried by 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 sediments, or may be derived from any combination of these sources.

Many plants and organisms carry trace amounts of uranium, possibly held in organic complexes which ultimately may become incorporated in petroleum. Results of investigations by Norton (personal communication regarding an unpublished paper "Inorganic constituents of marine plankton" by Daniel R. Norton) indicate the ratio of concentration of uranium in dried marine plankton to its concentration in sea water ranges from 28 to 1600 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. Hoffman (1941) has reported that algae growing in fresh water concentrate uranium and that the algal ash contains up to 9.1×10^{-4} percent uranium (9,100 parts per billion). The fresh water contains 10^{-6} grams uranium per liter (one part per billion). A. P. Pierce (written communication) reports the following concentrations of uranium in the ash of marine algae from the coast of Japan: Porphyra sp., 1,700 parts per billion; Laminaria sp., 800 parts per billion; Undularia sp., 3,000 parts per billion.

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 parts per billion 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 carry less than one part per million of uranium. Limestones and dolomites as a group are among the least uraniumiferous of all the sediments, but their uranium probably is the most readily extracted in nature. Sandstones, on the average, carry a few parts per million of uranium, a large portion of which may not be readily extractable because it may be a constituent of heavy refractory minerals 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 petroleum may make 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 than the petroleum itself. Those petroleum 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.

MANNER IN WHICH URANIUM IS HELD IN PETROLEUMS AND OTHER BITUMENS

The problem of how uranium is held in petroleum and other bitumens has not been fully investigated. No specific organo-uranium complexes have been identified in petroleum; therefore, it cannot be stated positively that uranium is held in this manner. Work by I. A. Breger and M. Deul (in preparation) and by A. W. Pierce, J. W. Mytton, and G. B. Gott (written communication) has shown that a major portion of 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 V). Many, if not all, crude oils and liquid asphalts carry finely divided mineral matter in suspension. Such matter ranges down to colloidal particles and commonly is very difficult to remove completely either by centrifuging or filtering. This material may include clays and other finely divided detritus picked up from rocks through which the oil has moved or from the reservoir rock; or 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; Stieff and Stern, 1952; Rosenzweig and others, 1952; Liebenberg, 1955; A. W. Pierce, J. W. Mytton, and G. B. Gott, written communication), but it is not known whether the uranium originally existed in the carbonaceous substance 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 resulting in the formation of uraninite. Hydrogen sulfide is present in most petroleum reservoirs, and it can be expected 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.

It is possible that some, if not all, uranium in petroleums and asphalts 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 uranium minerals 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 is a problem still to be solved.

HYPOTHETICAL ROLE OF PETROLEUM IN THE ORIGIN OF URANIUM
DEPOSITS IN SEDIMENTARY ROCKS

The common occurrence of uranium and petroleum deposits 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 carbonaceous substances, have led some geologists and geochemists to propose that uranium minerals may be deposited from oil field waters. Some of these hypotheses have received considerable publicity. Tomkejeff (1946) has supported a direct role for petroleum 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 crude oil. Many geologists engaged in the search for and development of uranium deposits apparently have accepted these ideas as facts rather than hypotheses as intended 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 sandstones 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 the same sandstones in the Cisco, Seiber, and Crescent Junction fields. Oil seeps have developed 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, California, and Cement, Oklahoma. 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 are substantially more uraniferous than those from any other region unless variations of one or two parts per billion caused by predominance of paraffinic, aromatic, or asphaltic constituents are considered significant. If petroleum plays 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 within mines or issuing from mineralized ground, uraniferous crude oils have not been found. The predominantly paraffin-base crude oils produced from Pennsylvanian and Mississippian formations in the Colorado Plateau area carry small fractions of a part per billion of uranium. Mixed-base crude oils produced from younger formation in the same area appear, on the average, to carry no more uranium than do the paraffin-base oils although one sample from the Boundary Butte field, San Juan County, Utah, was found to contain 4 parts per billion and one sample from the Crescent Junction field, Grand County, Utah, 3 parts per billion. Paraffin-base crude oils produced from Cretaceous and Tertiary formations of the Uinta Basin, Utah, and northwestern Colorado, carry fractions of a part per billion of uranium. Two samples of weathered asphaltic crude oils recovered from the upper part of the Permian Kaitab limestone at John's Valley and from a limestone in the Hermosa formation of Pennsylvanian age at Upper Valley, both in Garfield County, Utah, carried 39 and 8 parts per billion uranium respectively. These two crude oils appeared to consist of asphaltic residues which 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 carry greater quantities of uranium, possibly averaging about two parts per billion, probably because of their greater content of asphaltenes and aromatic constituents. No significant uranium deposits have yet been found in this area.

Crude oils from Wyoming and Montana, where substantial uranium deposits have been found, range from light paraffinic to heavy asphaltic types and generally carry about one part per billion of uranium.

Crude oils from the Riverton Dome, Beaver Creek, and Sand Draw fields, which are situated from 6 to 25 miles from uranium mines in the Gas Hills and Conant Creek districts of Wyoming do not contain anomalous quantities of uranium. Likewise, crude oils from the Crooks Gap, Sheep Creek, and Happy Springs fields situated within 6 miles of the Crooks Gap, Wyoming, uranium district do not contain anomalous quantities of uranium. The crude oils from all these fields, except Sheep Creek, are predominantly paraffin- or light mixed-base and are light green to brownish green in color. The crude oils are produced from several stratigraphic units ranging in age from Pennsylvanian to Cretaceous. The highest uranium concentration found was 2.7 parts per billion in a sample of black, asphaltic oil from the Sheep Creek field.

In the Frannie and Sage Creek fields, located in the northern part of the Big Horn Basin, Wyoming, crude oils are produced from the Mississippian Madison limestone and the Pennsylvanian Tensleep sand. These fields are situated approximately six miles from uranium deposits in the Madison limestone on Big Pryor Mountain. Crude oil from the Tensleep sand is mixed-base and contains less than 1 part per billion of uranium. Crude oil from the Madison limestone is a heavy, black, asphaltic type. A sample from the Sage Creek field contained less than 2 parts per billion of uranium whereas another sample from the Frannie field contained 476 parts per million. 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 parts per billion) was found in a sample of crude oil (No. 86636) from the Cement field, Caddo County, Oklahoma. This oil was produced from the Marchand sand at a depth of approximately 7,000 feet. It was a heavy, black asphaltic oil. Within the oil field, small, non-commercial deposits of uranium have been found within a few feet of the surface of the ground. No connection has been found between the petroleum at depth and the uranium near the surface.

On a regional basis no correlation can be established 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, as far as uranium contents are concerned. The occasional anomalous uranium concentrations found in crude oils appear to be strictly local conditions.

Many thousands of gamma-ray logs have been made of oil wells. There is no instance known to the author where a gamma-ray log indicates anomalous radioactivity that can be attributed to a concentration of uranium and its daughter products in petroleum. Likewise, no instance of a uraniferous deposit existing 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 petroleum is subsequently released under conditions that would permit substantial deposits to be formed in sedimentary rocks. It appears that uranium is tenaciously held and is released only when the petroleum is destroyed; such action may result from oxidation, nuclear irradiation, or leaching by certain acid or alkaline solutions; also, at the surface of the earth petroleum may be destroyed by certain bacteria, yeasts, and molds (ZoBell, 1946). Asphaltenes are among the most resistant major constituents of petroleum 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 monoclinical 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 Jurassic Morrison formation and the Triassic Chinle formation, 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 Permian Kaibab limestone, Pennsylvanian Paradox member of the Hermosa formation, 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 and petroleum deposits exist in the same sedimentary formations there is little likelihood that petroleum ever acts as an ore-forming fluid for uranium. A simple computation of the amounts 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 U contains 250 tons of uranium. As a first estimate it is assumed that a hypothetical petroleum ore-forming fluid contains one part per billion 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 1,500,000,000,000 barrels of petroleum is required. This minimum amount of petroleum required for the deposition of one rather small ore body is approximately fifty times greater than the total reserves of the United States. Because it is probable that crude oil carries somewhat less uranium than petroleum in the ground, the problem is recomputed on the assumption that the bitumen of rock asphalts acts as an ore-forming fluid. It is assumed that this bitumen is a petroliferous residue containing all of the metals that was present in the original petroleum. The uranium content of the bitumen is taken to be one part per million, 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 1,500,000,000 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 passage 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 is unlikely.

Because no evidence has been uncovered 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 SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 3, T. 32 N., R. 9 $\frac{1}{2}$ W., Fremont County, Wyoming. A pit approximately 250 feet long, 175 feet wide, and 30 feet deep has been dug in sandstones of the lower part of the Eocene White River formation (Van Houten, 1954), and a small amount of uranium ore has been recovered during the operation. The sandstone strata range from about an inch up to about five feet in thickness. Except for varying amounts of clay, each stratum consists of fairly well-sorted material that may be anywhere from silt size to coarse sand. Some strata are thoroughly saturated with asphaltic bitumen; other strata are lightly stained with the bitumen or contain it in a spotty distribution; some strata appear to contain no bitumen at all. It is evident that this bitumen is a petroliferous residue. Several oil fields are located within distances of 5 to 14 miles to the west and northwest. It is probable that petroleum has ascended along some of the faults of the area and has penetrated those near-surface strata that have favorable permeabilities. Most of the uranium is present 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 of bitumens of rock asphalts in general. One sample (No. 244376), taken from a bitumen-saturated layer contained 7.78 percent oil, of which the ash was 0.035 percent, and the uranium content of the oil ash was 5.72 percent, this being 20 parts per million of uranium (0.002 percent) in the bitumen. After extraction of the bitumen the sandstone residue contained 0.004 percent

uranium (40 parts per million). 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 bituminous sample was 0.007 percent (70 parts per million), and that of the nonbituminous sample was 0.10 percent (1,000 parts per million). The nonbituminous ore-bearing strata were not sampled, but it would be possible to select samples containing several tens of a percent of uranium. The rock asphalt is abnormally uraniferous, but it contains considerably less uranium than adjacent nonbituminous sandstone. The sequence of events appears 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 finally, oxidation of the primary uranium mineral. Uraniferous solutions undoubtedly penetrated the bituminous sandstone during the mineralization and oxidation 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 exist side by side.

It is possible that petroleum may play an indirect role in the formation of some uranium deposits. Petroleum carries 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 petroleum and attain significant concentrations under reducing conditions in the edge waters surrounding petroleum reservoirs, an environment may be established in which uranium could be precipitated. Uranium would have to be introduced by ground waters or hydrothermal solutions, and precipitation might be expected along interfaces of the two fluids. Many petroleum carries hydrogen sulfide, commonly in immense quantities. Inasmuch as hydrogen sulfide is highly soluble in water, the edge waters surrounding petroleum reservoirs become sulfurous, and reducing environments are established. It is known that hydrogen sulfide is an effective reducing agent and precipitant of uranium (Gruner, 1956). If uraniumiferous 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 present in edge waters are effective precipitants for uranium, it is reasonable to expect to find uranium deposits around the flanks of petroleum-bearing structures.

If petroleum plays 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 indicate the presence of a uranium deposit. The only parts of the United States where major deposits of both uranium and petroleum are known to exist are the Rocky Mountain region, the Colorado Plateau region, and the southeast Texas Coastal Plain, and in these areas no connection between the two materials 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 oil-field edge waters whereas uraniferous solutions have been lacking in some other petroliferous regions.

The total uranium contained in the petroleum of the United States appears to be very small compared to that present in mineral deposits in sedimentary rocks. If the average uranium content of crude oil is considered to be one part per billion, then the total uranium present in the reserves of the United States (30 billion barrels at end of 1956; World Oil, 1957) amounts to less than 5 tons. It is possible that petroliferous residua 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 to be made. 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 amount originally present 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 redeposited to form deposits such as exist in 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 some uranium deposits have been deposited from petroliferous fluids. Petroleum carry 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 position to another. In general it can be stated that petroleum from one region are no more uraniumiferous 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 petroleum, that is to a preponderance of paraffinic, naphthenic, or aromatic constituents, and to the asphaltene contents. The amount of uranium carried by petroleum appears to be small compared to that present in most common sedimentary rocks. The bulk of uranium carried by petroleum 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 uraniumiferous ground waters or hydrothermal solutions. It is only in the uranium province of the Rocky Mountain and Colorado Plateau regions that deposits are known to exist that might have been formed in this manner, and even here the relationship is hypothetical.

URANIFEROUS CARBONACEOUS SUBSTANCES CALLED "ASPHALTITE"

It has become a rather common practice to apply the term "asphaltite" to a large variety of native black organic substances that cannot readily be identified by a specific name. Some of these substances form commercially valuable uranium ores as in the San Rafael Swell area, Grand and Emery Counties, Utah. Others such as the nodules and pellets in the Azotea tongue of the Carlsbad limestone (formerly called Seven Rivers member of Chalk Bluff formation) of Permian age in southeastern New Mexico may carry substantial amounts of uranium but are too sparsely distributed in the host rocks to be utilized as uranium ores. Many of these uraniferous organic substances are called "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. The origins of these substances 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. It is probable that different deposits of "uraniferous asphaltite" 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.

PETROLEUM, ROCK ASPHALT, AND NATURAL BITUMENS AS RAW
MATERIALS FOR URANIUM

In common with most other naturally occurring substances, petroleum and its natural derivatives have been examined to determine their potential as possible sources of uranium. Although it is generally conceded that uranium is a minor trace element in petroleum and its natural derivatives, and that the amount of uranium that might be recovered from these materials is small, some over-optimistic estimates have been made concerning their potential. Any uranium recovered from petroleum, rock asphalt, and natural bitumens would have to be a byproduct extracted from refinery residues or from combustion residues.

The latest published estimates of the crude oil reserves of the United States indicate the amount to be 30 billion barrels (World Oil, 1957). On the basis of an average uranium content of one part per billion the total content of this crude oil is indicated to be less than 5 tons. If it is assumed that secondary recovery processes and improved methods of extraction ultimately may result in twice as much crude oil being produced, a possible potential of 10 to 15 tons of uranium is indicated. A somewhat higher uranium content in secondarily recovered crude oil is included in the latter figure.

It is known that a tarry or 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 carry greater percentages of trace metals than the recoverable crude oil. No data are available to indicate what the metallic content might be, but several or even a few tens of parts per billion uranium are possible. How this uranium could be recovered poses a difficult problem.

The bituminous constituent of rock asphalt carries, 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 bitumen, averaging about one part per million, rock asphalts do not present 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, California carry the highest concentrations of uranium of all the deposits sampled (table VI). 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 seven 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 parts per million 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 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 uranium content 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 parts per million uranium. These figures indicate there are approximately 220 tons of uranium in the deposit. About 630 tons of rock would have to be processed to obtain a 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 1,600,000,000 cubic yards of which one-half is assumed to contain at least 9 percent of bitumen by weight (Holmes and others, 1948). Analyses of eleven 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 parts per million 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, Texas. Total reserves of minable rock are 340,000,000 tons (Gorman and Robeck, 1945). Analyses of eleven 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 part per million 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 tabular form in table IV.

Table IV.--Bitumen and uranium contents of some rock asphalt deposits. ^{1/}

	(1)	(2)	Sunnyside,	Uvalde County,
	<u>Edna, Calif.</u>	<u>Edna, Calif.</u>	<u>Utah</u>	<u>Tex.</u>
Tons rock asphalt	282,880,000	282,880,000	1,416,000,000	340,000,000
Percent bitumen	11.0	11.0	9.0	8.5
Tons bitumen	31,116,800	31,116,800	127,520,000	28,900,000
Percent ash in bitumen	0.55	0.6	1.10	0.4
Tons ash in bitumen	174,000	183,600	1,402,720	124,270
Percent uranium in ash	0.376	0.122	0.021	0.002
Tons uranium in deposit	650	220	295	2.5
Uranium in bitumen, ppm	21	7	2	0.08
Tons rock/pound of uranium	215	630	2,400	68,500

(1) Average of 7 samples

(2) Average of 6 samples

^{1/} Source: Gorman and Robeck, 1945
Hail and others, 1956
Holmes and others, 1948
Page and others, 1944

There may be several hundred tons of uranium carried by bitumens in the rock asphalt deposits of the United States. This uranium is present in very low concentrations in the bitumen, only a few parts per million at best, and the bitumen in turn is 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, rock asphalts appear to be impractical source materials for uranium even if it should be recovered as a byproduct of bitumen production.

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