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Uranium in Carbonate Rocks

GEOLOGICAL SURVEY PROFESSIONAL PAPER 474-A

Prepared on behalf of the
U.S. Atomic Energy Commission

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Bell—URANIUM IN CARBONATE ROCKS—Geological Survey Professional Paper 474-A

Uranium in Carbonate Rocks

By KENNETH G. BELL

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

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A study of ore deposition and occurrence of uranium in carbonate environments, including analyses of 70 samples

U.S. DEPARTMENT OF THE INTERIOR
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URANIUM IN CARBONATE ROCKS

By Kenneth G. Bell

ABSTRACT

Carbonate rocks generally have been considered to be among the least uraniferous substances of the earth's crust. This conclusion has been based on analyses of a few samples. An investigation of the association of uranium with several types of carbonate rocks indicates that some revisions of the previous conclusion are necessary. Rocks that are composed almost wholly of carbonate minerals and that include only minute traces of other constituents generally contain about 0.0001 percent (1 gram per ton), or less, of syngenetically deposited uranium; they are among the least uraniferous rocks. The impure carbonate rocks, which form gradational series with many other kinds of sediments, may contain readily measurable quantities of syngenetically deposited uranium that is associated with the noncarbonate constituents. The quantities of such uranium may range from about 0.000X to 0.00X percent and reach a maximum of a few tens of grams per ton. The phosphatic constituent in some appreciably uraniferous limestones and dolomites is thought to hold the uranium; detrital constituents and possibly organic matter may hold uranium in other carbonate rocks. Uranium is deposited epigenetically in carbonate rocks under a variety of circumstances, and some of these deposits provide rich ores. Epigenetically deposited uranium minerals in carbonate host rocks are found in hydrothermal veins, in efflorescent deposits, in cavities of karst terrains, and as peneconcordant deposits in stratified carbonate rocks. The geochemical conditions that cause epigenetic deposition of uranium in carbonate rock environments, with the exception of those causing some efflorescent deposits, have not been determined.

INTRODUCTION

Limestones, dolomites, and other sedimentary carbonate rocks generally have been considered to be among the least uraniferous of all the rocks of the earth's crust, containing from almost none to about 4 parts per million uranium. This conclusion has been based on theoretical considerations and a few analyses of limestones and dolomites predominantly of marine origin. Recent investigations of carbonate rocks, both in the field and in the laboratory, have shown that, whereas most rocks that have carbonate minerals as major primary constituents have very little or possibly no uranium, nevertheless certain classes of these rocks may contain above-average quantities of uranium. The earlier conclusion has been revised, and some qualifying amendments have been made. The investigations described below have not been accomplished in sufficient detail to permit complete recognition of all the geochemical relations involved, but some valid relationships have been established.

OBJECTIVES OF THE INVESTIGATION

The principal objectives of this investigation were to determine (1) to what extent uranium is deposited syngenetically with carbonate sediments and what geochemical environments are essential for the inclusion or uraniferous substances with carbonate sediments and (2) some of the conditions under which uranium may be deposited epigenetically in carbonate rocks. Information leading toward attainment of these objectives was acquired by field examination of many carbonate rocks and by chemical analysis of a representative collection of these rocks and of carbonate source materials.

PREVIOUS INVESTIGATIONS

It was discovered during early investigations of the radioactivity of rocks and other terrestrial materials that carbonate rocks in general have very low levels of radioactivity. Consequently, little study has been made of radioactive constituents in carbonate rocks as compared with the amount of study of these constituents in other terrestrial materials. Because the uranium contents of many carbonate rocks are close to, or below, the threshold of analytical chemical procedures, many determinations by such methods are inconclusive. The results of some investigations have been reported in terms of radium contents, others as equivalent uranium contents—that is, actual uranium determinations were not accomplished.

There are few published data pertaining to the uranium contents of carbonate rocks. These data are not accompanied by detailed descriptions or even descriptions of the principal characteristics of the rocks that were tested. Evans and Goodman (1941, table 9) have reported uranium contents ranging from 0.30×10^{-6} to 2.6×10^{-6} g per g of rock (0.00003 to 0.00026 percent) for five samples of limestones from four localities. Lahner (1939) reported uranium contents ranging from 0.12×10^{-7} to 10.1×10^{-7} g per g of rock (0.000012 to 0.0001 percent) for 12 carbonate rocks of various kinds; the sample materials were taken from museum specimens. Bell (1956, p. 521) reported uranium contents ranging from 0.7 to 3.8 ppm (parts per million) (0.00007 to 0.00038 percent) for 11 typical marine limestones and dolomites. Baronov and others (Баронов, Ронов, и Кунашова, 1956) determined the uranium contents of 128 composites of carbonate rocks made up from 5,475 samples collected from the Russian platform; each composite represented a tier, division, or system of the stratigraphic scale; ages ranged from the late Precambrian to Quaternary. The uranium contents of the composites ranged from 1.2 to 5.4 ppm. Distinguishing characteristics of the carbonate rocks represented in each composite are not given. Inasmuch as the range of values is rather high it is suspected that a substantial number of more or less phosphatic carbonate rocks were represented in the sample material. (See p. A5.) Some determinations of uranium contents of carbonate rocks containing epigenetically deposited minerals have been published, but inasmuch as the investigations dealt with uranium ores or potential ores of variable grade, the analytical data are not considered to be characteristic of carbonate rocks as a group.

This rather meager collection of uranium determinations made on carbonate rocks indicates that, in general, uranium contents range from small fractions of a part per million to a few parts per million (probably in the range of $<0.0000x$ to 0.000x percent). Probably only syngenetically deposited uranium was present in the samples analyzed, but this condition cannot be taken for granted. The reports do not indicate whether variations in uranium contents can be attributed to depositional environments or to the kinds and amounts of noncarbonate constituents in these rocks.

THEORETICAL CONSIDERATIONS

The terms "limestone" and "dolomite" by definition designate sedimentary rocks composed predominantly of the carbonate minerals calcite and dolomite. The terms commonly are used to designate rocks containing roughly 50 percent or more by volume of carbonate minerals, and sometimes they are used questionably to designate rocks of which carbonate minerals are important constituents but constitute less than 50 percent of the volume. The noncarbonate constituents of different limestones and dolomites may consist of clastic detritus, clay minerals, iron oxides, manganese oxides, calcium phosphate minerals, calcium sulfate minerals, organic detritus, bitumens, various other organic derivatives of former plant and animal life, and many other substances. The carbonate-rich rocks therefore are parts of gradational series of which the end members are pure limestone or dolomite on the one hand and shales, siltstones, saline evaporites, and different varieties of organic-rich sedimentary rocks on the other hand.

The sedimentary carbonate rocks are deposited in aqueous environments. The chemical conditions may be either oxidizing or reducing, but a much larger volume of carbonate sediments probably is deposited under oxidizing or slightly reducing conditions than under strong reducing conditions. The oxidation-reduction potential of the medium from which carbonate sediments are deposited has no bearing upon the deposition of alkaline-earth carbonates that constitute the bulk of the carbonate rocks, but it does play a major role in the kind and amount of syngenetically deposited chemical impurities.

Carbonate sediments are formed by biogenic and chemical processes. Some reef limestones and coquinas are formed almost entirely of skeletal parts and shells of organisms; other limestones are composed almost wholly of precipitated calcium carbonate; many carbonate rocks are composed of a mixture of bioclastic and chemically precipitated components. The noncarbonate constituents in carbonate rocks may be deposited by any one of the sedimentary processes.

It has been known for a long time that uranium in the oxidized, hexavalent or uranyl, state is highly soluble in the presence of substantial concentrations of carbonate or bicarbonate ions, and this property is utilized by analytical chemists in making quantitative separations of uranium from several other metallic elements (Fresenius and Hintz, 1895; Rodden and Warf, 1950, p. 16, 31). It follows that in natural environments where the carbonate or bicarbonate ion concentration is high with respect to that of the uranyl ion, uranium should not be precipitated along with carbonate sediments. Nearly pure carbonate rocks that were deposited in oxidizing environments cannot be expected to contain appreciable quantities of syngenetically deposited uranium.

Uranium in the tetravalent, or uranous, state is thought to form a soluble complex with the carbonate ion. This conclusion is based on the fact that uraninites, or pitchblendes, which contain a mixture of hexavalent and tetravalent uranium, will dissolve completely in some carbonate solutions, and uranium oxide (presumably uraninite) does not precipitate from all uraniferous carbonate solutions that are subjected to the reducing action of hydrogen sulfide. The behavior of the uranous ion in the presence of high concentrations of the bicarbonate and carbonate ions apparently has not been fully investigated.

Theoretical considerations indicate that uranium should not be deposited syngenetically with nearly pure carbonate rocks laid down in reducing environments. For example, a nearly pure limestone, even though characterized by a fetid odor due to hydrogen sulfide or sulfurous organic substances, normally cannot be expected to be appreciably uraniferous.

Inasmuch as uranium has a strong tendency to remain in solution in the presence of high carbonate-ion concentrations and is not coprecipitated with carbonate minerals, that uranium which is a syngenetic constituent of carbonate rocks must be intimately associated with the impurities or noncarbonate constituents of these rocks. Common constituents, or impurities, that occur in various carbonate rocks, and which are capable of holding small amounts of uranium, are certain heavy mineral resistates, sedimentary or marine apatite, fluorite, some kinds of organic matter, and possibly other less-abundant substances.

Heavy mineral resistates may be present in impure carbonate rocks, especially those that contain clastic sediments. Zircon, sphene, igneous apatite, monazite, and other resistates commonly contain small amounts of uranium. Although these minerals contribute to the total uranium content of the host rock, the amount of the contribution generally is very small.

Marine apatite is an important constituent of many marine limestones and dolomites, in fact, a completely gradational series exists between nearly pure carbonate rocks at one end and nearly pure phosphate rocks at the other end. The uranium content of primary marine apatite characteristically ranges from 0.005 to 0.02 percent; phosphatic sediments that have been reworked in marine environments may have uranium contents ranging from 0.005 to 0.1 percent; it is thought that this uranium substitutes for calcium in the apatite structure, and it has been shown that uranium can be secondarily leached from or introduced into the apatite structure (Altschuler and others, 1958). If it is assumed that all the phosphate content of carbonate rocks is in the form of apatite, then the quantity of this mineral commonly is more than adequate to account for all the uranium. Some carbonate rocks contain substantial amounts of phosphatic fossils that hold small quantities of uranium. This uranium probably was introduced into the shells and skeletons after death of the organisms and is not strictly syngenetic, but for the purpose of this discussion it is considered to be so.

Some fluorite, particularly the purple varieties, may contain small quantities of uranium. Most fluorite in sedimentary carbonate rocks probably is an epigenetic constituent, but small grains of this mineral are found in some limestones that are not metamorphosed and show no evidence of alteration or introduction of material by hydrothermal or other solutions.

Organic matter is an important constituent of many sedimentary carbonate rocks. Again there are gradational series ranging from nearly pure carbonate rocks to nearly pure organic rocks. The hexavalent uranyl ion and the tetravalent uranous ion are known to form complexes with many organic substances, and several such combinations are utilized in analytical chemistry (Rodden and Warf, 1950, p. 11, 13). Undoubtedly many other organo-uranium combinations exist that have not been fully investigated or that are unrecognized. A part of the syngenetic uranium in some carbonate rocks probably is attached to organic matter. Inasmuch as the precise composition and identity of organic matter in sedimentary rocks are little-investigated subjects, only general statements can be made about the association of uranium with organic matter. Some forms of humic matter have a high capacity for taking up uranium (Szalay, 1957; Manskaya and others (Манская, Дроздова, и Емельянова, 1956); Vine and others, 1958), but the precise composition and character of the organo-uranium combination are unknown. Many organic acids, some of which occur in nature in small or minute quantities, can form uranium salts. Hydrocarbons that are major constitutents of petroleums, asphalts, and most native bitumens apparently have no capacity for taking up uranium (Bell, 1960b), but some of the organic acids that are very minor constituents of petroliferous substances may readily form uranium salts. Some organic-rich carbonate rocks contain above-average quantities of uranium.

This discussion of theoretical considerations so far has dealt primarily with syngenetic deposition of uranium in carbonate rocks. Epigenetic deposition of uranium in carbonate rocks is known to occur under a variety of widely differing conditions, but no complete explanation for the origin of some epigenetic uranium deposits in carbonate rocks can be provided at this time.

Solutions that transport uranium are likely to be either appreciably acid or alkaline rather than neutral. Uraniferous acid solutions can be of hydrothermal origin or can form from ground water in the zone of oxidation where sulfide minerals become oxidized. Acid solutions that flow through substantial amounts of carbonate rocks become neutralized, or they even may become slightly alkaline. Some uranium may be deposited as the pH changes. Alkaline carbonate-rich solutions readily transport uranium, and it is evident that the minerals of many uraniferous hydrothermal veins were deposited from such solutions. Some of these veins are found in carbonate rocks. The conditions that cause deposition of both uranium and carbonate minerals are not fully understood. Very few paragenetic studies of such deposits have been made; additional thorough studies are needed to provide more information on the order of deposition and the influence of wallrock and to furnish clues concerning the precise chemical and physical conditions that existed at time of deposition.

The conditions that cause deposition of uranium in hydrothermal deposits undoubtedly are physically and chemically complex. It is possible to write chemical equations, based on experiments made at room temperature and approximately atmospheric pressure, that might represent reactions occurring during the depositional processes, but one does not have complete assurance that these reactions always occur in the range of physical and chemical environments that exist during genesis of hydrothermal deposits. The effects of temperature and pressure on the solubility relations between various ions in the ore-forming fluids, and on phase relations of the solid and dissolved portions of the reacting constituents are virtually unknown to the geologist. The same statement can be made concerning most epigenetic deposition of uranium in sedimentary rocks under conditions other than hydrothermal.

SELECTION OF SAMPLE MATERIAL

During this investigation, 70 samples of sedimentary carbonate rocks and carbonate source materials were collected and analyzed to determine their contents of uranium and principal constituents. In addition, eight samples obtained from well cuttings were checked for uranium contents only; the small size of these samples precluded determinations of other constituents.

Most of the samples that were collected and analyzed represent carbonate rocks in which the uranium contents are probably wholly syngenetic. These rocks contain very small quantities of uranium and no visible or identifiable uranium-bearing minerals except possibly some clastic resistates and sedimentary marine apatite. A few carbonate rocks containing uranium minerals of undoubted epigenetic origin were sampled primarily for determination of their phosphate and fluoride contents; samples of such rocks having wide ranges of uranium contents can be selected at will because the epigenetic minerals usually are readily visible and identifiable, and it was thought that the possible presence of fluorides and phosphates that might have been associated with the uranium mineralization would be of greater interest.

The number of samples analyzed was limited by the available capacity of the laboratory for this work. The sampling seems very sparse in relation to the almost infinite variety of carbonate rocks. An attempt was made to get a wide coverage of carbonate rocks of varying compositions that were deposited in different environments. The collection includes marine and nonmarine rocks, calcitic and magnesian limestones, dolomites, marls, marlstones, fetid and nonfetid rocks, calcareous shells, and predominantly carbonate rocks having as impurities substantial amounts of phosphate minerals, clastic detritus, clays, iron oxides, and organic matter.

The rock samples were taken from individual beds or from vertical sections a few inches thick because the character and composition of sedimentary carbonate rocks commonly change abruptly within short vertical distances, even from stratum to stratum within some thinly bedded series. The purpose of this selectivity was to limit each sample, insofar as practicable, to a unit representing a single depositional environment. About 50 pounds of rock was taken from most of the units sampled; the original sample was broken into small fragments and by successive quartering was reduced to approximately a 2-pound sample. The latter was pulverized in a grinder equipped with ceramic plates and then was further reduced by quartering to about 100 grams of material which was sent to the laboratory for analysis.

ANALYTICAL PROCEDURES

All the sample material collected during this investigation was analyzed in the Geological Survey Laboratory at Denver, Colo. The constituents that were determined are: uranium, acid-insoluble matter, calcium as calcium oxide, magnesium as magnesium oxide, total R_2O_3, iron as ferric oxide, phosphorous as phosphoric pentoxide, and fluorine. The results of the analyses are tabulated in table 2.

Total uranium in the samples was determined by the ethyl acetate extraction-fluorimetric method. Details of the procedure are described by Grimaldi and others (1954).

Acid-insoluble matter was determined as follows: To 2 g of the sample was added 50 ml of 1:1 hydrochloric acid, and the mixture was heated to a boil on a hot plate. The sample was then digested 1 hour on a steam bath, 50 ml of hot water was added, and the sample was filtered through tared sintered glass crucibles and washed with 1-percent hydrochloric acid. The crucibles and insoluble matter were dried at 105°C and weighed.

Acid-soluble calcium oxide and magnesium oxide were determined by titration with versene (Shapiro and Brannock, 1956).

R_2O_3 was determined by ammonium hydroxide precipitation from an aqua regia solution.

Total iron was determined colorimetrically with *o*-phenanthroline (Cuttitta, 1952).

Total phosphate was determined by the volumetric method of the Association of Official Agricultural Chemists (1950, p. 8–10).

Total fluorine was determined colorimetrically by the method of Icken and Blank (1953) following distillation by the method of Willard and Winter (1933).

An approximate mineral composition was calculated for all samples in order to make a rough check of material balances and to assure that no important constituent was overlooked. All phosphate was assumed to be in the form of apatite, $(CaF)Ca_4(PO_4)_3$; all fluorine not accounted for in apatite was assumed to be in fluorite (CaF_2); all calcium in excess of that assumed to be in apatite and fluorite was assumed to be in calcium carbonate ($CaCO_3$); all magnesium was considered to be in magnesium carbonate ($MgCO_3$); uranium was assumed to be in the form of the oxide, U_3O_8; the percentages of insoluble matter and R_2O_3 were used as determined. The summation of these assumed constituents is 100 ± 3 percent for most of the samples. Deficiencies greater than 3 percent for a few samples reasonably can be accounted for by constituents such as manganese oxides or carbonate, sulfide minerals, organic matter, silicate minerals, and other minor constituents known to be in the rocks.

A petrographic examination of the rocks was made for the purpose of observing textural features and identifying the principal noncarbonate constituents. The observations are included in table 2.

CLASSIFICATION OF CARBONATE ROCKS

The carbonate rocks and source materials sampled and analyzed during this investigation are divided into 18 categories. The division is based in part upon well-defined characteristics and in part is arbitrary. This classification, used in the discussion and in presenting analytical data in table 2, is simply one possible method of classifying these rocks; obviously many classification schemes can be devised.

The principal point of interest in this discussion is the uranium content of carbonate rocks; therefore, they are divided into two major categories, those containing only syngenetically deposited uranium, and those containing epigenetically deposited uranium. Further subdivisions are based on combinations of the following features: (1) marine versus nonmarine origin, (2) unmetamorphosed versus metamorphosed rocks, (3) principal carbonate constituent, that is, calcitic limestones composed predominantly of calcite and containing less than 4 percent magnesium carbonate, magnesian limestones containing more than 4 percent and less than 30 percent magnesium carbonate, and dolomite which is arbitrarily considered to include all the rocks containing more than 30 percent magnesium carbonate, and (4) fetid versus nonfetid rocks. Carbonate-bearing concretions, tufas, and shells of organisms are placed in separate categories. The separation of fetid from nonfetid rocks was made because some of the fetid rocks may have been deposited in reducing environments that commonly are thought to be conducive to the precipitation of uranium.

SYNGENETIC URANIUM IN CARBONATE ROCKS

Minute quantities of uranium can be deposited syngenetically with carbonate sediments by at least four mechanisms:

1. Uranium can be a minor constituent of some substances that may be coprecipitated with carbonate sediments; an example is calcium fluophosphate, or marine apatite, in which a small quantity of uranium can substitute for calcium.
2. Uranium may be adsorbed on clay, gelatinous silica, and some forms of organic matter that are deposited simultaneously with the carbonate sediments.
3. Uranium may become incorporated in the sediments shortly after deposition and, while the sediments still are in contact with the aqueous medium from which deposition occurred, by base exchange; an example of this mechanism is the increase of uranium in marine apatites that remain in contact with ocean water (Altschuler and others, 1958).
4. Uranium can be a minor constituent of some heavy mineral resistates that are present in clastic detritus deposited with some impure carbonate sediments.

It is essential to notice that uranium deposited by these mechanisms is contained in impurities adventitiously deposited with carbonate sediments. No primary uranium carbonate minerals are known to be deposited syngenetically with carbonate sediments.

The analytical data presented in table 2 indicate that the most characteristic feature of carbonate rocks containing only syngenetic uranium is the generally very low content of this element, which in most of the samples ranges from less than 1 ppm (<0.0001 percent) to about 4 ppm (0.0004 percent). Among 51 samples of carbonate rocks in which the uranium content is thought to be wholly syngenetic, 15 samples had uranium contents of less than 1 ppm, and 10 samples had uranium contents of 1 ppm. These 25 samples include marine and nonmarine rocks, calcitic limestones, magnesian limestones, dolomites, fetid and nonfetid rocks, and metamorphosed and unmetamorphosed rocks. The rocks in this group were deposited under a wide variety of sedimentary conditions.

The most significant feature of this group of samples is that it includes most of the nearly pure carbonate rocks that were analyzed (examples: Upper part of the Burlington Limestone, I–A, No. 260486; upper part of the Madison Limestone, I–A, Nos. 260492 and 260493; Franklin Limestone, I–E, No. 249713, and I–B, No. 249714; Niagara Group, I–G, Nos. 249702 and 249703; dolomites from the Stockbridge Limestone, I–I, Nos. 249704 and 260487). The group includes several fetid rocks (examples: Pinery Limestone Member of the Bell Canyon Formation, I–C, No. 260483; Edwards Limestone, I–D, No. 260448; Hueco Limestone, I–D, No. 260488; limestone bed in Pierre Shale, I–D, No. 249717). The group also includes some carbonate rocks that contain a few percent of impurities in the form of acid insoluble matter, iron and aluminum oxides, and probably other minor constituents (examples: St. Louis Limestone, I–A, No. 249711; Sinbad Limestone Member of Moenkopi Formation, I–A, No. 260542; limestone from Maysville Group, I–A, No. 249710; limestone from Chaffee Formation, I–D, No. 260457; Pony Express Limestone Member of Wanakah Formation, I–J, No. 260479). Only one conclusion can be drawn from this assemblage of data, that is, uranium is not syngenetically deposited in significant quantities with most carbonate rocks. This conclusion is in accordance with the theoretical consideration that uranium compounds, under most circumstances, are not deposited from solutions in which carbonate, or bicarbonate, or carbonate and bicarbonate ion concentrations are high with respect to those of various uranium ions.

The fact that the fetid rocks do not contain significant quantities of uranium merits a brief comment. If the sediments that constitute these rocks had been deposited from sulfurous waters where reducing conditions prevailed, they might be expected to contain greater quantities of uranium than nonfetid rocks having otherwise identical compositions. The quantities of uranium would be dependent upon rates of sedimentation and availability of uranium in the aqueous medium. Rapid sedimentation generally would result in low uranium contents. Sediments oftentimes may be deposited on the ocean bottom or a lake bottom under oxidizing conditions and, after a particular layer becomes buried at a slight depth, putrefaction of a small content of organic matter creates a sulfurous reducing environment. The available uranium is limited to the minute quantity present in the connate water and, consequently, the sediment cannot become appreciably enriched with the element. No attempt was made during this study to determine whether the fetid character of the rocks was acquired contemporaneously with deposition or by subsequent alteration of primary sediments.

The tabulated data indicate that, when substantial quantities of phosphate are present in carbonate rocks as an impurity, the uranium contents may be considerably increased. For example, the limestone sample from the Uinta Formation (I–F, No. 260490) contained 0.28 percent P_2O_5 and 0.021 percent uranium, a dolomite sample from the Kittatinny Limestone (I–I, No. 249706) contained 0.40 percent P_2O_5 and 0.0020 percent uranium, and a sample from the Milton Dolomite (I–I, No. 249708) contained 3.06 percent P_2O_5 and 0.0030 percent uranium. The sample of limestone from the Uinta Formation, which is of nonmarine origin, was taken from a bed about 4 inches thick; this sample contained a small quantity of organic matter of undetermined character that probably holds some of the uranium. The Kittatinny Limestone and Milton Dolomite are of marine origin and have thick, slightly phosphatic beds that can be traced for considerable distances. There is no constant ratio between the phosphate and uranium contents of carbonate rocks. Some of the most phosphatic samples collected during this investigation, such as one from the Bigby Limestone (I–A, No. 260445) that contained 2.85 percent P_2O_5 and one from the Hermitage Limestone (I–B, No. 260446) that contained 6.87 percent P_2O_5, contained only slightly more uranium than the general run of nonphosphatic rocks, that is, 0.0002 and 0.0004 percent respectively.

Four samples of slightly phosphatic and uraniferous limestone containing a substantial amount of organic matter (III–A, Nos. W66873, W67241, W67247, and W90218) from the Bear River Formation of Cretaceous age, Fall River area, Bonneville County, Idaho, (collected by J. D. Vine of the Geological Survey) have been analyzed, and the results are included in table 2. These limestone samples contained about 1 percent P_2O_5 and 0.01 to 0.024 percent uranium. The phosphate-uranium ratios are unusually high, and some of the uranium probably is associated with the organic matter. The Fall River locality has not been examined by the author, and it cannot be stated definitely whether all the uranium in this limestone is syngenetic or whether some of it may represent a late enrichment. For this reason these samples are not listed with those believed to contain only syngenetic uranium.

A lack of correlation between phosphate and uranium in apatites and phosphorites has been noted by several investigators (Hébert, 1947; Davidson and Atkin, 1953; Altschuler and others, 1958). Recent investigations by Altschuler and others (1958) indicate that uranium probably enters the apatite structure in isomorphous substitution for calcium, and the substitution can take place as the mineral is formed and at any time thereafter when ocean water, ground waters, or other aqueous solutions make uranium available. The phosphatic constituents of carbonate rocks probably are predominantly forms of apatite, fluorapatite, and carbonate-apatite. The introduction of uranium into lacustrine and marine limestones and dolomites most likely occurs between the time the sediment is deposited on the bottom and its burial by the next suceeding layer. The quantity of uranium that can be introduced is dependent upon its concentration in the water and the length of time the sediment remains unburied. These conditions are conducive to highly variable uranium-phosphate ratios, particularly when the rate of sedimentation fluctuates.

None of the samples listed in table 2 as containing only syngenetically deposited uranium contained megascopically visible fluorite although a few of them contained a few hundredths of a percent of fluorine in excess of that which would be held in fluorapatite if all the phosphate constituent exists in this mineral. (Examples: Bigby Limestone, I–A, No. 260445; Hermitage Limestone, I–A, No. 260446; Mahogany oil shale bed (of economic usage) in the Parachute Creek Member of the Green River Formation, I–F, No. 260464; marlstone from the Green River Formation, I–K, No. 260485). The maximum uranium content of these samples was 0.0004 percent, and it cannot definitely be associated with any particular constituent. The Salem Limestone (Spergen Limestone of former usage) locally contains scattered small crystals of purple fluorite. The two samples of this rock, I–A, No. 249720, and I–D, No. 260463, that were selected for analyses did not contain any visible fluorite and contained only 0.0004 and 0.0003 percent uranium respectively. During wet periods, thin efflorescent films of a carnotite-type mineral, which apparently is a transient substance here, appear on some joint surfaces and parts of quarry faces in this rock (Muilenburg and Keller, 1950; Gott and others, 1952, p. 34).

Uranium, in many places, is associated with various native organic substances that, in general, have not been precisely identified. There is substantial evidence that uranium tends to associate with humic-type organic substances (Vine and others, 1958; Manskaya and others (Манская, Дроздова, и Емельянова, 1956)) and shuns sapropelic-type organic substances, including petroleum hydrocarbons (Bell, 1960b) and sapropelic solids. Different carbonate rocks contain a wide variety of native organic substances as impurities.

Several of the samples of carbonate rocks analyzed during this investigation contained readily noticeable quantities of organic matter. A sample of dark-gray fetid Madison Limestone (I–C, No. 260450) that contained many fossil brachiopods contained 0.0004 percent uranium. A sample from the Sinbad Limestone Member of the Moenkopi Formation (I–A, No. 260452) that contained about 2 or 3 percent of heavy petroliferous residue and a sample of dolomite from the Niagara (I–G, No. 249703) that contained enough residual petroliferous matter to give the rock a dark brown color contained 0.0001 and less than 0.0001 percent uranium, respectively. These determinations confirm the earlier observations that petroliferous substances are not carriers of significant quantities of uranium (Unkovskaya, 1940; Bell, 1960b). Two samples of metamorphosed Franklin Limestone (I–E, No. 249713, and I–B, No. 249714) that contained abundant flakes of graphite both contained less than 0.0001 percent uranium. A sample of marlstone from the Mahogany oil shale bed in the Parachute Creek Member of the Green River Formation (I–F, No. 260464) that contained at least 25 percent kerogen contained only 0.0004 percent uranium. This determination supports the observation that sapropelic substances are not carriers of significant quantities of uranium. The samples that were analyzed did not indicate any tendency for uranium to concentrate in the organic-rich carbonate rocks.

During the course of investigating the distribution of uranium in salt-pan deposits (Bell, 1960a), several samples of drill cuttings from the Hermosa Formation of the Paradox basin, southeastern Utah, were checked for uranium contents. This collection included seven samples of dolomite. The small amounts of material that were available permitted only uranium determinations to be made. A few thin beds of slightly uraniferous black shale (maximum uranium content was 0.0057 percent) are interspersed in the dolomite. The dolomite samples contained no megascopically visible shaly material. All the samples were oil stained and emitted an odor of crude petroleum when crushed. The analytical data are listed in table 1. No unusual concentrations of uranium are indicated, and it is thought that the slight traces of uranium were deposited syngenetically with the carbonate sediments.

A few conclusions can be drawn from the preceding discussion and from the analytical data presented in table 2: Uranium is an insignificant syngenetic constituent of rocks composed almost wholly of carbonate minerals and of only traces of phosphates, fluorides, and organic substances of humic origin. The uranium contents of these rocks reasonably can be considered to range from 0 to 0.0001 percent (1 gram per ton).

The almost pure carbonate rocks are end members of gradational series with many other kinds of sedimentary rocks. As the proportions of noncarbonate constituents increase, the uranium contents likewise

TABLE 1.—*Uranium content of dolomite from the Hermosa Formation, Paradox basin, San Juan County, Utah*

[Analysts: C. G. Angelo, J. P. Schuch, and E. J. Fennelly]

Sample	Description	Uranium (percent)
252225	Dolomite	0.0004
252226	do	.0011
252227	do	.0003
252228	Dolomite and anhydrite	.0003
252248	Dolomite	.0002
252253	do	.0001
252256	do	.0005

Source of samples:
Nos. 252225, 252226, 252227, 252228 from Shell Oil Co. 1 North Boundary Butte well, CSW¼NE¼ sec. 33, T. 42 S., R. 22 E., San Juan County, Utah, at depths of 4,221 ft 6 in, 4,622 ft, 4,623 ft, and 4,625 ft, respectively.
No. 252248 from Superior Oil Co. 1–28 Navajo well, CNW¼NW¼ sec. 28, T. 41 S., R. 26 E., San Juan County, Utah, at depth of 6,073 to 6,074 ft.
No. 252253 from Shell Oil Co. 1 Desert Creek well, SW¼SE¼NW¼ sec. 2, T. 42 S., R. 23 E., San Juan County, Utah, at depth of 5,128 ft 6 in.
No. 252256 from Reynolds Metal Co. 1 Hatch well, sec. 4, T. 39 S., R. 24 E., San Juan County, Utah, at depth of 5,799 to 5,800 ft.

may increase appreciably. The presence of phosphate, presumably as calcium phosphate in some form of apatite, commonly has a significant effect on uranium content. Many phosphatic carbonate rocks contain quantities of uranium that are measurable by routine chemical methods (in excess of 0.0001 percent or 1 gram per ton). This uranium probably substitutes for calcium in the apatite structure, and the quantities of uranium in such rocks are dependent upon environments existing at times of sedimentation and upon subsequent geological histories. There is no consistent ratio between the uranium and the phosphate contents in these rocks; in fact, some phosphatic limestones are almost devoid of uranium, and the quantities of uranium in other phosphatic limestones may reach a few tens of grams per ton. The uranium in carbonate rocks containing substantial amounts of detrital sediments is most likely to be in uraniferous heavy mineral resistates. The association of uranium with organic-rich carbonate rocks has not been thoroughly investigated. Available data indicate that carbonate rocks containing sapropelic derivatives such as kerogen and petroleum hydrocarbons are not enriched in uranium. It is pointed out in the discussion of epigenetic uranium deposits in carbonate rocks that some of these rocks which contain rich uranium deposits are strongly fetid. Analyses of several fetid limestone and dolomite samples show that these rocks, as a group, are not at all enriched with syngenetically deposited uranium.

Finally, no useful result can come from any attempt to establish average uranium contents of comparatively impure carbonate rocks on the basis of available data. The uranium contents of these rocks are associated with the noncarbonate constituents rather than the carbonates, and, to have any meaning at all, average uranium contents should be expressed in relation to quantities of specific impurities in the carbonate rocks; sufficient analytical data to justify such expressions have not been assembled.

EPIGENETIC URANIUM DEPOSITS IN CARBONATE ROCKS

Uranium is deposited epigenetically in carbonate rocks under a wide variety of circumstances. In the discussion that follows these deposits are divided into four types: (1) hydrothermal veins, (2) efflorescent deposits, (3) deposits in karst terrains, and (4) peneconcordant deposits. The term hydrothermal vein should need no explanation. The efflorescent deposits form at or near the earth's surface by evaporation of uraniferous solutions. Many minerals can be deposited in caves, solution channels, and other cavities in the carbonate rocks of karst terrains; uranium minerals are included in this group. The peneconcordant deposits are formed in permeable sedimentary rocks. Epigenetic uranium deposits may originate from hydrothermal processes, from supergene enrichment processes, may be efflorescent, or even may form as results of combinations of these processes.

URANIUM IN HYDROTHERMAL VEINS

Large uraninite-bearing veins of hydrothermal origin cut across sedimentary carbonate rocks in the Shinkolobwe district, Republic of Congo (Thoreau and du Trieu de Terdonck, 1933, 1936; Bain, 1950; Derriks and Vaes, 1956), and in the Lake Athabaska region, Saskatchewan, Canada (Alcock, 1936, p. 36; Christie and Kesten, 1949; Bowie, 1955; Robinson, 1955). Uranium-bearing veins have been discovered in carbonate rocks at several localities in Central Asia; the uranium minerals near the surface are mainly carnotite and tyuyamunite and are accompanied in different deposits by barite, sulfide minerals, and secondary copper minerals. Available descriptions hint that the primary mineralization in some of these deposits may have been hydrothermal. Such deposits at Kan-sai in the Tadzhik S.S.R. are described by Arapov (Арапов, 1936); deposits at Tyuya-Muyun in the Uzbek S.S.R. are described by Alexandrov (Александров, 1922), Pavlenko (Павленко, 1933), and Betekhtin (Бетехтин, 1946); deposits at Agalyk in the Uzbek S.S.R. are described by Gorbunov (Горбунов, 1935) and Gotman (Готман, 1937); and deposits at Taboshar in the Tadzhik S.S.R. are described by Vol'fson (Вольфсон, 1940).

The uraninite-bearing hydrothermal veins at Shinkolobwe are enclosed by dolomite in which there are some schist, sandstone, and siliceous beds. The structure, mineralogy, and geological history of these deposits are complex. The deposits have been deeply weathered, and above the present ground-water table the secondary ores, which have been largely mined out, consist of a great variety of secondary uranium minerals and oxidation products of primary sulfide and selenide minerals. Descriptions of the deposits by Thoreau and du Trieu de Terdonck (1933) and Derriks and Vaes (1956) indicate that a large proportion of the carbonate constituents in the oxidized zone has been removed, apparently by weathering processes. Below the water table, in the unoxidized zone, uraninite is the only uranium mineral, and carbonate minerals, both in the veins and in the wallrock, are intact. The mineralization process apparently included at least two phases of vein carbonate mineral deposition, one preceding and one following uraninite deposition (Derriks and Vaes, 1956, p. 127). Several sulfide minerals, those of nickel and cobalt being most abundant and including iron, molybdenum, and copper sulfides, were deposited after the uraninite. Descriptions of the deposits indicate that uraninite replaces some of the earlier carbonate minerals, and, in turn, is replaced by later carbonate minerals; uraninite and sulfide minerals tend to be concentrated in separate veins.

Uraninite-bearing veins in the Lake Athabaska region, Saskatchewan, Canada, are enclosed in a sequence of Precambrian rocks that includes gneisses, chlorite schists, diabases, basalts, quartzites, conglomerates, and dolomites. The vein materials consist principally of carbonate and sulfide minerals and lesser amounts of uraninite and other minerals. Uraninite-bearing parts of the veins occur within all the rocks of the region, but published descriptions seem to indicate that the quantities of uraninite are least where dolomite forms the wallrock. About 40 percent of the uraninite occurs as colloform masses, 5 percent as dusty or sooty powder, and most of the remainder as massive pitchblende or uraninite (Robinson, 1955, p. 61).

There is little information available to the author about the uraniferous veins of Central Asia. The obtainable literature reports only the presence of secondary uranium minerals in these deposits; this indicates that the descriptions probably apply to oxidized zones. Some of the veins in the Tyuya-Muyun locality originally may have consisted of minerals of hydrothermal origin. The hydrothermal activity could have been associated with nearby igneous intrusions according to Pavlenko (Павленко, 1933) and Shimkin (1949). Arapov (Арапов, 1936) has described uraniferous deposits within limestone, which in places has been converted to skarn, along the contact with a granodiorite batholith in the vicinity of Kan-sai. Other uranium deposits within limestones and near contacts with igneous intrusive rocks that are situated near Agalyk in the Uzbek S.S.R. have been described by Gorbunov (Горбунов, 1934), Zil'bermintz (Зильберминц, 1935), and Zil'bermintz and Samoilo (Зильберминц и Самойло, 1935).

Slightly uraniferous apatite and traces of a powdery yellow uranium mineral have been found in a fault zone in the Kittatinny Limestone at the Mulligan quarry, Clinton, N.J. The traces of secondary yellow uranium mineral may have been derived from the apatite or may be a slight supergene enrichment of uranium leached from the carbonate rock itself or from formations that formerly overlay the Kittatinny but have been eroded from the locality. The rock exposed in the Mulligan quarry is dolomite or has the chemical composition of dolomite. Two samples (I–I, Nos. 249706 and 249707) taken from the quarry contained 0.0020 and 0.0006 percent uranium respectively; sample 249706 was taken from a bed of slightly phosphatic rock approximately 10 feet thick.

In summary, it is pointed out that, although carbonate rocks would seem on the basis of theoretical considerations to provide unfavorable environments for the deposition of uranium minerals from hydrothermal solutions, such deposits do exist and some furnish rich ores. This situation indicates a gap in our knowledge of the chemical behavior of uranium. Carbonate gangue minerals are abundant in the known deposits. At Shinkolobwe, uraninite veins are enclosed in predominantly carbonate rocks; on the other hand, in the Lake Athabaska region carbonate rocks form a small part of the stratified sequence, and the richest parts of the uraninite-bearing veins are adjacent to siliceous rocks. An interesting observation has been made by Derriks and Vaes (1956, p. 106) in describing the Shinkolobwe deposits. They state, "The uraninite is always crystalline. We have never observed at Shinkolobwe the colloform type which occurs at Great Bear Lake and St. Joachimstal." The following question arises: Is uraninite deposited in a carbonate rock environment likely to be crystalline and that deposited in a silicate rock environment likely to be colloform?

EFFLORESCENT DEPOSITS OF URANIUM MINERALS

Superficial deposits of efflorescent epigenetic uranium minerals are found in some places on walls of solution cavities and open fractures and even on surfaces of outcrops of all kinds of rocks. Tyuyamunite, carnotite, uranophane, bayleyite, and schroeckingerite are the most common constituents of such deposits, but other secondary uranium minerals may be deposited. The distribution of uranium minerals is generally erratic and commonly is so sparse that the minerals are barely visible. Such deposits are fairly common in semiarid regions and are rather uncommon elsewhere. The uranium minerals in some deposits are associated with substantial amounts of chalcedony and(or) opal and in other deposits with secondary calcite or with nonuraniferous efflorescent minerals. All these substances are deposited because the solutions that transport them evaporate. A change of pH as the solutions enter a carbonate rock environment probably is a secondary factor causing deposition.

The largest efflorescent deposits that have been found in carbonate rocks in the United States are in the Miller Hill area of Carbon County, Wyo. Here they are small uranium deposits on and within a few feet of outcrops of a thin lenticular lacustrine algal limestone bed in the North Park(?) Formation of Pliocene(?) age. The limestone is more resistant to erosion than the soft sandstone above it. The limestone is exposed in small cliffs and on benches ranging from a few feet to a few hundred feet in width behind the cliffs. The only visible uranium mineral is uranophane that is spottily distributed in fractured and brecciated parts of the limestone. This mineral apparently does not occur in the rock along the cliff faces; it is most abundant in a zone of variable width on the benches extending from the margin of the overlying sandy sediments towards the cliffs.

Slightly uraniferous chalcedony and opal, mostly dark gray to black, have been deposited in fractures, vugs, and solution cavities in the limestone. These minerals, which have a greater distribution than the uranophane, definitely are epigenetic constituents of the rock. The chalcedony and opal were deposited from ground-water solutions carrying both silica and uranium. A part of the silica seems to have been deposited as a result of evaporation, but reactions between silica-rich solutions and the carbonate rock may have caused a substantial part of the deposition of silica.

The uranophane in this limestone seems to be a strictly efflorescent mineral. It has been found only in the upper part of the limestone bed where it crops out or is covered with a thin soil mantle; it has not been found on cliff faces because it can be readily leached in such places. Uranophane evidently is being formed by evaporation of uraniferous ground-water solutions, and capillary action is instrumental in bringing the solutions toward ground surface. Uranophane is a rather soluble uranium mineral; it is more soluble than carnotite and tyuyamunite. There is probably a slow, but continuous, movement of uranium across the limestone benches; uraniferous ground water draining from the more elevated terrain behind the benches evaporates from the porous limestone exposed along the benches; through the medium of successive resolution and redeposition, the uranium moves toward the cliff faces and finally is carried away in the surface drainage. Uranium that becomes incorporated in uranophane is not leached from chalcedony and opal.

Uranium deposits in the Miller Hill area also have been described briefly by Love (1953) and by Vine and Prichard (1959) who suggest that the uranium was leached from tuffaceous beds in the upper part of the North Park(?) Formation and transported to sites of deposition by ground water.

Small pockets of ore-grade material are found in the Miller Hill area. The deposits discovered up to 1958 ranged from a few hundred pounds to possibly a ton of ore-grade rock. The small size of these deposits, and an erratic distribution of the uranium mineral make them unfavorable for profitable exploitation.

Uranophane is locally rather abundant in the uppermost part of the Todilto Limestone, Grants district, McKinley County, N. Mex., but not in sufficient quantity to constitute ore. It has been deposited in vugs, solution cavities, and along open fractures. This uranophane seems to be in the form of efflorescent deposits.

Similar deposits found in carbonate rocks elsewhere in the United States produce interesting specimens but not ores. Such minor deposits in the Hueco and Edwards Limestones of west Texas are described by Eargle (1956). Carnotite and tyuyamunite form thin films on fracture surfaces and walls of cavities in these limestones and on surfaces of boulders and pebbles in the alluvial mantle. The uranium probably has been leached from thin clay and shale beds in the limestone formations by ground and surface waters. Yellow secondary uranium minerals occur in cavities and fractures in limestone beds of Mississippian and Pliocene(?) age in the vicinity of Clarkdale and Jerome, Ariz. Minor deposits of uranium minerals occur in the limestone facies of the Hermosa Formation, Gypsum Valley area, San Miguel County, Colo. Stephens (1954) has described briefly minor deposits of secondary uranium minerals in cherty limestone of the Browns Park(?) Formation of Miocene(?) age in the Saratoga area, Carbon County, Wyo.; these deposits are similar to those in the Miller Hill area. Isachsen and others (1955, p. 129) mention the presence of copper-uranium mineral concentrations in the uppermost parts of the Kaibab Limestone of Permian age near Williams, Ariz.

Thin films of carnotite coat fracture surfaces and cavities in dolomite wallrock of hydrothermal fluorspar pipes in the Thomas Range district, Utah (Thurston and others, 1954, p. 5 and 29). The fluorite in these deposits is slightly uraniferous, and near-surface weathering probably has released some uranium that has been redeposited in carnotite.

Yellow coatings of carnotite, or a carnotite-type mineral sporadically appear on rock faces of quarries in the Salem Limestone (Spergen Limestone of former usage) near Ste. Genevieve, Mo. The limestone itself does not seem to contain unusually large amounts of uranium; the two samples (I–A, No. 249720 and I–D, No. 260463) analyzed during this investigation contained 0.0004 and 0.0003 percent uranium, respectively. A few thin seams of dark-gray to black clays and shales are interspersed among the limestone strata. A sample of shale collected by G. B. Gott, U.S. Geological Survey, contained 0.48 percent uranium oxide as U_3O_8. Uranium probably is being leached from the clays and shales by ground waters and is being deposited in carnotite where these waters evaporate from rock surfaces.

URANIUM DEPOSITS IN KARST TERRAINS

Rich deposits of secondary uranium minerals are found in caves, solution channels, and fractures in carbonate rocks of karst terrains at Tyuya-Muyun, Fergana district, Uzbek S.S.R., U.S.S.R., and in the Pryor Mountains-Bighorn Mountains area of Montana and Wyoming. According to Alexandrov (Александров, 1922), the Tyuya-Muyun deposits have been known for several centuries and were worked sporadically by the Chinese for the copper minerals that they also contain. The deposits in the Pryor and Bighorn Mountains were discovered in 1955.

TYUYA-MUYUN, FERGANA DISTRICT, UZBEK S.S.R.

The ore deposits for which the Tyuya-Muyun locality is especially noted consist mainly of incrustations of calcite, barite, and several secondary uranium, vanadium, and copper minerals that partly or wholly fill a series of caves, solution channels, and fractures in metamorphosed limestones of Paleozoic age. The deposits are in the northern foothills of the Alai Range, and according to Pavlenko (Павленко, 1933) they are close to an area where a series of younger volcanic rocks have been erupted upon a sedimentary terrain. The ores have been mined to depths exceeding 175 meters. The incrustations locally reach a thickness of 1.5 meters and consist of successive layers that vary in number, thickness, and to some extent in order of deposition from one cavity to another; the general sequence of mineral layers, in order of deposition as stated by Betekhtin (Бетехтин, 1946), is as follows: (1) calcite interspersed with thin argillaceous-carbonaceous bands, (2) coarse-grained calcite with tyuyamunite, turanite ($5\,CuO \cdot V,O_5 \cdot 2H_2O$), and other minerals, (3) barite, both red and honey yellow and red quartz, (4) barite breccia cemented with younger barite and carbonate minerals, and (5) dense calcite and earthy red clays.

The Tyuya-Muyan deposit, as described by Fersman (Ферсман, 1928), is in the midst of a vein field. According to Shimkin (1949), at least 5 barite veins containing uranium, vanadium, and copper minerals, and at least 30 pure barite veins are known in the locality. No report that describes completely the possible origin and emplacement of the uraniferous ores has been available to the author. No direct association between the uraniferous barite veins and the fillings of the karst cavities has been demonstrated. Pavlenko (Павленко, 1933) has proposed the following general sequence of mineral deposition within the cavities: (1) a thermal ore process which was dependent upon solidification of diabase rocks and during which calcite and then calcite and ore minerals were deposited, (2) a thermal barite process during which barite was deposited, (3) a typical first "karst" process during which banded crusts were deposited, and (4) a second "karst" process during which previously deposited barite was reworked and quartz and then aluminous sediments were deposited. Pavlenko's conclusions and the presence of many barite veins containing metallic constituents suggest that the uranium may be of hydrothermal origin. No published reports available to the author stated that primary uranium minerals, such as uraninite, have been found in the locality. Unsubstantiated reports indicate that uraninite has been found in deep mines of the locality.

BIGHORN-PRYOR MOUNTAINS, WYOMING AND MONTANA

A karst terrain that was formed in the upper part of the Madison Limestone of Mississippian age during Late Mississippian or Early Pennsylvanian time is now exposed on the westward-facing slopes of the Pryor Mountains of south-central Montana and the northern part of the Bighorn Range of north-central Wyoming. Some of the caves and solution channels formed during the main karst-forming stage subsequently have become partly or wholly filled with an assortment of debris, and some of this debris is mineralized with tyuyamunite.

The materials within individual caves and solution channels may include blocks of limestone that have fallen from the backs and walls, chert nodules and other insoluble residue from the limestone, clay, silt, and sand washed in from the surface of the ground or from rocks that formerly overlay the Madison, and in some caves large quantities of siliceous sinter. Some of the fine-grained sediments are stratified and indurated and form masses of siltstone or sandstone. The rubble in some of the caves is unconsolidated, and in other caves it is cemented by siliceous sinter or by secondary calcite.

The uranium deposits are restricted to the rubble, sinter, and sediments within the caves and to scaly crusts on the walls of caves, solution channels, and fractures. Tyuyamunite is the only uranium mineral that has been identified from these deposits. Tyuyamunite occurs in powdery form dispersed in silt and siliceous sinter, as powdery films on secondary calcite, as scaly crusts on walls of cavities and caverns, and as films and scaly crusts on limestone rubble and chert nodules. Some caves in the area have not been mineralized. The controlling factors of the mineralization process have not been determined. The deposits range from insignificant accumulations of tyuyamunite within a single small opening to those occupying series of connected caves, channels, and fractures extending over distances of several hundred feet horizontally and to a known depth of 175 feet. The quantity of uranium in the mineralized material ranges from mere traces to several percent and tends to be erratically distributed.

The uranium was introduced into the cave fillings from some source outside of the limestone. Although cave walls may be coated with highly uraniferous incrustations, limestone an inch or so back from the incrustations generally is nonuraniferous except along surfaces of connected fractures and solution cavities. This observation was checked by uranium determinations on two samples of limestone broken from the walls of heavily mineralized caves, one at Big Pryor Mountain in Montana and the other at the Little Mountain locality near the north end of the Bighorn Mountains in Wyoming. The two samples (I–A, Nos. 260492 and 260493) contained less than 0.0001 percent uranium.

The source of the uranium has not been determined. The two most likely methods of emplacement seem to be: (1) the deposits are supergene enrichments of uranium leached from formations that are younger than the Madison Limestone and which formerly covered the area, and (2) the tyuyamunite is the oxidized residue of hydrothermal deposits.

The principal point in favor of the supergene enrichment hypothesis is the presence, in the Mesozoic and Tertiary rocks of the region, of several formations containing an abundance of arkosic and tuffaceous material. The most uraniferous of these sediments are in the Tertiary section. An obstacle to strict supergene enrichment is the presence of several more or less impervious mudstone, clay, and shale formations and strata distributed throughout the sedimentary sequence. Shale and clay beds in the Amsden Formation of Pennsylvanian age that directly overlies the Madison would seem to prevent a normal type of supergene enrichment. It is possible that as the present Madison surface was exposed through erosion, surface and ground waters carrying uranium leached from surrounding terrain may have deposited it in the cave and solution channels in the limestone.

Evidence supporting a possible hydrothermal origin for the uranium likewise is meager. Very few features that might be attributed to hydrothermal activity were seen by the author while examining several dozen prospects. Fluorite and barite are common, although minor, constituents of the material filling fractures and caves of the Big Pryor Mountain locality; these minerals were not observed in the limestone wallrock. Several hundred pounds of massive pyrite within a fracture zone was exposed in a prospect in the Little Mountain locality. Secondary calcite, commonly in the form of dog-tooth spar, occurs in many of the deposits and is very abundant in the Little Mountain locality. Siliceous sinter partly fills some caves and has been deposited in large quantities along some fracture zones in the Big Pryor Mountain locality; it is either a minor constituent or does not occur in deposits of the Little Mountain locality. Most of the limestone in the upper part of the Madison is very pure, and the effects of hydrothermal solutions upon it would be mainly solution and redeposition of calcite. No sulfide minerals or oxidation products of sulfide minerals except pyrite, limonite, and possibly other iron oxides have been observed.

The problem of the genesis of uranium ores in karst terrains of the Madison Limestone probably cannot be solved until exploration has progressed to depths below the zone of oxidation. Disappearance of the uranium mineral with increasing depth will be a point in favor of supergene enrichment. The presence of primary uranium and sulfide minerals at deeper levels will favor the hydrothermal hypothesis. The physical characteristics of some of these ores, especially those occurring in silt-filled caves, are, in general, similar to many sandstone uranium ores from the Colorado Plateau region. The bulk of the tyuyamunite in all the deposits is within siliceous cave and fracture fillings, and the mineralized zones tend to end abruptly on or very close to the limestone walls. Uraniferous solutions probably entered the channels and caves where a slight reaction with the carbonate wallrocks changed the pH enough to cause precipitation of a uranium mineral.

PENECONCORDANT URANIUM DEPOSITS IN CARBONATE ROCKS

The largest and richest uranium deposits in carbonate rocks within the United States are of the type called peneconcordant by Finch (1959). These deposits are "tabular, lenticular, or irregularly shaped masses of widely differing size that are, in general, concordant to the gross sedimentary structures of the enclosing rock but that, in detail, cut across sedimentary structures. This local discordance is a diagnostic characteristic indicating that the deposits are epigenetic rather than syngenetic." The uranium deposits in limestone beds of the Todilto Limestone of Late Jurassic age in northwestern New Mexico definitely can be placed in this category. Some small uranium deposits in limestone lenses at the base of the Sundance Formation of Late Jurassic age in Wyoming have similar characteristics. All these deposits in limestones have physical features like those of most uranium deposits in sandstones of the Colorado Plateau region.

URANIUM DEPOSITS IN THE TODILTO LIMESTONE, NEW MEXICO

A few large and several small uranium deposits have been discovered in limestone beds of the nonmarine Todilto Limestone in the Grants district, McKinley and Valencia Counties, N. Mex. Other small deposits in this formation have been discovered in the Laguna district, Valencia County; in the Sanostee area, Apache and San Juan Counties; and in the Rio Cebolla and Arroyo del Agua areas, Rio Arriba County. Only the Grants district has produced a substantial amount of ore.

The Todilto was deposited in a nearly elliptical basin about 300 miles long in an east-west direction and 100 miles wide (Rapaport and others, 1952, p. 23). The formation consists of two members. The lower member is a sequence of supposedly fresh- to brackish-water beds of limy shale, silty limestone, and limestone that reaches a maximum thickness of about 40 feet. The upper member, of considerably smaller areal extent, consists mainly of gypsum and anhydrite that was deposited in the basin sink; it attains a thickness of at least 95 feet in the northern part of the Lucero uplift near Laguna (Rapaport and others, 1952, p. 23). The Todilto rests upon the nonuraniferous Entrada Sandstone.

The Summerville Formation, Bluff Sandstone, Morrison Formation, all of Late Jurassic age, and the Dakota Sandstone of Early(?) and Late Cretaceous age overlie the Todilto in the order given in the Grants district. The Summerville and Dakota are weakly mineralized with uranium in a few places. Some of the largest known uranium deposits in the United States are in the Morrison Formation of the Ambrosia Lake district a few miles northwest of the Grants district; a large ore body has been mined out of the Morrison Formation at Poison Canyon on the north edge of the Grants district.

It is desirable to point out some features that characterize the limestone member of the Todilto and which possibly influenced the deposition of uranium because substantial uranium deposits are uncommon in limestones. The Grants district is described in some detail because the largest known deposits are in this district and because outcrops and mining operations have provided excellent exposures.

The limestone member of the Todilto in the Grants district is a part of the southern rim of the San Juan Basin and is on the north flank of the Zuni uplift. The upper gypsiferous member is absent in this locality. The limestone is underlain, apparently conformably, by the Entrada Sandstone, and these formations are exposed on low southward-facing cliffs that form the steep slope of a dissected cuesta about 15 miles long and a half a mile to about 2 miles wide. The back slope of the cuesta is a gentle dip slope formed on the upper part of the Todilto; its surface is made somewhat irregular by minor structural features and variable thicknesses of residual soil and alluvium. The Todilto passes under younger formations that are exposed on southward-facing cliffs several hundred feet high and which form the main part of the southern rim of the San Juan Basin.

The limestone ranges in thickness from about 18 to about 30 feet. Much of it is thinly bedded and tends to split along bedding planes. Several thin units can be recognized, but only three persist throughout most of the district. These are a basal, or near basal, very fine grained dense limestone; a middle unit of very thinly bedded fine-grained crinkly limestone; and an upper unit of coarse-grained recrystallized limestone, which in most places is rather coarsely crinkled. These three principal units are separated locally from one another and from the underlying Entrada Sandstone and the overlying Summerville Formation by lenticular, thinly laminated shaly and silty beds that range from a feather edge to about a foot in thickness; other lenticular shaly and silty beds are interspersed within the main limestone units. These partings vary in thickness and number from place to place.

The Grants district probably lies along, or close to, the strand line of the upper gypsiferous member of the Todilto where thin layers of gypsum or anhydrite formerly were interspersed with limestone beds or where a mixture of calcium sulfate and calcium carbonate was deposited. Subsequently, anhydrite, where that was the primary sulfate mineral, was hydrated to gypsum, and the attendant swelling helped produce the crinkly features of the upper unit of the limestone member. The gypsum along the strand line eventually was leached from the rock. Results of the leaching were formation of a porous texture, completion of crinkling of the thinly laminated limestone, and erratic recrystallization of the calcite constituent.

The limestone is strongly fetid. It has a brownish color except in places where it has been recrystallized, and there the colors are usually white and light shades of pink, yellow, and gray; locally the presence of hematite is the cause of a red color. It generally has been assumed that the odor and brown color are due primarily to a small amount of petroliferous substance. Attempts to extract organic matter from several samples of limestone collected in the Grants district have been unsuccessful. Several kinds of organic solvents were used in the experiments. It is concluded that this rock is not now petroliferous, and that it probably never has been petroliferous. The limy sediments undoubtedly contained significant amounts of organic matter as they were being deposited, and the traces that remain give the rock its brown color. The exact nature of the organic matter cannot be stated. The only fossils that have been recognized in the Todilto are remains of ostracodes (Swain, 1946), and the author has found remains of small fishes. The scarcity of readily recognizable fossil forms suggests that most of the organic matter likely was derived from minute organisms of which plankton might have been the principal members. The organic matter, brown color, and fetid odor have been eliminated from some of the thoroughly recrystallized rock.

The sediments that formed the limestone member of the Todilto were composed principally of chemically precipitated carbonates, minor amounts of clay- and silt-size detritus, and traces of organic matter. The analyses reported in table 2 (II–C, Nos. 260469–260477) show that the rock is a normal high-calcium limestone containing approximately 1 percent of magnesium carbonate. It contains less than 0.01 percent P_2O_5 and variable amounts of acid-soluble R_2O_3 ranging from about 0.8 to about 3.8 percent. Most of the limestone contains less than 10 percent of clastic sediments, but some lenses are marlstone and calcareous siltstone, and some thin stringers are composed almost wholly of detrital quartz and feldspars.

The limestone is mostly very thinly stratified and consists of alternating layers of dense finely crystalline calcite and calcite mixed with silt. The silty layers generally are thinner than the dense calcite layers, but they evidently have been quite permeable because epigenetic minerals locally have been deposited in them and have given the rock a banded appearance.

The calcareous sediments consisted of very fine grained material that was deposited in an aqueous environment, and they probably were subjected to considerable compaction before lithification occurred. Layers of dense material inhibited vertical movement of water and solutions; hence, the main flow was laterally along bedding planes and through relatively more permeable silty lenses. This condition has had a readily noticeable effect on the deposition of epigenetic minerals. Secondarily induced permeability in the limestone resulting from leaching of calcium sulfate minerals and development of vertical fractures has been an important factor in redistribution of secondary uranium minerals.

Four types of deformation have affected the Todilto Limestone in the Grants district. The first is tectonic folding that has produced broad, slightly undulating structures in all the formations of the area; these folds are a mile or more wide and have closures of only a few tens of feet and axes that trend approximately northward. The second type of deformation is small-scale folding that is almost wholly confined within the limestone beds and has affected adjacent formations in only a few scattered places; these folds probably were caused by hydration of calcium sulfate and subsequent leaching of this material. These folds range from a few inches to some 30 or 40 feet in width, but most are less than 10 feet in width; they range from a few feet to a few hundred feet in length and have closures of a few inches up to 5 or 6 feet; the numbers of these folds vary greatly from place to place, the limestone in some localities being almost devoid of them and in other localities being tightly crumpled by closely spaced series of such folds. The third type of deformation consists of northward- and northeastward-trending fault zones that cross the district; there is but little vertical displacement along these faults; the amount of horizontal displacement has not been determined. Finally, the entire section was tilted as the present regional structures of the San Juan Basin and Zuni uplift formed.

An interesting feature of the Grants district is the recrystallized character of much of the uppermost few feet of the limestone. The results of this alteration vary considerably from place to place. The limestone, where altered, generally has been more or less recrystallized to depths of about 5 feet below its upper surface, but locally it is recrystallized to depths of as much as 10 to 12 feet below the upper surface. The rock in the latter places is coarsely crystalline, vuggy, and is streaked with hematite stain. The cause of this recrystallization has not been determined. It may have been caused by warm water, of undetermined origin, moving through porous strata and along fractures. Recrystallized limestone has considerably greater areal distribution than rock enriched with uranium minerals and fluorite.

Ore bodies mined or discovered in the Grants district up to 1960 tend to be clustered along zones of major faults. These fractures are unmineralized except for minor amounts of secondarily redistributed uranium minerals. The primary uranium mineralization occurred mainly in the small anticlinal structures within the limestone adjacent to fault zones; this feature suggests a structural control. What role, if any, was played by the major fractures is not clear. The masses of primary or "black" ore, of which uraninite is the important constituent, are mostly small and range from insignificant pods to bodies about 30 feet wide, 200 x 300 feet long, and about 3 feet thick. At some places two or more bodies of primary ore, in adjacent small anticlines, can be mined from the same pit, particularly if the intervening rock has been heavily mineralized with secondary uranium minerals. The uraninite in some ore bodies has been altered almost completely to secondary uranium minerals. Secondary minerals are likely to be redistributed along fracture surfaces, in vugs, and in solution cavities for substantial distances from sites of the primary deposition. The redistributed yellow secondary minerals are especially conspicuous in the upper, crinkly layers of the limestone. Ore bodies of predominantly secondary uranium minerals tend to be irregulary rounded rather than elongate.

Several epigenetic minerals, and some that possibly are authigenic, occur in the mineralized parts of the limestone. There are two categories of these minerals, those that are primary, and those that are alteration products of the primary minerals. In the primary category are pyrite, fluorite, uraninite, barite, some calcite, and probably hematite. It seems unlikely that all these minerals were deposited during the same phase of mineralization. The alteration products of the primary epigenetic minerals include carnotite, tyuyamunite, uranophane, and limonite. Redistributed calcite is abundant. Small, probably authigenetic manganese-bearing nodules, possibly composed predominantly of psilomelane(?), are widely, though not abundantly, distributed in the limestone. These nodular masses rarely exceed an eighth of an inch in diameter. There is no evidence to indicate that any of these minerals are mainly syngenetic except for some fine-grained pyrite in parts of the limestone that are otherwise unmineralized. None of the minerals listed above is confined to any particular stratum, and none is even approximately uniformly distributed within a particular stratum. The bulk of the primary minerals are concentrated in zones of former bedding-plane porosity and generally are further controlled by the small anticlinal structures; the banded appearance of rock so mineralized commonly does not extend more than a few feet from the flanks of the folds. The secondary minerals, particularly those of uranium, in most places have been redistributed beyond the limits of the primary deposits and are concentrated mainly in fractures.

The primary uranium mineral, uraninite, is preserved mainly in the fine-grained dense limestone of the lower units. Ore in lots of a few tons containing several percent uranium can be handpicked from places where uraninite is especially abundant. The limestone generally has been recrystallized to the point where stratification features are obscure or eliminated; the uraninite occurs as small grains, irregular masses, and small stringers that show some indication of following the former stratification but also in many places cut across it; lenticular masses of nearly pure uraninite about half an inch thick and a few inches long that obviously replace the limestone are found in this rich ore. Small grains and nodular masses of uraninite definitely follow bedding planes and give the rock a somewhat discontinuous banded appearance around the flanks of rich ore bodies and in places where there has been relatively little primary uranium mineralization as well as little or no recrystallization of the limestone. This feature indicates that bedding plane permeability exerted considerable control over localization of uraniferous solutions. No direct association between uraninite and organic matter has been observed.

Fluorite is rather widespread in the Grants district and locally attains concentrations ranging from a trace to possibly 5 percent. It occurs as minute grains and as aggregates of microscopic grains. Some of the fluorite is purple, some is colorless, and some of the aggregates consist of mixtures of purple and colorless grains. Although some of the fluorite is uraniferous, it does not seem to be associated directly with uraninite. Some aggregates of fluorite grains have cores of uranophane, a peculiar feature that cannot now be explained. Fluorite-rich parts of the limestone are not characteristically mineralized with uraninite, in fact, some fluorite-rich rock seems to be devoid of uraninite. Some of the richest concentrations of fluorite occur in the small anticlinal structures, particularly those adjacent to major fractures. In those parts of the limestone that are not extensively recrystallized, fluorite, like uraninite, follows the stratification, and some of the rock is conspicuously banded. No conclusive evidence has been found indicating that fluorite and uraninite belong to the same period of mineralization. It is possible that the two minerals were deposited at different times from unrelated solutions.

Hematite, or some other reddish iron oxide, is a conspicuous constituent of some of the mineralized limestone. Most of this mineral is extremely fine grained and tends to color the rock a dull red. It probably does not amount, at the most, to more than 1 percent of the rock. Hematite also has a tendency to follow bedding planes and is more likely to accompany uraninite than is fluorite, but hematite and fluorite are not always found together in mineralized zones devoid of uraninite.

Known uranium deposits in the Todilto Limestone outside of the Grants district are small and are distributed along the margins of the San Juan Basin or at points within the basin sink where the upper gypsiferous member is missing. Only secondary uranium minerals have been found in these deposits.

Although the source of the uranium in the Todilto Limestone has been a subject of much speculation by many geologists, no completely satisfactory answer has been found. The author believes that the uranium in the limestone was derived from the same source as that which furnished the uranium in the overlying sandstone formations and that it was deposited at the same time. When the origin of uranium deposits in sandstones is determined, it is expected that the deposits in the Todilto Limestone also will be explained.

Limestones generally are not favorable host rocks for uranium deposits; therefore, some unusual conditions had to exist to cause deposition of uraninite in the Todilto. This limestone probably contains no significant amount of syngenetic uranium. The validity of this statement cannot be established completely on the basis of analyses of samples collected in the Grants district. All the rock seems to contain redistributed uranium in the form of secondary minerals. All the samples collected by the author contained visible traces of yellow minerals even though considerable effort was expended to obtain rock free from such constituents. Even so, it should be noted that samples 260469 and 260471 contained only 0.0005 and 0.0006 percent uranium, respectively (table 1, II–C). The analyses of nine samples also show that the Todilto is almost nonphosphatic, the maximum quantity of P_2O_5 being only 0.08 percent. It already has been pointed out in the discussion of syngenetic uranium in carbonate rocks that only those carbonate rocks that have a few tenths of 1 percent or more of P_2O_5 are likely to contain syngenetic uranium in quantities exceeding about 0.0004 percent. It is concluded that the possibility that a minor amount of syngenetic uranium in the Todilto could have been concentrated and redeposited is nil. The uraninite, as well as fluorite, hematite, and some other less abundant minerals, are distributed in the limestone in a manner indicative of epigenetic deposition.

The ore-forming solutions responsible for deposition of uranium in the sandstone units overlying the Todilto fluids, structural features for entrapment of the fluids, and chemical environments causing precipitation of ore minerals. Within the Todilto, structural features are readily visible, and the availability of ore-forming fluids can be easily explained, but the precise nature of the chemical environment in which the uranium was precipitated cannot be fully explained.

The ore-forming solutions responsible for deposition of uranium in the sandstone units overlying the Todilto Limestone in the area also must have deposited the uranium in the Todilto; no evidence has been uncovered to the contrary, and there is no evidence of more than one period of primary uranium mineralization in the area. It is reasonable to assume that uraniferous solutions migrated through several permeable strata of the local section and that, wherever structural and chemical conditions were favorable uranium was deposited.

Structural features in the Todilto that trapped ore-forming fluids were mainly the small folds that are confined to the limestone itself. Generally the overlying Summerville Formation, composed mostly of shales and mudstones, had formed an impervious cap over the limestone. Ore-forming solutions may have flowed along fractures in the limestone to some extent, but the major movement was controlled by stratification features and was along thin permeable beds that average only a small fraction of an inch in thickness. This circumstance is indicated by the predominant deposition of uraninite, fluorite, and hematite along bedding planes. Bedding-plane permeability seems to have been an inherent feature of the lower units of the Todilto in the Grants district.

The geochemical environment that existed as the uraninite was deposited is not fully understood. The pH of the mineralizing solutions must have been nearly neutral or slightly alkaline. Large masses of the limestone have been almost completely recrystallized, but are not characteristically mineralized with uraninite. Those parts of the limestone that contain the uraninite show relatively little recrystallization and only minor extraction of the carbonate constituent; this condition would not exist if the mineralizing solutions had been acid. Even moderately acid mineralizing solutions would have dissolved substantial amounts of the limestone; conversely, strongly alkaline solutions, or solutions nearly saturated with carbonate ions, probably would not have permitted replacement of calcite by uraninite. It is concluded that recrystallization of the limestone was not an essential feature of the mineralizing process and that the fact that uraninite occurs in some of the least recrystallized parts of the limestone is indicative of nearly neutral or moderately alkaline solutions.

The environment was undoubtedly reducing and sulfurous as uraninite was being deposited. The uranium ores of the Ambrosia Lake district are characterized by an abundance of very fine grained iron sulfides that are dispersed throughout the mineralized parts of the rock. Iron sulfides also are present in ores of the Todilto Limestone, althought not so abundantly. The limestone itself is a fetid rock.

The state of the uranium as it was introduced into the limestone is a subject that can only be speculated upon. Some, and possibly all, of the uranium may have existed in the uranyl form, most likely as a uranyl carbonate complex. The sulfide ion readily reduces the uranyl ion under some conditions, and it probably was the reducing agent in the Todilto Limestone.

Phase relations that exist with varying temperatures and pressures in complex solutions containing uranyl, uranous, sulfide, and carbonate ions, and which may be in contact with solid phases of uranium oxides, are virtually unknown. The presence of uraninite in the Todilto Limestone seems to indicate that reduction of uranyl uranium by sulfide ions may occur in a carbonate environment, but the concentrations of reacting constituents, and the Eh and pH of the solutions, cannot be stated from present knowledge. The only alternative is that uranium might be transported in the uranous state and be deposited by some process that cannot be explained on the basis of present knowledge.

URANIUM DEPOSITS IN THE SUNDANCE FORMATION, WYOMING

Some small, low-grade uranium deposits are found in lenticular limestone beds at the base of the Sundance Formation in Wyoming. These deposits have some features similar to those of deposits in the Todilto Limestone and therefore are classed as peneconcordant.

The largest known deposits in the Sundance Formation are in sec. 3, T. 44 N., R. 83 W., in Johnson County. This locality is on the east flank of the Bighorn Mountains and about 2 miles southwest of the abandoned Mayoworth post office. The formations exposed in the vicinity of the uranium deposits are the Chugwater, Sundance, and Morrison. The upper part of the Chugwater, of Triassic and Permian age, consists of a thick section of massive to crossbedded fine-grained red sandstone. The Sundance Formation, of Jurassic age, consists of a basal lenticular limestone having a maximum thickness of about 20 feet that is overlain by beds of nonglauconitic sandstone and shale approximately 200 feet thick and an upper sequence of glauconitic shale and sandstone about 150 feet thick; all these units contain marine fossils. The Morrison Formation, of Jurassic age, consists of shale and sandstone. The only uraniferous material that has been found in these formations in this locality, other than the deposits in the limestone, is fossil dinosaur bone in the Morrison Formation (Love, 1954, p. 3).

The formations at the Mayoworth locality strike approximately N. 30° W. and dip 12° to 15° NE. The largest exposure of the limestone at the base of the Sundance Formation is within an area of several acres on a northeastward-facing dip slope in the SW¼ sec. 3. This limestone bed feathers out within distances of about a mile to the northwest and southeast.

The limestone consists predominantly of calcitic oölites cemented with calcite. It is mostly dull grayish brown, but in places it is reddish because of local abundance of iron oxides. The freshly broken rock is strongly fetid. The limestone contains no recognizable organic matter, and organic solvents extract no material from it. Chemically the rock is a calcitic nonphosphatic limestone (table 2, II–B, No. 249721).

Metatyuyamunite is irregularly distributed within the limestone, some forming coatings on fracture surfaces and some replacing, or partly replacing, oölites and calcite cement. These two modes of deposition do not everywhere occur together; consequently, the most richly mineralized parts of the limestone are small pockets where the two occur together. The uranium content of the rock generally is substantially less than 0.1 percent except for a few small pockets. A petrographic description of the rock has been presented by Guilinger and Theobald (1957).

Inasmuch as most of the metatyuyamunite on fracture surfaces obviously is redistributed, it seems that the primary uranium deposition involved replacement of the oölites and calcite cement. Whether metatyuyamunite is the primary uranium mineral or an alteration product of some previously existing mineral is unknown. No structural control of deposition has been observed, perhaps because observations have been restricted to the upper surface of the limestone and to a few prospect pits not exceeding 5 feet in depth.

The source of the uranium in the limestone is a subject for speculation. The author has observed no features that indicate syngenetic deposition of the uranium. The limestone can be considered to be nonphosphatic (table 2, II–B, No. 249721 contained less than 0.05 percent P_2O_5) and is a type not likely to contain above-average quantities of syngenetic uranium. The uranium probably was carried into an originally porous limestone by ground-water solutions and was precipitated in the reducing environment of the fetid rock. There is no apparent source of uraniferous solutions in the immediate vicinity. No other appreciable concentrations of uranium minerals are known to exist for considerable distances around the Mayoworth locality. There are no intrusive igneous rocks or hot-spring deposits nearby that could point to possible hydrothermal solutions. The uranium may have been leached from other rocks of the region and concentrated in the limestone. Love (1954) has suggested that it might have been leached from volcanic ash in the White River Formation of Oligocene age, which was deposited unconformably upon the upturned edges of the Jurassic formations but which subsequently was eroded from the area.

The uranium probably was deposited epigenetically in the limestone. If uraniferous solutions entered the limestone and a reducing environment was encountered, it is reasonable to assume that the primary mineral was uraninite; because the known deposits are within 5 feet of the surface of the ground where oxidation is complete, no trace of uraninite has been found.

SUMMARY

Uranium deposits can be formed epigenetically in carbonate rocks by several mechanisms. Some of these mechanisms produce deposits that furnish interesting mineralogical specimens but generally do not provide ores; most of the efflorescent deposits belong in this category. Other mechanisms have produced a few deposits that have been mined profitably primarily for their uranium contents alone; examples of these deposits are the hydrothermal veins at Shinkolobwe, Republic of Congo, the peneconcordant deposits in the Todilto Limestone in New Mexico, and deposits in the karst terrains of the Pryor Mountains in Montana and the Bighorn Range in Wyoming.

Carbonate rocks are less favorable host rocks for epigenetic uranium deposits than are clastic sedimentary rocks, metamorphosed clastic sedimentary rocks, and igneous rocks. Carbonate rocks that contain significant epigenetic uranium deposits are in the so-called uranium provinces of the earth, and even in these regions the deposits generally seem to be restricted to a single carbonate rock formation.

The exact physical and chemical conditions that cause primary deposition of uranium in carbonate rocks are virtually unknown. Uraninite seems to be the only primary uranium mineral deposited in the hydrothermal veins. Tyuyamunite, uranophane, uraniferous fluorite, and possibly other minerals may be deposited as primary constituents in some of the other types of deposits, but this point has not been established definitely. It cannot be stated that the same chemical conditions existed during mineralization of deposits having different physical characteristics. The fact that uraninite can be deposited in carbonate rocks, and apparently from solutions rich in carbonate, or bicarbonate, or carbonate and bicarbonate ions, seems to be puzzling, but this circumstance merely points out a gap in our knowledge of the chemical behavior of uranium.

Only a few favorability criteria can be suggested that might aid in the discovery of epigenetic uranium deposits in carbonate rocks. The known significant deposits are in uranium provinces, and this circumstance would seem to define favorable regions. Uraniferous hydrothermal veins in carbonate rocks are most likely to be found in districts where similar veins occur in other types of rocks. Uranium deposits in karst terrains are most likely to exist where there has been deep-seated hydrothermal activity; a less favorable criterion is the presence, or former presence, of tuffaceous or arkosic sediments that could have furnished uranium for supergene enrichment. The only known peneconcordant deposits are in fetid limestones.

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TABLE 2.—*Analyses in percent of some carbonate rocks and source materials*

[Analysts: R. P. Cox, E. J. Fennelly, D. L. Ferguson, W. D. Goss, Claude Huffman, H. H. Lipp, E. C. Mallory, Wayne Mountjoy, W. W. Niles, L. F. Rader, D. L. Schafer, J. P. Schuch, and D. L. Skinner]

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
I. ROCKS AND SOURCE MATERIALS CONTAINING ONLY SYNGENETIC URANIUM																			
A. Marine limestones—no significant metamorphism, nonfetid																			
260486	Burlington Limestone.	Early Mississippian.	Road cut, U.S. Highway 60, east bank James River, Galloway, Mo.	0.1	55.4	<0.5	0.15	0.030	0.02	-------	<0.0001	0.1	98.87	<1.05	0.05	-------	0.15	99.1+	Light-gray medium-grained limestone. Contains a few fossil brachiopods and fragments of crinoid stems. Composed of calcite and traces of very fine grained clay-size material.
260492	Madison Limestone.	Mississippian	Open pit, Tripacer claims, T. 58 N., R. 94 W., Bighorn County, Wyo.	<.1	55.3	<.5	.13	.020	<.01	-------	<.0001	<.1	98.75	<1.05	<.02	-------	.13	98.9+	Buff fine-grained dense limestone. Contains poorly preserved microfossils. Composed of minute calcite grains (about 35 percent) in a matrix of extremely fine grained calcite. Calcite is the only mineral that can be identified under the microscope.
260449	Washita Group	Cretaceous	Top of Kings Mountain, 4 miles northeast of McCamey, Tex.	1.2	54.1	.6	.42	.121	<.01	-------	.0003	1.2	96.60	1.26	<.02	-------	.42	99.5	Buff fine-grained dense limestone. Contains some small macrofossils and many microfossils. Composed of an extremely fine grained matrix of calcite in which there are scattered small grains and stringers of clear colorless secondary calcite, some replacing fossils, and a few minute quartz grains.
260493	Madison Limestone.	Mississippian	Sec. 4, T. 9 S., R. 27 E., Carbon County, Mont.	2.5	53.4	.6	.02	.020	<.01	-------	<.0001	2.5	95.36	1.26	<.02	-------	.02	99.1+	Buff fine-grained dense limestone. Composed of an extremely fine-grained calcite matrix in which there are small grains of calcite and minute grains of quartz.
249720	Salem Limestone.	Late Mississippian.	Upper bench Busson's quarry, Ste. Genevieve, Mo.	1.75	53.2	<1.0	.20	.11	<.05	-------	.0004	1.75	95.00	<2.09	<.12	-------	.20	97.0+	Gray medium-grained oölitic limestone cemented with calcite. Microfossils are abundant, many with aggregates of minute quartz grains or cryptocrystalline silica in the interior parts. There are a few minute grains of detrital quartz.
249711	St. Louis Limestone.	Late Mississippian.	Abandoned quarry, N½ sec. 34, T. 3 S., R. 4 E., near Corydon, Ind.	3.47	53.2	<1.0	1.30	.82	.05	-------	<.0001	3.47	94.89	<2.09	.12	-------	1.30	99.8+	Dark-gray fine-grained fossiliferous limestone. Composed of calcite grains, macrofossils, microfossils, and oölites(?). Many of the fossils are composed of cryptocrystalline silica. There are some small aggregates of fine-grained clay-size material and many minute pyrite granules.
260453	Sinbad Limestone Member of Moenkopi Formation.	Early Triassic	SW¼ sec. 6, T. 21 S., R. 13 E., Grand County, Utah.	4.1	52.7	.8	1.4	.81	.12	0.005	.0001	4.1	93.84	1.67	.28	-------	1.4	101.3	Dark-gray fine-grained dense limestone. Composed chiefly of extremely fine grained calcite; minor constituents are fine-grained detrital quartz (about 2 percent), pyrite and other opaque minerals, and traces of petroliferous residue.
249710	Maysville Group.	Late Ordovician.	Road cut, U.S. Highway 60, 5 miles west of Frankfort, Ky.	4.55	52.1	1.1	2.11	.88	.13	.021	<.0001	4.55	92.71	2.30	.31	0.02	2.11	102.0	Gray medium-grained fossiliferous limestone. Rock is about 25 percent fossils. Composed of fine-grained calcite, minor quantities of detrital quartz, clay, phosphatic material, and a very minute quantity of pyrite.

TABLE 2.—*Analyses, in percent, of some carbonate rocks and source materials*—Continued

I. ROCKS AND SOURCE MATERIALS CONTAINING ONLY SYNGENETIC URANIUM—Continued

A. Marine limestones—no significant metamorphism, nonfetid—Continued

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
260444	Nicholas Limestone. Member of Cynthiana Formation.	Middle Ordovician.	Abandoned quarry 2 miles east of Carlisle, Ky.	5.6	51.1	<.5	2.3	0.90	0.07	0.007	0.0002	5.6	91.09	<1.05	0.16	-------	2.3	99.2+	Gray fine-grained fossiliferous limestone. Rock is about 5 percent fossils. Composed of fine-grained calcite, minor quantities of detrital quartz, clay, phosphatic material, and a very minute quantity of pyrite.
260447	Catheys Limestone.	do	Road cut, U.S. Highway 31, 2 miles north of Columbia, Tenn.	4.9	50.3	1.5	2.2	.54	.59	.064	.0002	4.9	88.41	3.14	1.40	0.02	2.2	100.1	Fine-grained, mottled gray and brown, fossiliferous limestone. Composed chiefly of irregular-sized calcite grains, phosphatized microfossils (2 to 3 percent), small quantities of detrital quartz and clay, and scattered minute granules of pyrite. Macrofossils are composed of calcite.
260445	Bigby Limestone.	do	do	2.2	52.3	.7	5.2	.20	2.85	.39	.0002	2.2	86.32	1.46	6.75	.29	5.2	102.2	Medium-grained mottled gray and brown limestone. Composed chiefly of calcite. Many phosphatized microfossils (3 to 4 percent), detrital quartz (about 1 percent), a few minute pyrite granules, and specks of iron oxide.
260451	Belden Formation.	Pennsylvanian.	West slope of Vail Pass, Eagle County, Colo.	11.9	47.0	.6	4.0	.74	.13	.016	.0006	11.9	83.62	1.25	.31	.01	4.0	101.1	Dark-gray fine-grained fossiliferous limestone. Composed chiefly of calcite. Many microfossils, some phosphatized. Some small granules of phosphatic material are interstitial to calcite grains. There are very small quantities of detrital quartz, minute pyrite granules, and a black opaque mineral. Bulk of insoluble matter seems to be finely divided clay.
260446	Hermitage Formation.	Middle Ordovician.	Road cut, U.S. Highway 31, 2 miles north of Columbia, Tenn.	24.3	34.0	1.2	13.7	.50	6.87	.71	.0004	24.3	44.35	2.51	16.26	.20	13.7	101.3	Dark-gray fine-grained arenaceous limestone. A few fossil brachiopods; many microfossils, most of which are phosphatized. Composed of calcite matrix, about 15 percent recognizable phosphatic material, 10 percent detrital quartz, 2 percent detrital feldspar, come clay, and a few minute pyrite granules.
260480	Twin Creek Limestone.	Middle and Late Jurassic.	Road cut, U.S. Highway 40, Parleys Canyon, Utah.	32.2	33.6	1.2	8.3	.19	.12	.056	.0004	32.2	59.62	2.51	.28	.09	8.3	103.0	Gray fine-grained argillaceous limestone. Slaty cleavage. Only recognizable constituents are minute grains of quartz, muscovite(?), and pyrite. Almost opaque in thin section.

B. Marine Limestone—metamorphosed, completely recrystallized, nonfetid

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
249718	Leadville Limestone.	Mississippian.	Abandoned Strauss quarry, Marble, Colo.	0.03	56.1	<1.0	0.18	0.08	<0.05	-------	0.0003	0.03	100.17	<2.09	<0.12	-------	0.18	100.4+	White medium-grained marble. Almost pure calcite.
249705	Stockbridge Limestone	Cambrian and Ordovician.	Quarry at Farnams, Mass.	.75	56.0	<1.0	.30	.11	<.05	-------	.0002	.75	100.00	<2.09	<.12	-------	.30	101.1+	Light-gray medium-grained marble. Contains a few grains of detrital quartz, numerous granules of graphitic carbon, and a few granules of pyrite.

249714	Franklin Limestone.	Precambrian	Abandoned quarry at McAfee, N.J.	1.59	54.5	<1.0	.22	.16	<.05	------	<.0001	1.59	97.32	<2.09	<.12	------	.22	99.1+	White very coarse-grained limestone. Composed of coarse calcite crystals, a few grains of quartz and graphite, aggregates of epidote, and pyrite granules.
260491	Leadville Limestone.	Mississippian	Quarry at Garfield, Colo.	.3	53.5	1.7	------	------	<.01	------	.0003	.3	95.53	3.55	<.02	------	------	99.4+	Gray medium-grained limestone. Contains traces of graphitic carbon, minute pyrite granules, and granules of colorless zoisite(?) or epidote(?).
249716	Hermosa Formation.	Middle Pennsylvanian.	Bank of Yule Creek, Marble, Colo.	4.07	53.4	1.0	.55	.23	.06	0.017	.0004	4.07	95.19	2.09	.14	0.02	.55	102.0	Gray fine-grained limestone. Contains minute grains of quartz, colorless zoisite(?) or epidote(?), and tiny granules of pyrite and graphitic carbon.

C. Marine Limestone—no significant metamorphism, fetid

260450	Hueco Lime stone.	Permian	Abandoned road cut, U.S. Highway 62, 1 mile west of Hueco Inn, Hudspeth County, Tex.	1.5	54.3	0.5	0.29	0.055	<0.01	------	0.0002	1.5	96.96	1.05	<0.02	------	0.29	99.8+	Light-tan fine-grained dense limestone. Contains about 45 percent poorly preserved microfossils, a few aggregates of cryptocrystalline silica, and specks of powdery iron oxide probably formed by alteration of pyrite.
260478	Madison Limestone.	Mississippian	Center E½ sec. 14, T. 3 S., R. 7 E., Wasatch County, Utah.	.5	53.2	1.7	.14	.030	<.01	------	.0004	.5	95.00	3.56	<.02	------	.14	98.7+	Dark grayish-brown fine-graine limestone. Composed chiefly of very fine grained calcite enclosing scattered large crystals of calcite, a few small aggregates of cryptocrystalline silica, and traces of clay. Rock contains scattered macrofossils and microfossils. Color probably is due to organic matter.
260481	Unknown	------	Road cut, U.S. Highway 50, 40.2 miles east of Eureka, Nev.	2.9	53.4	.7	.70	.14	.20	0.030	.0001	2.9	94.87	1.46	.47	0.02	0.70	100.4	Light-brown fine-grained dense limestone containing small chert nodules. Sample analyzed contained no chert nodules. Composed chiefly of fine-grained calcite and a small amount of detrital quartz and feldspar, and scattered tiny specks of iron oxide probably formed by alteration of pyrite.
260483	Pinery Limestone Member of Bell Canyon Formation.	Permian	Outcrop on south side of U.S. Highway 62, 1 mile east Salt Flat, Tex.	1.5	53.4	<.5	.42	.18	.07	.018	.0001	1.5	95.18	<1.05	.17	.02	.42	97.3+	Brown fine-grained dense limestone. Composed chiefly of very fine grained calcite and scattered small grains of colorless calcite, a few tiny grains of detrital quartz, small aggregates of cryptocrystalline silica, and minute pyrite granules; microfossils are abundant.

D. Marine magnesian limestone—no significant metamorphism, fetid

260448	Edwards Limestone.	Early Cretaceous.	South slope King Mountain, 2 miles northeast of McCamey, Tex.	1.8	48.8	4.5	1.1	0.54	0.02	------	0.0001	1.8	87.09	9.41	0.05	------	1.1	99.50	Light-tan fine-grained dense limestone containing small chert nodules. Composed chiefly of very fine grained calcite and tiny grains of detrital quartz, aggregates of cryptocrystalline silica, and specks of iron oxide. Rock is partly stained brownish, possibly by organic matter. There are a few microfossils.
260488	Hueco Limestone.	Permian	Road cut, U.S. Highway 62, Hueco Gap. Hudspeth County, Tex.	4.0	49.4	3.1	.42	.030	<.01	------	<.0001	4.0	88.21	6.48	<.02	------	.42	99.1+	Light-brown fine-grained limestone. Composed chiefly of fine-grained calcite and scattered larger grains; microfossils are abundant; some seem to be phosphatized and others are composed partly of cryptocrystalline silica. Specks of iron oxide, probably formed from pyrite, are abundant.

Table 2.—*Analyses, in percent, of some carbonate rocks and source materials*—Continued

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
I. ROCKS AND SOURCE MATERIALS CONTAINING ONLY SYNGENETIC URANIUM—Continued																			
D. Marine magnesian limestone—no significant metamorphism, fetid—Continued																			
260452	Sinbad Limestone Member of Moenkopi Formation.	Early Triassic	SW¼ sec. 6, T. 21 S., R. 13 E., Grand County, Utah.	6.2	49.0	2.2	2.1	0.84	0.04	0.011	0.0002	6.2	87.39	4.60	0.09	0.02	2.1	100.4	Gray medium-grained asphaltic limestone having many small cavities; petroleum stained. Composed of fine-grained calcite and coarser grained secondary calcite lining cavities. Small detrital quartz grains are abundant. Rock contains about 0.3 percent pyrite and many microfossils, a few of which are phosphatized.
260457	Chaffee Formation.	Late Devonian.	Road cut, U.S. Highway 6–24, east end of Glenwood Canyon, Garfield County, Colo.	11.4	38.2	9.0	2.3	.44	.06	.025	.0001	11.4	68.05	18.83	.14	.04	2.3	100.7	Dark-gray fine-grained dense limestone. Composed of an extremely fine grained matrix in which there are many small calcite grains and detrital quartz grains. Scattered granules and small stringers of pyrite constitute about 0.1 percent of the rock. There are a few macrofossils.
260463	Salem Limestone.	Late Mississippian.	Middle bench, Busson's quarry, Ste. Genevieve, Mo.	18.1	33.2	8.8	4.3	1.24	.05	.048	.0003	18.1	59.05	18.41	.12	.09	4.3	100.1	Gray fine-grained argillaceous limestone. Composed chiefly of very fine grained carbonate minerals and substantial amounts of detrital quartz and clay; small blebs and stringers of an opaque black substance probably are carbonized organic residue. Rock contains a few tiny granules of pyrite.
249718	Pierre Shale	Late Cretaceous.	Road cut U.S. Highway 40, 5 miles west of Kremmling, Colo.	17.8	38.9	3.5	5.59	2.45	.65	.037	.0001	17.8	67.95	7.32	1.54	------	5.59	100.2	Gray fine-grained argillaceous limestone. Composed of an extremely fine grained, almost opaque matrix, 2 to 3 percent detrital quartz and feldspar, 2 to 3 percent phosphatic material, abundant shreds and blebs of black opaque material that is probably an organic residue, and many granules and tiny veinlets of pyrite.
260458	Carmel Formation.	Middle and Late Jurassic.	Northeast end ot San Rafael Swell, Emery County, Utah.	27.6	35.8	2.5	4.7	.75	.12	.025	.0002	27.6	63.62	5.23	.28	.03	4.7	101.5	Grayish-brown fine-grained dense limestone. Contains about 5 percent detrital quartz and feldspar and a considerable amount of clay and iron oxide.
E. Marine magnesian limestone—metamorphosed, completely recrystallized, nonfetid																			
249713	Franklin Limestone.	Precambrian	Abandoned quarry at Franklin, N.J.	0.17	51.8	3.3	0.45	0.26	<0.05	------	<0.0001	0.17	92.50	6.90	<0.12	------	0.45	100.0+	White, very coarse grained limestone. Composed of large grains of carbonate minerals and a few flakes of graphite and phlogopite.

F. Nonmarine magnesium limestone—no significant metamorphism, nonfetid

260490[1]	Uinta Formation.	Eocene	Near Pariette gilsonite mine, Uintah County, Utah.	9.4	40.2	3.6	3.5	1.90	0.28	0.054	0.021	9.4	71.07	7.53	0.66	0.04	3.5	92.20	Brown, extremely fine grained limestone containing small quantities of organic matter, manganese oxide(?), detrital quartz and feldspar, and analcite(?).
260464	Mahogany oil shale bed of Parachute Creek. Member of Green River Formation.	do	NW¼ sec. 20, T. 10 S., R. 25 E., Uintah County, Utah.	55.0	14.8	6.7	7.6	2.41	.09	.11	.0004	55.0	25.89	14.01	.21	.25	7.6	103.0	Dark-brown marlstone containing at least 25 percent kerogenous organic matter. Rock is mostly too fine grained and opaque to permit identification of constituents. It contains at least 5 percent analcite in visible grains, 1 to 2 percent pyrite, and scattered small grains of detrital quartz.

G. Dolomite—no significant metamorphism, nonfetid

249702	Niagara Group	Middle Silurian.	Quarry at Genoa, Ohio.	0.23	31.1	22.3	0.21	0.10	<0.05	-------	0.0001	0.23	55.54	46.65	<0.12	-------	0.21	102.6+	White medium-grained dolomite. No recognizable constituent other than dolomite.
249703	do	do	do	.45	31.0	21.1	.19	.07	<.05	-------	<.0001	.45	55.36	44.14	<.12	-------	.19	100.1+	Brown fine-grained dolomite. No recognizable constituent other than dolomite. Rock is petroleum stained.
249712	Little Falls Dolomite.	Late Cambrian.	Abandoned quarry at Canajoharie, N.Y.	5.72	29.5	19.8	1.43	.69	<.05	-------	<.0001	5.72	52.68	41.42	<.12	-------	1.43	101.3+	Grayish-brown fine-grained dolomite. Contains a small quantity of detrital quartz, small aggregates of cryptocrystalline silica, and minute granules of a pyrobitumen generally called anthraxolite.

H. Dolomite—no significant metamorphism, fetid

249715	Fremont Limestone.	Late Ordovician.	Sec. 24 and 25, T. 48 N., R. 5 E., Saguache County, Colo.	0.43	30.6	22.4	0.33	0.20	<0.05	-------	0.0004	0.43	54.64	46.86	<0.12	-------	0.33	102.3+	Grayish-brown fine-grained dolomite. No recognizable constituent other than dolomite. Rock is slightly stained by a brown substance.

I. Dolomite—metamorphosed, completely recrystallized, nonfetid

249717	Leadville Limestone.	Mississippian	Strauss quarry, Marble, Colo.	0.56	31.1	20.6	0.82	0.72	<0.05	-------	<0.0001	0.56	55.54	43.09	<0.12	-------	0.82	100.0+	Light-gray fine-grained dolomite. Contains a few tiny aggregates and stringers of cryptocrystalline silica and minute pyrite grains.
249704	Stockbridge Limestone.	Cambrian and Ordovician.	Quarry at Farnams, Mass.	2.05	30.7	20.2	.48	.28	<.05	-------	<.0001	2.05	54.82	42.25	<.12	-------	.48	99.6+	Light-gray fine-grained dolomite. Contains about 1 to 1½ percent quartz and a few minute muscovite grains.
240487	do	do	Abandoned quarry at Ashley Falls, Mass.	3.5	32.7	17.4	.93	.18	.02	-------	<.0001	3.5	58.34	36.40	.05	-------	.93	99.2	White medium-grained dolomite. Contains about 1 to 1½ percent tremolite, a few small quartz grains, and some minute muscovite flakes.
269706	Kittatinny Limestone.	Late Cambrian and Ordovician.	Mulligan quarry, Clinton, N.J.	8.59	28.4	19.4	2.64	.36	.40	0.05	.0020	8.59	49.72	40.58	.95	0.03	2.64	102.5	Gray fine-grained dense dolomite. Contains a few small quartz grains and tiny quartz veinlets and minute granules of an iron mineral.
429707	do	do	do	9.85	27.7	18.9	2.69	.67	.05	-------	.0006	9.85	49.34	39.54	.12	-------	2.69	101.5	Dark-gray fine-grained dense dolomite. Contains a few small quartz grains and tiny veinlets filled with quartz, pyrite, and graphitic carbon(?). There are many very minute pyrite granules distributed throughout the rock.

See footnote at end of table.

TABLE 2.—*Analyses, in percent, of some carbonate rocks and source materials*—Continued

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
I. ROCKS AND SOURCE MATERIALS CONTAINING ONLY SYNGENETIC URANIUM—Continued																			
I. Dolomite—metamorphosed, completely recrystallized, nonfetid—Continued																			
249708	Milton Dolomite.	Late Cambrian.	Outcrop on east side of U.S. Highway 7, south of Milton, Vt.	13.80	28.4	17.1	4.80	1.06	3.06	.29	.0030	13.80	43.50	35.77	7.24	.04	4.80	105.13	Gray fine-grained siliceous dolomite. Contains about 10 percent quartz and about 2 percent of a brown to black substance that seems to be an organic residue; phosphatic constituent probably is mixed with this residual substance. Extremely fine grained pyrite is dispersed throughout the rock. (R_2O_3 probably includes some $(PO_4)^{-3}$.)
249709	do	do	do	22.45	24.0	15.8	3.46	1.16	.70	.078	.0014	22.45	41.18	33.05	1.66	.03	3.46	101.8	Gray fine-grained siliceous dolomite. Composed chiefly of cloudy carbonate mineral and about 10 percent quartz and cryptocrystalline silica. Some of the cloudiness seems to be due to clay-size detritus. Contains a few minute pyrite granules.
J. Nonmarine limestone—not metamorphosed, nonfetid																			
260482	Flagstaff Limestone.	Late Paleocene and early Eocene(?).	Abandoned Bird's Eye quarry, sec. 30, T. 10 S., R. 4 E., Utah County, Utah.	1.4	53.9	<0.5	0.62	0.16	0.05	0.008	0.0001	1.4	96.12	<1.05	0.12	0.008	0.62	98.3+	Light-brown, extremely fine grained dense limestone. Only constituent that can be identified is calcite.
260465	Fresh-water marl.	Modern	Lake bottom, 1½ miles south of Charlo, New Brunswick, Canada.	2.8	52.2	.5	1.0	.11	.03	.005	<.0001	2.8	93.11	1.05	.07	.004	1.0	98.0	Buff unconsolidated marl currently being deposited. Composed chiefly of extremely fine grained calcium carbonate and a small quantity of clay and silt.
260479	Pony Express Limestone Member of Wanakah formation.	Late Jurassic	Abandoned quarry, Sawpit, Colo.	5.0	51.1	.5	.91	.19	.02	-------	.0001	5.0	91.20	1.05	.05	-------	.91	98.2	Very dark gray, extremely fine grained dense limestone; contains about 3 percent detrital quartz, some detrital feldspar, and minute granules of pyrite.
K. Nonmarine magnesian limestone—not metamorphosed, nonfetid																			
260485	Green River Formation.	Eocene	SW¼ sec. 14, T. 10 S., R. 6 E., Utah County, Utah.	16.8	29.1	10.8	3.7	1.00	0.17	0.085	<0.0001	16.8	51.37	22.59	0.40	0.15	3.7	95.0	Buff, extremely fine grained marlstone. Mostly too fine grained for identification of constituents. Contains a few tiny grains of a carbonate mineral, quartz, and pyrite.
L. Calcareous tufa from uraniferous district—not metamorphosed, nonfetid																			
260456	Tufa	Recent	S½ sec. 24, T. 30 N., R. 90 W. Fremont County, Wyo.	7.2	49.7	1.6	0.68	0.03	0.12	0.050	0.0004	7.2	88.36	3.35	0.28	0.08	0.68	100.0	Buff fine-grained deposit of extinct spring. Composed chiefly of calcite and contains about 3 percent quartz and cryptocrystalline silica, traces of organic matter, limonite, and some clay.

M. Shells of Modern organisms

260489	Land snail	Modern	Sec. 29, T. 6 S., R. 4 E., Utah County, Utah.	0.1	55.0	<0.5	0.09	0.011	0.02	------	<.0001	0.1	98.16	<1.05	0.05	------	0.09	98.4+	Includes small amount of chitin. Snails lived on a terrain of Flagstaff Limestone.
260468	Barnacle	do	Falmouth, Mass.	<.1	54.0	<.5	.11	.020	<.01	------	<.0001	<.1	96.43	<1.05	>.02	------	.11	96.5+	Shells contained small amount of organic matter.
260467	Clam, *tivela stultorum.*	do	Lions Head, Santa Barbara County, Calif.	<.1	53.2	<.5	.11	.013	<.01	------	<.0001	<.1	95.00	<1.05	>.02	------	.11	95.1+	Includes a small quantity of chitin and other organic matter.
260489	Blue mussel, *mytilus edulis.*	Modern	Hull, Mass	.2	50.0	<.5	.42	.020	.06	.006	<.0001	.2	89.12	<1.05	.14	.002	.42	89.7+	Includes some chitin and other organic matter.

II. ROCKS CONTAINING EPIGENETIC URANIUM

A. Marine limestone—not metamorphosed, nonfetid

260484[2]	Tansill Formation.	Permian	SE¼ sec. 21, T. 22 S., R. 25 E., Eddy County, N. Mex.	0.05	55.0	<0.5	0.34	0.14	0.05	0.010	0.0054	0.5	98.09	<1.05	0.12	0.01	0.34	99.1+	Brownish-gray fine-grained vuggy limestone. Vugs are lined with secondary calcite. Small specks and stains of reddish-brown iron oxide are distributed throughout the rock. Traces of a powdery yellow mineral, probably tyuyamunite, occur on some vug walls.

B. Marine limestone—not metamorphosed, fetid

249721	Sundance Formation.	Late Jurassic	Sec. 3, T. 44 N., R. 83 W., Johnson County, Wyo.	5.11	52.8	<1.0	0.86	0.44	<0.05	------	0.055	5.11	94.28	<2.09	<0.12	------	0.86	100.2+	Mottled reddish-brown and gray öolitic limestone containing about 0.2 percent metatyuyamunite on fracture surfaces and irregularly distributed throughout the rock, about 4 percent detrital quartz and feldspar, 1 percent cryptocrystalline silica, and stains of reddish-brown iron oxide.

C. Nonmarine limestone—not metamorphosed, fetid

260469	Todilto Limestone.	Late Jurassic	NW¼ sec. 31, T. 13 N., R. 9 W., McKinley County, N. Mex.	4.7	53.2	0.5	0.89	0.13	0.04	0.020	0.0005	4.7	94.87	1.05	0.09	0.03	0.89	101.6	Brownish-gray fine-grained dense limestone. Contains about 3.5 percent detrital quartz and feldspar, a few minute specks of iron oxide, and traces of tyuyamunite on fracture surfaces.
260470	do	do	do	2.7	52.7	<.5	.78	.16	.02	------	.031	2.7	94.05	<1.05	.05	------	.78	97.6	Brownish-gray fine-grained dense limestone. Contains about 2 percent detrital quartz and feldspar, traces of iron oxide and tyuyamunite.
260471	do	do	do	10.6	46.9	.8	2.8	.35	.06	.024	.0006	10.6	83.55	1.67	.14	.04	2.8	98.8	Light brownish-gray fine-grained thin-bedded silty limestone. Contains about 10 percent detrital quartz and feldspar, a few minute granules of iron oxide and pyrite, and thin films of tyuyamunite.
260472	do	do	do	8.2	49.1	.5	1.3	.25	.08	.018	.0032	8.2	87.46	1.05	.18	.02	1.3	98.2	Brownish-gray fine-grained dense limestone. Contains about 7 percent detrital quartz and feldspar, and a few specks of reddish-brown iron oxide. There are traces of tyuyamunite on fracture surfaces.

See footnote at end of table.

TABLE 2.—*Analyses, in percent, of some carbonate rocks and source materials*—Continued

Laboratory sample	Source	Age	Locality	Chemical composition								Approximate mineral composition							Remarks
				Acid-insoluble matter	CaO	MgO	R_2O_3	Fe as Fe_2O_3	P_2O_5	F	U	Acid-insoluble detritus	$CaCO_3$	$MgCO_3$	$(CaF)Ca_4(PO_4)_3$	CaF_2	R_2O_3	Total	
II. ROCKS CONTAINING EPIGENETIC URANIUM—Continued																			
C. Nonmarine limestone—not metamorphosed, fetid—Continued																			
260473	Todilto Formation.	Late Jurassic	NW¼ sec. 31, T. 13 N., R. 9 W., McKinley County, N. Mex.	15.5	44.9	0.5	2.1	0.22	0.07	0.025	0.023	15.5	79.98	1.05	.16	0.04	2.1	98.8	Brownish-gray fine-grained dense limestone. Contains about 15 percent detrital quartz and feldspar, a few specks of reddish-brown iron oxide and pyrite granules. There are traces of tyuyamunite on fracture surfaces.
260474	do	do	do	16.1	45.4	.4	1.9	.14	.04	.009	.0039	16.1	80.98	.84	.09	.01	1.9	99.9	Brownish-gray fine-grained dense limestone. Contains about 15 percent detrital quartz and feldspar and a few specks of iron oxides. There is tyuyamunite on fracture surfaces.
260476	do	do	do	1.5	56.1	<.5	.88	.10	.08	.85	.45	1.5	97.78	<1.05	.18	1.73	.88	102.0+	Light brownish-gray fine-grained dense limestone. Contains about 1 percent detrital quartz, many tiny fluorite grains, and traces of tyuyamunite.
260475	do	do	do	1.5	53.7	<.5	.93	.45	.04	.048	.033	1.5	95.70	<1.05	.09	.09	.93	98.3+	Recrystallized limestone that is bleached and partly stained by iron oxides. The altered equivalent of sample 260469. Contains about 1 percent quartz in rounded and corroded grains, small aggregates of powdery tyuyamunite, and iron oxide stains.
260477	do	do	Sec. 25, T. 13 N., R. 9 W., McKinley County, N. Mex.	10.2	46.6	<.5	3.8	.51	.06	.067	1.19	10.2	82.91	<1.05	.14	.13	3.8	97.2+	Brownish-gray fine-grained dense limestone spotted and streaked with red iron oxide and uraninite. Contains about 8 percent detrital quartz and feldspar. Mineralized parts consist of a mixture of extremely fine grained reddish-brown substance (hematite?) and uraninite interstitial to, and replacing, calcite, and abundant minute pyrite granules.
III. ROCKS IN WHICH THE GENETIC CHARACTER OF THE URANIUM WAS NOT DETERMINED																			
A. Brackish water limestone—not metamorphosed, fetid																			
W66873[3]	Bear River Formation.	Early Cretaceous.	Sec. 4, T. 1 S., R. 42 E., Bonneville County, Idaho.	10.9	46.5	0.7	3.1	0.93	0.86	0.15	0.024	10.9	80.80	1.46	2.04	0.15	3.1	98.5	Gray fine-grained limestone containing a substantial quantity of organic matter.
W90218[3]	do	do	do	11.0	46.5	.6	4.1	.86	1.35	.17	.012	11.0	79.73	1.26	3.20	.10	4.1	99.4	Dark-gray thinly laminated limestone with thin coaly partings. Contains about 10 percent organic matter, 0.5 percent pyrite, and a few quartz grains. Phosphatic constituent probably is mixed with the dark coaly substance.
W67247[3]	do	do	do	12.6	45.8	.5	4.8	1.1	.91	.12	.011	12.6	79.55	1.05	2.15	.08	4.8	100.2	Gray fine-grained limestone containing a substantial quantity of organic matter.

W67241[3]	Bear River Formation.	Early Cretaceous.	Sec. 4, T. 1 S., R. 42 E., Bonneville County, Idaho.	36.7	30.9	.9	9.4	4.0	.34	.08	.022	36.7	54.26	1.88	.80	.10	9.4	103.1	Gray fine-grained argillaceous limestone with a substantial quantity of organic matter.

B. Carbonate concretions in marine shales—not metamorphosed, nonfetid

260454	Mancos Shale	Late Cretaceous.	Road cut, U.S. Highway 40, 1 mile west of Steamboat Springs, Colo.	20.6	41.0	1.1	5.8	1.66	0.10	0.016	0.0001	20.6	72.98	2.30	0.24	0.01	5.8	101.9	Gray fine-grained concretion in shale. Consists chiefly of very fine grained calcite, about 15 percent clay, 5 percent detrital quartz, a small quantity of organic matter, and a few pyrite granules.
260455	Monterey Shale	Miocene	Road cut, U.S. Highway 101, 2 miles north of Shell Beach, San Luis Obispo County, Calif.	24.4	19.5	14.2	6.2	2.25	.20	.047	.0005	24.4	43.00	29.70	.48	.06	6.2	103.8	Brownish-gray fine-grained concretion in shale. Consists chiefly of extremely fine grained material in which no minerals can be recognized, and contains about 15 percent detrital quartz and feldspars, a few granules of pyrite, and a trace of organic matter.

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[1] Collected by E. P. Beroni.
[2] Collected by A. P. Pierce and J. W. Mytton.
[3] Collected by James D. Vine.