(200)
T67r

Geology and Mineralogy

This document consists of 102 pages,
Series A

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

ORIGIN OF URANIUM DEPOSITS*

By

V. E. McKelvey, U. S. Geological Survey
D. L. Everhart, U. S. Atomic Energy Commission
R. M. Garrels, U. S. Geological Survey

March 1955

Trace Elements Investigations Report 504

---

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

USGS - TEI-504

GEOLOGY AND MINERALOGY

Distribution (Series A)	No. of copies
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Battelle Memorial Institute, Columbus	1
Carbide and Carbon Chemicals Company, Y-12 Area	1
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Butte	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	2
Division of Raw Materials, Hot Springs	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, St. George	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Washington	50
Division of Research, Washington	1
Dow Chemical Company, Pittsburg	1
Exploration Division, Grand Junction Operations Office	6
Grand Junction Operations Office	1
National Lead Company, Winchester	1
Technical Information Service, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Fuels Branch, Washington	10
Geochemistry and Petrology Branch, Washington	15
Geophysics Branch, Washington	15
Mineral Deposits Branch, Washington	20
E. H. Bailey, Menlo Park	5
A. L. Brokaw, Grand Junction	35
N. M. Denson, Denver	5
C. E. Dutton, Madison	1
W. L. Emerick, Plant City	1
J. H. Eric, Washington	1
R. M. Garrels, Washington	1
M. R. Klepper, Spokane	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
J. D. Love, Laramie	1
V. E. McKelvey, Menlo Park	1
L. R. Page, Washington	1
P. C. Patton, Denver	10
C. B. Read, Albuquerque	1
Q. D. Singewald, Beltsville	2
A. E. Weissenborn, Spokane	5
TEPCO, Denver	25
TEPCO, RPS, Washington, (including master)	5
	245

CONTENTS

ILLUSTRATIONS

TABLES

ORIGIN OF URANIUM DEPOSITS

By V. E. McKelvey[1], D. L. Everhart[2],
and R. M. Garrels[1]

ABSTRACT

Uranium is concentrated in certain silicic and silica-alkalic igneous rocks, pegmatites, veins, lenticular sandstones and conglomerates, low-rank high-ash coals, asphaltic materials, marine black shales, and phosphorites. Its distribution in igneous rocks, pegmatites, and veins shows its tendency to concentrate in late stage differentiates. In the granitic rocks, uranium occurs mainly as a minor constituent of accessory minerals that have cations (such as rare earths, thorium, and calcium) for which uranium can substitute isomorphously, but it also occurs as an acid-soluble interstitial constituent. In pegmatites, uranium occurs both in uraninite and in other uranium minerals in combination with niobium, thorium, and rare earths. Uranium is found in both high temperature veins, where it is mainly in the titanium minerals davidite and brannerite, and low temperature veins, where it is nearly always in pitchblende, the botryoidal variety of uraninite, although the mineral coffinite is being found in increasing amounts. The low temperature veins are of several overlapping types, but all are characterized by sulfides and many contain disseminated iron oxide. Whereas thorium is associated with uranium in igneous rocks and pegmatites, it is rare in the vein deposits of uranium. This separation may be accomplished by oxidation of U^{+4} at a late magmatic stage to $(UO_2)^{+2}$ in which form it is carried away from the unoxidizable Th^{+4}. Subsequently $(UO_2)^{+2}$ is reduced and deposited as pitchblende along with sulfides and other low-valent minerals in veins.

The sandstone uranium deposits resemble the pitchblende veins in their mineralogic assemblage except that many of the sandstone deposits also contain vanadium, a metal not abundant in veins.

[1] Geologist, U. S. Geological Survey

[2] Geologist, U. S. Atomic Energy Commission

Isotopic studies indicate that the Plateau deposits are epigenetic and they suggest that the uranium was derived from a deep-seated source. It is possible, however, that the uranium might have been derived from volcanic ash or other dispersed sources within the sedimentary pile and transported to the site of deposition by circulating ground waters or petroleum. Whatever the source, reduction (in large part related to decaying organic matter) evidently played an important role in the precipitation of uranium and associated metals.

The uranium in coal and associated carbonaceous shale beds occurs in the form of metallo-organic compounds but secondary uranium minerals like meta-autunite are found in coals that contain more than 0.1 percent uranium. The uranium in some coals may be derived from volcanic ash, though in others it may be derived from the weathering of igneous rocks or from hydrothermal solutions. The uranium is probably taken up by the coal from solutions that migrate along adjacent permeable beds.

The uranium in marine black shales and phosphorites is derived from sea water. The precipitation of uranium in the shales probably is brought about by chemical adsorption by living or dead plankton, but reduction evidently plays an important role in its precipitation and stabilization in the shale. Uranium in the phosphorites substitutes for calcium in the apatite structure. Its adsorption by apatite is hindered by abundance of calcium ions, with which it competes for lattice positions in the structure, and by carbonate and by hydroxyl ions, which compete with phosphate groups for structure positions and form less stable compounds with uranium.

INTRODUCTION

The intensive search for uranium underway all over the world since 1944 has tremendously expanded knowledge of the occurrence and distribution of uranium (Nininger, 1954). Because chief emphasis necessarily has been placed on economic objectives, growth of knowledge of the genesis of uranium has been less rapid. Nevertheless, important data have accumulated that outline the problems of genesis and, for some types, provide an understanding that may aid in the search for additional deposits. Our purpose here, therefore, is to summarize information available on the origin of uranium deposits to help define critical problems and to indicate some economic applications of the data in certain fields. Because of space limitations we will limit the discussion to a few of the most important types of uranium deposits, and we will devote most space to those hypotheses that seem to us the most reasonable.

Before discussing the origin of specific types of deposits, we will summarize briefly the geochemistry of uranium and its mode of occurrence to provide background and prospective to the main problem.

GEOCHEMISTRY OF URANIUM*

Uranium belongs to the actinide group of elements consisting of the elements of atomic numbers 89 and above. Of the naturally occurring elements actinium, thorium, protactinium, plutonium and uranium, only thorium and uranium occur in appreciable quantities in nature. Actinium and protactinium have such short half lives that their abundance is vanishingly small. Only minute quantities of natural plutonium (94) have been detected in pitchblende, fergusonite, monazite, and carnotite. The uranium-plutonium ratio is of the order of 10^{-12} (Seaborg and Levine, 1951).

Uranium makes up about 1 to 2 ppm of the earth's crust. Its average concentration in some typical geologic entities is given in table 1.

Table 1

Average uranium concentration in some typical geologic entities

Geologic Entity	Concentration of Uranium (ppm)
1/ Low silica igneous rocks	<1
1/ Intermediate igneous rocks	2
1/ High silica igneous rocks	4
1/ Sedimentary rocks	2
2/ Ground and stream waters	.0002
1/ Ocean waters	.002
3/ Oil	.1

1/ Holland and Kulp, 1954
2/ Based on unpublished analyses by F. R. Bruce and D. Ferguson.
3/ Erickson, and others, 1954.

---

*Much of the information for this discussion has been integrated from five general sources: Goldschmidt, 1954; Seaborg and Katz, 1954; Katz and Rabinowitch, 1951; Rankama and Sahama, 1950; and Tomkieff, 1946.

Uranium ore deposits range from approximately 1,000 ppm upwards and represent, therefore, significant concentrations over that found in ordinary rocks. The concentration factor, however, is not remarkable among the factors necessary for ore elements as a group; the crustal abundance of uranium is greater than that of antimony, bismuth, mercury, silver, and gold, and about the same or slightly less than that of cobalt, lead, and molybdenum (Green, 1953, p. 1012).

Solution and mineral chemistry of uranium

The chemistry of uranium in aqueous solutions at low temperatures is well known from experimental work; its behavior in high temperature aqueous solutions has received little attention in the laboratory; its behavior in silicate systems, almost none. Fortunately, its behavior in low temperature aqueous solutions seems to be a useful guide to that under more stringent physico-chemical conditions; the geologic evidence is interpretable by reasonable extrapolation of the information available at low temperature, plus the fragmentary data at higher temperatures and pressures.

The uranium atom, despite its 92 electrons, has a crystal radius of 1.38 Å (Green, 1953, p. 1012*), essentially the same as tungsten and molybdenum. It has six valence electrons. Its tendency to lose these electrons is indicated by the following ionization equations, which give the energy released when uranium metal dissolves to give a solution of unit activity (approximately 1 molar) in water (Latimer, 1952, p. 302).

---

*All succeeding ionic radii are taken from Green's table.

$U_{metal} \longrightarrow U^{+3}_{aq.} + 3e$ $\Delta F = -124.4$ kilocalories

$U_{metal} \longrightarrow U^{+4}_{aq.} + 4e$ $\Delta F = -138.4$ kilocalories

$U_{metal} + H_2O \longrightarrow (U^{+6}O_2)^{+2} + 2H^{+} + 4e$ $\Delta F = -179.7$ kilocalories

U^{+} and U^{+2} ions are unknown in aqueous solution; U^{+3} ion can be obtained in the laboratory but is markedly unstable with respect to the liberation of hydrogen from water (Latimer, 1952, p. 301).

Because it decomposes water at a finite rate in the laboratory, it appears unlikely that U^{+3} ion is important in nature, a conclusion borne out by the absence of mineral species containing uranium in this valence.

U^{+4} ion is by far the most abundant species in nature. It is stable under reducing conditions, as in magmas, or in sedimentary environments in which organic material is preserved. It has a radius of about 0.97 Å. The combination of relatively large size and high charge probably accounts for its very limited substitution in the structures of the common rock-forming minerals. Calcium ion (0.99 Å) is the only high abundance cation with a similar radius, and U^{+4} does occur in some calcium-bearing minerals, notably sphene, apatite, and fluorite. Its absence in other common calcium minerals--anorthite, calcite, and gypsum, for example--probably is related to the discrepancy in charge. Substitution is unlikely except where the difference can be accommodated by special structural features (C. L. Christ, oral communication).

The U^{+4} oxide ($U^{+4}O_2$) is very slightly soluble in water. The dissociation constant for the reaction:

$$U^{+4}O_2 + 2H_2O \longrightarrow U^{+4} + 4OH^{-}$$

is but 10^{-52} at 25° C and 1 atmosphere pressure (Garrels, 1954, p. 12) and is little changed by increase in temperature up to 120° C. This great stability of $U^{+4}O_2$ (under reducing conditions) probably accounts for the preponderance of uraninite as the primary uranium ore mineral.

The only element with a 4-valent cation essentially identical to U^{+4} is thorium. This similarity is evidenced by extensive isomorphism in (U, Th) (SiO_4). Although U^{+4} also shows a limited amount of substitution for other 4-valent cations, such as zirconium, tungsten, and molybdenum, the discrepancy in radius (Zr = 0.79; W = 0.70; Mo = 0.70 Å) is such that the percentage of uranium in minerals containing these elements generally is not large. U^{+4} occurs also in a whole series of complex tantalates, niobates, and various yttrian rare earth oxides and phosphates, where it may substitute for rare earths, calcium, niobium, or tantalum. Its concentration in these minerals ranges up to about 20 percent; the maximum uranium content of compounds of this type is about 40 percent in brannerite, $(U, Ca, Fe, Y, Th_3)Ti_5O_{16}$.

Uraninite is easily oxidized and destroyed on weathering, but most of the other U^{+4} minerals are not. Presumably continued oxidation of the U^{+4} ion in fairly pure UO_2 to the 6-valent state is permitted by the removal of friable and soluble oxidation products, whereas, in those compounds in which U^{+4} is a minor substituent, it is protected from attack by the surrounding unoxidizable ions. In general, the U^{+4} tantalates, niobates, and phosphates are durable and highly insoluble as well as unoxidizable, so that they appear in the clastic sediments.

The U^{+4} ion in aqueous solution can be oxidized easily at a finite rate to the uranyl ion $(U^{+6}O_2)^{+2}$ rather than to U^{+6}. The reaction is:

$$U^{+4} + 2H_2O \longrightarrow (U^{+6}O_2)^{+2} + 2H^+ + 2e$$

A variety of oxidizing agents present in many natural systems are sufficient for the task. Very roughly it can be said that U^{+4} is stable under the same conditions as H_2S, HS^-, S^{-2}; $(U^{+6}O_2)^{+2}$ coexists with SO_4^{-2} and HSO_4^-. A $(U^{+5}O_2)^+$ ion can be formed experimentally, but it is metastable, and disproportionates to U^{+4} and UO_2^{+2}, so that the U^{+4} - $(UO_2)^{+2}$ couple is the significant pair (Latimer, 1952, p. 301). Again the experimental behavior extrapolates to geologic conditions: $(U^{+5}O_2)^+$ – containing minerals are not known.

The $(U^{+6}O_2)^{+2}$ ion is so stable that it can be considered a complex ion like NH_4^+, and maintains its identity through various chemical transformations from solution to solid and vice versa. The oxygen atoms are on opposite sides of the uranium atom, forming a dumbell-shaped group as shown in figure 1 (Connick and Hugus, 1952, p. 6012).

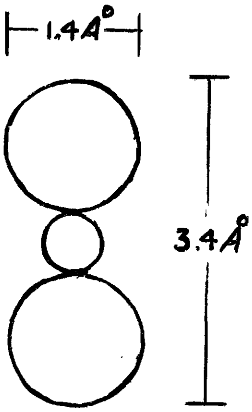

Figure 1. The uranyl ion.

In solids, the other atoms tend to arrange themselves around this group so as to "key" the uranium into a layer structure. The compounds are of the general type:

$(Me^{+})_2(U^{+6}O_2)_2^{+2}(R^{+5}O_4)_2^{-3}$ or $(Me^{+2})(U^{+6}O_2)_2^{+2}(R^{+5}O_4)_2^{-3}$

where Me^{+} or Me^{+2} are mono or di-valent cations such as K^{+}, Na^{+}, Ca^{+2}, Mg^{+2}, or Cu^{+2}, and R^{+5} is V^{+5}, As^{+5}, or P^{+5}. The stable group in the solid is the $\left[(U^{+6}O_2)(R^{+5}O_4)\right]^{-1}$ complex; it forms a continuous layer structure. The Me^{+} or Me^{+2} is much more loosely held; so much so that it can be added or removed by a base exchange reaction without destroying the $\left[(U^{+6}O_2)^{+2}(R^{+5}O_4)^{-3}\right]^{-1}$ layer structure (Murata, and others, 1951, p. 323).

The $(U^{+6}O_2)^{+2}$ ion does not bind strongly with most anions and hence forms few insoluble solids. Moreover, the few insoluble compounds are not combinations with the major rock-forming elements, but with elements that are not abundant in natural waters, such as As, V, and P. The two important soluble complexes, on the other hand, are formed from the two chief dissolved constituents of natural waters: carbonate and sulfate. The sulfate complex is largely un-ionized $(U^{+6}O_2)(SO_4)$ (Brown, and others, 1952); the carbonate forms two complexes $\left[(U^{+6}O_2)(CO_3)_3\right]^{-4}$ and $\left[(U^{+6}O_2)(CO_3)_2(H_2O)_2\right]^{-2}$ (Bullwinkel, 1954). Consequently, the solubility of uranium in oxidizing solutions is increased by increase in sulfate content, and is essentially independent of pH; it is also increased by increase in total carbonate present $(H_2CO_3 + HCO_3^{-} + CO_3^{-2})$, and the effect is increased at high pH, as the carbonate dissociation is shifted toward formation of CO_3^{-2} ion at the expense of H_2CO_3 and HCO_3^{-}.

The general relations between tetravalent uranium compounds and hexavalent uranium compounds in aqueous solution are illustrated by figure 2, a plot of the stability fields of the U^{+4} and U^{+6} oxides as a function of pH and oxidation potential (Garrels, 1954). The activity of U^{+4} ion, a rough measure of the dissociation of uraninite, is extremely small even in solutions of pH 3. On the other hand, the activity of $(U^{+6}O_2)^{+2}$ ion is appreciable (greater than 10^{-5}) at pH 5. Furthermore, no effective complexes of U^{+4} ion are known, so that the activity of the ion is probably an index of the solubility of uraninite, whereas the UO_2^{+2} ion is strongly complexed by sulfate and carbonate and the activity shown is probably a small fraction of the total solubility.

The uranium cycle

The foregoing material provides a basis for the interpretation of most of the geologic occurrences of uranium.

In igneous rocks uranium is present in the 4-valent state in primary minerals. In low silica rocks the magmatic concentration is so low that the uranium is taken up in the ordinary rock minerals. In the high silica rocks the magmatic concentration commonly is sufficiently high so that removal in major rock minerals is not sufficient to prevent concentration in the magma phase, with consequent late stage enrichment of uranium in accessory minerals. In granitic rocks, uranium is concentrated in the accessory minerals that have 4-valent cations for which U^{+4} can substitute, such as thorite, zircon, monazite, and xenotime, and in those with calcium ion and unusual structural properties permitting valence adjustment, such as apatite and sphene. In addition, it appears that uranium may remain in solution until the ultimate stage of solidification, so that it is finally deposited as a film on grain surfaces of the major minerals. As much as 40 percent of the uranium of some rocks is easily leachable with dilute hydrochloric acid (Brown and others, 1953) and may represent the film of material on grain surfaces. Concentration in the last magmatic stage also is indicated by the high uranium content of some pegmatite minerals, such as uraninite, uranothorite, monazite, and complex tantalates and niobates.

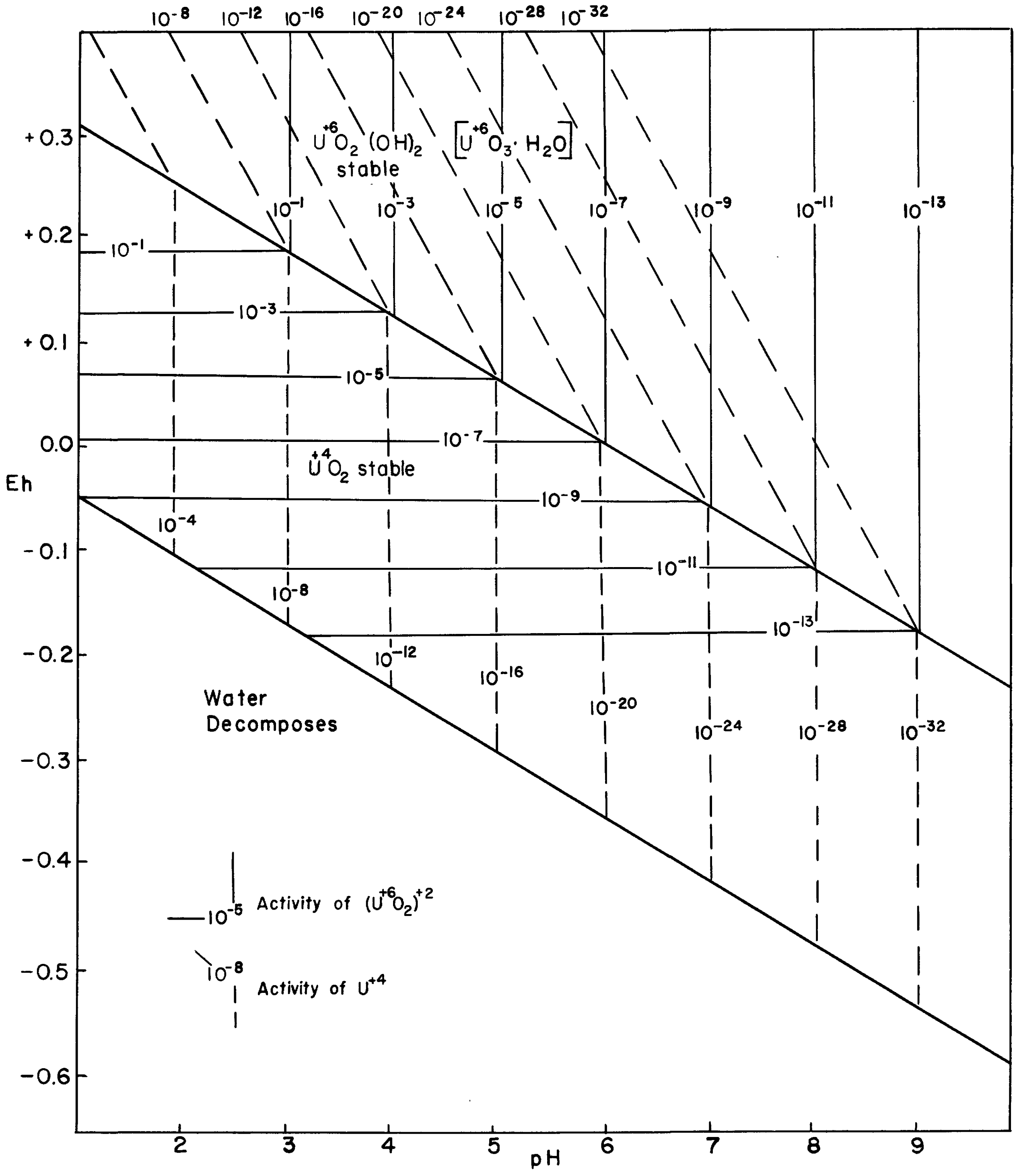

Figure 2. Stability fields of $U^{+4}O_2$ and $U^{+6}O_2(OH)_2$. Superimposed contours show equilibrium activity of U^{+4} and $(U^{+6}O_2)^{+2}$ ions.

In igneous rocks (including pegmatites) uranium and thorium are intimately associated; hydrothermal veins are notable for their low thorium content. In them uranium occurs chiefly as uraninite. This segregation of uranium suggests the possibility that an oxidation of uranium to the 6-valent state may precede deposition in veins. In other words, an oxidation of U^{+4} to $(U^{+6}O_2)^{+2}$ at a late magmatic stage might permit the $(U^{+6}O_2)^{+2}$ to be carried away in solution, and separated from the unoxidizable Th^{+4}. In turn $(U^{+6}O_2)^{+2}$ might be reduced to form pitchblende in veins. Phair's studies (1952) of high and low uranium bostonite dikes indicate that uranium is released to vein solutions by an oxidation reaction. The widespread association of uraninite and hematite in vein deposits also may be explained by such an hypothesis. The reaction:

$3H_2O + 2Fe^{+2} + U^{+6}O_2)^{+2} \longrightarrow Fe_2O_3 + U^{+4}O_2 + 6H^+$ goes to completion $((U^{+6}O_2)^{+2} < 10^{-6})$ at 25° C at pH 4 and above over a wide range of Fe^{+2} concentration.

Where original uranium concentrations are exposed at the surface, uraninite oxidizes rapidly. If the uraninite is associated with iron sulfides, the $(U^{+6}O_2)^{+2}$ may be retained for some time at the outcrop by adsorption on the ferric oxide of the gossan. Under humid conditions, uranium is removed by ground and surface waters. Under arid or semiarid conditions, in the absence of V, P, and As, a complex suite of hydrated uranyl oxides and hydroxides, basic sulfates, and carbonates may form essentially as an efflorescence (Weeks and Thompson, 1954, p. 21). In the presence of P, V, and As, the slightly soluble metal uranyl phosphate, vanadate or arsenate is formed. Most prominent among these, of course, is hydrated $K_2(UO_2)_2(VO_4)_2$ (carnotite), until recently the major ore mineral of the Colorado Plateau.

Under most circumstances uranium rather quickly enters ground or stream waters and is eventually carried to the sea. There it is precipitated largely with muds containing organic material, or with phosphatic sediments. It is likely that the precipitation is caused by a reduction process, for although the mineral species containing uranium are not known, the sedimentary environments in which uranium is concentrated appear to be sufficiently reducing to cause the change from $(U^{+6}O_2)^{+2}$ to U^{+4}. Organisms participate complexly in the marine processes involving uranium, but the gross reaction appears to be removal from ocean water by reduction and precipitation or adsorption.

The uranium cycle is illustrated schematically in figure 3. The recurrent association of uranium with a variety of carbonaceous materials is striking. In pegmatites and veins uranium may occur in intimate association with "asphaltic" material. Petroleum may contain several parts per million uranium, and asphaltic pellets in sediments as much as several percent (Erickson, and others, 1954). On the Colorado Plateau fossil wood is commonly replaced by pitchblende or by coffinite (Rosenzweig, and others, 1954), and it appears probable that the fixation has been effected by the reducing effect of the wood. Some coals that have no uranium minerals contain hundreds of parts per million uranium. Many black shales (see before) contain comparable concentrations. At present no clear picture has emerged as to the exact nature of the uranium-bearing compounds; some may be uranium-organic complexes; others may be finely disseminated uraninite; and the uranium in some deposits may be held by adsorption.

OCCURRENCE OF URANIFEROUS DEPOSITS

Concentrations of uranium of more than 10 times the average in the earth's crust are associated with rocks formed as a result of igneous, sedimentary, and weathering processes. The nearly ubiquitous geologic distribution of uranium stems, of course, from some of its aforementioned chemical and physical properties, particularly its polyvalence, its high chemical reactivity, the relative solubility of some of its common compounds in aqueous solutions, and its relative abundance compared to some other ore metals. These attributes permit it to form compounds with many other elements, to enter the structure of a wide variety of minerals, to take part in many chemical reactions, and hence, to be deposited in many rocks and minerals of diverse origins and compositions, as summarized below. Its wide geologic distribution means also that it is dispersed, so that concentrations of uranium are not as great as those of other, less active metals of comparable abundance, such as lead and molybdenum.

Certain silicic and silica-alkalic igneous rocks (Evans and Goodman, 1941), pegmatites (Page, 1950), and migmatites (Mawdsley, 1952), contain uranium in amounts of 0.001 to 0.02 percent. The uranium in these deposits occurs mainly in accessory minerals--zircon, monazite, apatite, sphene, or multiple oxides

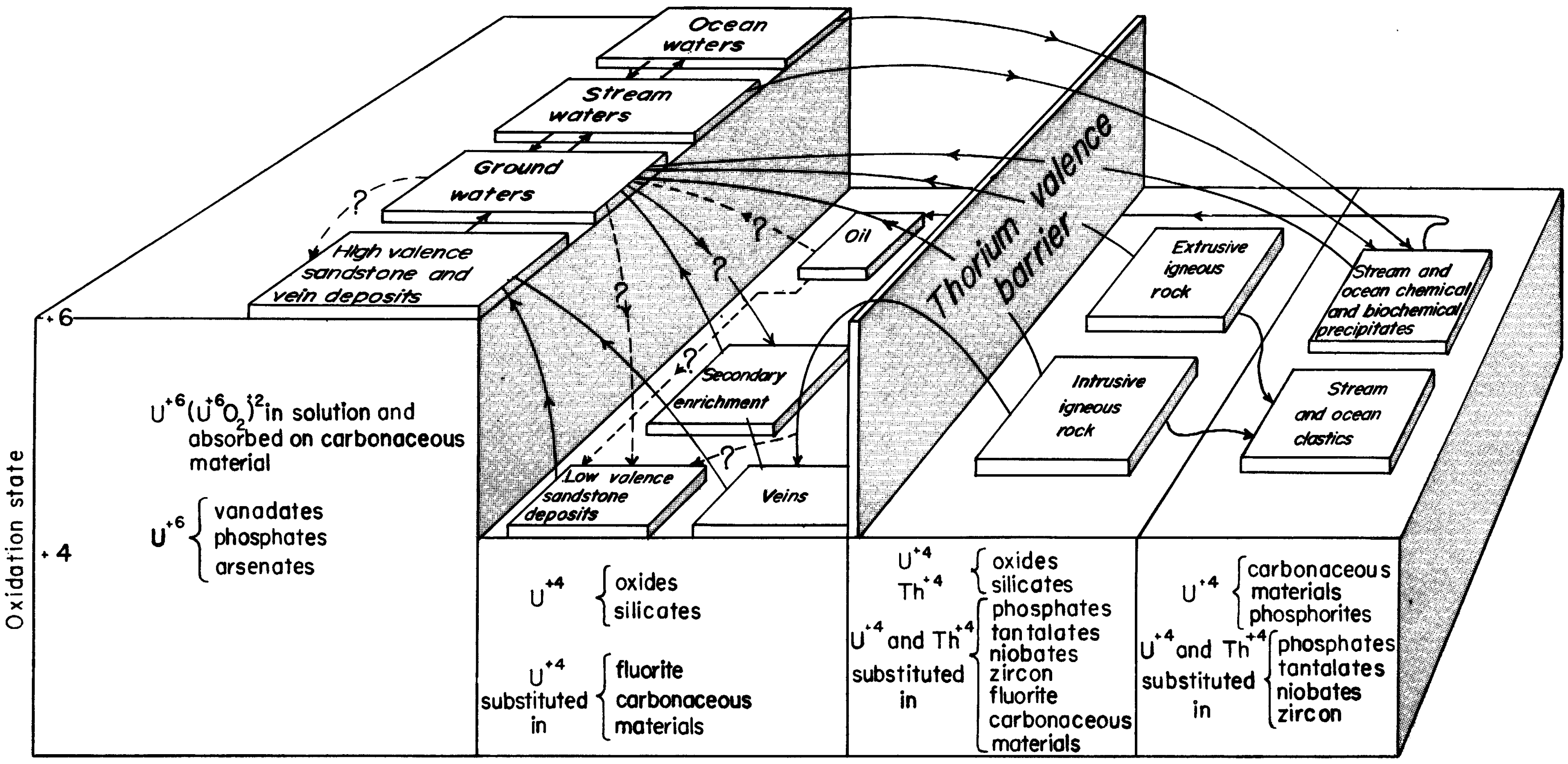

Figure 3. Schematic representation of some of the major aspects of the geochemical cycle of uranium.

78444

like pyrochlore--but some occurs in uraninite or interstitial acid-soluble form (Hurley, 1950; Brown and others, 1953). The riebeckite granites of Nigeria (Mackay and Beer, 1952), the bostonite dikes of the Colorado Front Range (Phair, 1952), and the pegmatite deposits of Madagascar (Turner, 1928) are important examples of these types.

The greatest concentrations of uranium are those found in veins and in replacement deposits. With few exceptions, they are the only important source of ores that contain more than 0.5 percent uranium. The uranium in unoxidized veins is mainly in the form of pitchblende (the colloform variety of uraninite), but in some it is in brannerite, davidite, or fluorite. Two prominent varieties of pitchblende veins have been recognized (Everhart and Wright, 1953): 1) a simple type that contains pyrite, quartz or chalcedony and possibly galena and small amounts of other sulfides, and occurs chiefly in felsic rocks; and 2) a complex type that contains sulfides of nickel, cobalt, and copper as well as pyrite and native silver in a quartz or a carbonate gangue; this type occurs mainly in metasedimentary rocks. The deposits in the Urgericia, Portugal and Wolsendorf, Germany districts are examples of the first type and those at Great Bear Lake, Canada, and Shinkolobwe, Belgian Congo (Bain, 1950; Everhart and Wright, 1953) are examples of the second. Many intermediate types are found but regardless of metal content nearly all uraniferous veins contain sulfides, some variety of SiO_2, fluorite, and hematite. Thucholite or similar varieties of uranium-bearing carbonaceous materials are sometimes present also. Secondary minerals like autunite, torbernite, and schroeckingerite are found in the oxidized parts of uraniferous veins but notable zones of supergene enrichment are unknown. Replacement deposits are uncommon. In the known important deposits, pitchblende replaces paragneiss and schist in the Gunnar deposit, Beaverlodge district, Saskatchewan, carbonaceous shale and schist in the Rum Jungle district of Australia (Sullivan and Matheson, 1952), limestone at Grants, N. Mex., (Bucher, 1953), and trachyte in British Columbia (F. C. Armstrong, personal communication, 1953) and davidite replaces femic rocks in Mozambique (Davidson and Bennett, 1950).

Pitchblende, along with pyrite and other sulfides, low-valent vanadium oxides and silicates, and several types of organic matter, is found also in sandstones and conglomerates as pore-space fillings and replacements of carbonaceous matter and clay galls. The uranium content of these deposits, of which those on the Colorado Plateau (Fischer, 1950) and the Witwatersrand (C. F. Davidson, 1953) are the most important examples, ranges from about 0.05 to 0.5 percent. Oxidized portions consist of secondary minerals such as carnotite and tyuyamunite.

In most other occurrences, uranium is in secondary minerals or is held by adsorption or ionic substitution in other minerals in which it is not an essential constituent. Secondary minerals are found along fractures and joints in tuffs and tuffaceous sediments (Wyant and others, 1952) and in a few phosphorites (Arambourg and Orcel, 1951). Variable concentrations of uranium attached to other materials rather than in uranium minerals are found in certain coals and non-marine carbonaceous shales, particularly in those associated with volcanic ash (Denson, Bachman, and Zeller, _in_ Vine and Moore, 1952), and in aluminum phosphates derived from the weathering of marine carbonate-fluorapatite deposits (Cathcart and others, 1953). The uranium content of most of these deposits ranges from 0.005 to 0.01 percent. Uniform or highly persistent concentrations of uranium, mostly in the range of 0.005 to 0.03 percent, are found in marine black shales and marine carbonate-fluorapatite bearing phosphorites. Uranium also occurs in certain petroleums, asphaltites, thucholite, and other related materials. In petroleum and asphaltite it appears to be in an organic compound (Erickson and others, 1954), but in thucholite and other similar materials it seems to be in disseminated grains of uraninite (Davidson and Bowie, 1951).

Uranium is not abundant in placers (C. F. Davidson, 1953) and where it does occur it is mainly in monazite, zircon, or other refractory, accessory minerals typical of igneous rocks and pegmatites.

We may orient these data on occurrence in terms of genesis by saying that concentrations of uranium of about 10 to 100 times the average in the earth's crust (i.e., 0.002-0.02 percent U) are deposited by rock-forming processes in several igneous and sedimentary rocks. Concentrations of more than 100 times the average in the earth's crust are generally formed only by ore-forming processes as they are ordinarily conceived, i. e., deposition from hypogene solutions associated with late stages of igneous activity or from ground water solutions associated with some form of weathering. Most concentrations of more than about 2,000 times that in the earth's crust (i. e., more than about 0.4 percent U) are clearly formed from hypogene solutions. Deposits whose origin is problematical or controversial generally have concentrations that lie in the range of 100 to 2,000 times that in the earth's crust.

Of these various types of deposits, further discussion will be limited to those in igneous rocks, hydrothermal veins, sandstones, coals, phosphorites, and black shales.

URANIFEROUS IGNEOUS ROCKS

As indicated in the foregoing section on the geochemistry of uranium, certain types of igneous rocks, particularly those high in silica content, are more uraniferous than any of the other general rock types. Furthermore, the uranium in igneous rocks of several different types has been regarded by many geologists as a source, or an important clue to the source, of many of the minable and productive ore deposits of the world. In the following paragraphs, the intrusive rock types, the pegmatites, and the extrusives that have been found to be significantly uraniferous are discussed, and the mode of uranium occurrence and available information concerning possible origin are presented. The most comprehensive work on uranium content of igneous rocks has been done by Evans and Goodman (1941), Keevil (1944), and Senftle and Keevil (1947).

Intrusive rocks

Of the major types of intrusives, the granitic rocks, certain syenites, migmatites, and felsic porphyries appear to be the most uraniferous. These represent in general the more felsic intrusives. Mafic and ultramafic intrusives are with few exceptions, only slightly uraniferous.

Granitic rocks

Available data suggest that almost every granitic body in the earth's crust contains uranium in amounts greater than those in the average of all rocks of the crust. The uranium content of granitic intrusives, however, varies considerably and seems to be related to their petrography and structure. Only a few uranium-bearing granites, mainly in the United States, Nigeria, South Australia, and Canada, have been studied in detail; but, as described below, these show patterns in uranium concentration and distribution that appear to apply widely.

Nigerian albite-riebeckite granite.--A distinctive albite-riebeckite granite has been described and extensively studied in four districts of Nigeria--in the Kaffo Valley, the Darowa district, the Teria district, and the Kigom Hills (Beer, 1951). The major minerals of this granite are quartz, albite, perthite, and riebeckite; minor minerals include cryolite, pyrochlore (the uranium-bearing mineral), astrophyllite, zircon, topaz, and thorite. In the Kaffo Valley a sampled granite area of 195 acres was found to average 0.012 percent U_3O_8. Three chemical analyses of the pyrochlore $\left[(Na, CaU)_2 (Cb, Ta)_2O_6F\right]$ average 3.1 percent U_3O_8. The uranium probably replaces calcium in the crystal structure of this complex mineral.

Plutonic rocks of New Hampshire.--Perhaps the best known granites in the United States, from the standpoint of uranium content, are those that form a part of four magma series in New Hampshire. (See table 2.) Here, according to Billings and Keevil (1946), one of the high-alkali granites contains double the average radioactivity of the granites of similar character from all North America.

Table 2

Average amounts of uranium in the four magma series in New Hampshire

	Uranium in Parts Per Million*
Granite	52
Quartz syenite	48
Syenite	34
Monzodiorite	33
Quartz Monzonite	31
Granodiorite	21
Gabbro	20
Nepheline sodalite syenite	18
Diorite	15
Quartz diorite	12
Norite	09
Average	38

* Calculated from α-activity, assuming Th/U = 3.3

In the White Mountain granites the only appreciably radioactive minerals apparently are allanite (about 0.1 percent of the rock) and zircon (0.03 to 0.13 percent of the rock). These minerals occur principally in the more alkalic White Mountain granites. The radioactivity of the White Mountain granitic rocks in general is not due to such minerals as apatite, epidote, sphene, biotite, or the potash feldspars, as is the case in many other common granites.

From Keevil's and Billings' studies, the highest uranium content appears to be in the youngest phase of the magmatic series--the Conway biotite granite. This is preceded in the magmatic sequence by a hastingsite-riebeckite phase similar to the Nigerian granite described above.

Other granites in the United States.--Common characteristics of the Nigerian and White Mountain granites have been noted by Coats (1952) to include: post-tectonic age and richness in alkalis (mostly indicated by a high content of sodic ferromagnesian minerals), fluorite, and iron-rich biotite. Using these and other characteristics associated with high uranium content as a guide, the Geological Survey has attempted to find other unusually uraniferous granites in the United States. Of twelve selected granitic bodies examined in Montana, Idaho, Oregon, Washington, and California, two indicated abnormally high amounts of uranium by chemical analysis, and in all twelve, the radioactive minerals were restricted to allanite and zircon. One of the uraniferous bodies containing 0.001 percent U is a schlieren rich in biotite, forming one phase of a granite exposed in the floor of Grand Coulee near Steamboat Rock, Wash. The other body is a small mass of anorthoclase trachyte porphyry containing 0.008 percent U in the Eureka quadrangle, California. This reconnaissance found only high uranium rocks; the data are not necessarily applicable to the great bulk of granitic bodies. More typical, perhaps, is a summary of the most recent work on uranium content and distribution in granites of the United States by Larsen and Gottfried (TEI-440, p. 202)[1].

---

[1] U. S. Geological Survey reports TEI-330, 390, 440, and 490 include progress reports by many authors. For the sake of brevity, the reports are listed only once in the bibliography, with the U. S. Geological Survey shown as author, rather than by the author of various sections to which reference will be made. Reference to individual sections will be given as above.

which includes results of mineral and chemical analyses of rocks from the Southern California batholith, the Adams Tunnel, Colorado and the New Hampshire, Oliverian, and Highlandcroft magma series of New England. Significant analyses of the Southern California batholith are as follows:

Table 3

Uranium content of minerals of the Southern California Batholith

Mineral	No. of samples	No. of analyses	Range U content (ppm)	Average U content (ppm)
Olivine	1	1		0.01
Ilmenite	1	1		.1
Plagioclase	20	27	0.07 - 6.0	1.6
Orthoclase	15	20	0.16 - 8.2	1.9
Quartz	18	22	0.20 - 6.0	2.2
Fluorite	1	3	3.0 - 4.0	3.5
Diopside	1	1		3.7
Hypersthene	5	6	0.01 -14.0	4.7
Biotite	19	44	0.3 -29.0	5.7
Magnetite	13	20	0.68 -24.0	7.1
Augite	6	8	0.8 -39.0	7.7
Muscovite	1	2	7.9 - 8.1	8.0
Hornblende	18	27	0.1 -85.0	18.0
Garnet	2	3	5.5 - 7.5	6.0
Epidote	3	4	15.0 -50.0	32.0
Apatite	8	9	31.0 - 130.0	67.0
Allanite	3	6	51.0 - 360.0	180.0
Sphene	4	7	27.0 - 350.0	196.0
Monazite	1	1		820.0
Zircon	14	17	90 -4,600	1367.0
Xenotime	2	2	360.0 -12,700	6630.0

In summary, most of the work done to date indicates that radioactivity (attributable to both uranium and thorium) in the granitic rocks of the United States is concentrated in zircon, allanite, monazite, xenotime, and sphene.

Granite from Haliburton County, Ontario.--The character and distribution of uranium in Precambrian granite from Monmouth township, Haliburton County, Ontario has been intensively studied by Tilton and others (1954) and by Brown and others (1954). In this granite, it has been found that marked differences exist in the distribution of uranium, thorium, and lead. So-called stably bound uranium (and also thorium) were found to be concentrated, for the most part, as in the granites from the United States, in the accessory minerals zircon, sphene, and apatite. A substantial fraction of the uranium, however, was found to exist in environments in the rock from which it is easily released by acid, and presumably not in the usual minerals. The uranium in this form is so loosely bound that approximately 34 percent of the total content in the rock can be removed from a pulverized sample by five minutes of agitation in cold 6 M hydrochloric acid. This confirms the work of Hurley (1950) and Picciotto (1950) who by leaching experiments and by radio-autograph techniques showed that a large fraction of the radioactive elements present in some granite rocks is in the mineral interstices and intra-crystalline fractures, with most of the remaining fraction in accessory minerals. Thus the loosely bound uranium is assumed to originate from the inter-crystalline interstices (see Newmann, 1948, for a general description of the origin of such material). An additional source of such highly soluble uranium may possibly be allanite.

Granite from Crocker Well area, South Australia.--In the Crocker Well area of South Australia, Archean rocks consist of granite intruding metamorphosed and granitized sediments (King, 1954).

Certain uranium and rare earth minerals in these rocks are apparently of late magmatic origin, occurring mainly as segregations in pegmatite and as fracture fillings in the parent rocks. They are dominantly oxides. Except for apatite and fluorite, minerals that reflect richness in volatiles are notably deficient. The deposits lack structural controls in the usual sense of the term but were apparently formed in pegmatites and fissures at a late stage of magmatic cooling when the parent rock was largely consolidated.

The uranium mineral davidite is found almost exclusively in coarse crystalline aggregates in pegmatite or pegmatitic quartz veins along with magnetite and rare earth minerals including fergusonite, polymignite, xenotime, euxenite and orthite.

Another brannerite-like uranium mineral is essentially in the form of disseminated fracture fillings found only in a leucocratic phase (adamellite) of the granitoid rocks. This mineral usually occurs in intergrowth with granular rutile and in association with biotite, apatite and blue opalescent quartz, and the paragenetic sequence in all observed exposures is clearly biotite-apatite, followed by quartz and rutile-"brannerite".

In summary, the uranium minerals in the South Australian granites do not occur as true accessory constituents, but either in pegmatitic apophyses or disseminations in fissures of a variety of types within the granite or adjacent country rock. There are locally concentrations of fracture fillings in favorable structural environments such as shatter zones, and although the controlling structural features are irregular in nature and distribution, they have an important bearing on the localization of potentially commercial uranium deposits in the area.

Syenite

Syenitic rocks, although not as extensively studied for radioactivity as granitic intrusives, are known to be abnormally uraniferous in some areas. Perhaps the most thoroughly tested are the syenites of the Adirondack Mountains complex of New York (Narten and McKeown, 1952). Here, the order of magnitude of uranium content is approximately equivalent to that of the granitic units (0.00X percent U), as well as can be ascertained from the analytical methods used.

Migmatite

Several areas underlain by migmatite in Canada have received considerable study and mining exploration because of the uranium content. Many of the deposits of radioactive minerals are in granite pegmatite and intruded biotite-rich schist or gneiss that are so thinly banded as to constitute true migmatite (A. H. Lang, 1952). Elsewhere the country rock consists either of wider, parallel or en echelon lenses of pegmatite intruding more dominant schist or gneiss, or of granitic rocks with numerous altered inclusions of biotite schist. Deposits of one or another of these types are found north of the East Arm of Great Slave Lake, in the Black Lake and Charlebois Lake areas of Saskatchewan, and in the Greenville region of Ontario.

The most common radioactive mineral is very finely disseminated uraninite occurring almost wholly in intimate association with the abundant biotite of the rocks. Uranothorite also contains some of the uranium. Molybdenite and zircon are common, and chalcopyrite, pyrite and pyrrhotite are found sparingly disseminated throughout the rocks.

Exploration to date suggests possibilities for considerable tonnages of rock in selected areas, averaging from several hundredths to 0.1 percent U_3O_8.

Felsic porphyry

It has been noted in several localities that felsic porphyry intrusives, chemically in the granite to quartz monzonite range, are highly uraniferous. One of the most thoroughly documented studies of such rocks is that of Phair (1952) in the bostonite porphyries of the Central City district, Colorado. Here results of the analyses of 117 samples indicate that a porphyry sequence of Tertiary age includes some of the most radioactive igneous rocks in the world. (See table 4.)

Table 4

Sequence of Tertiary intrusions in Central City district, Colorado

	Average percent U	Petrography
Monzonite porphyry	0.002-0.007	Plagioclase phenocrysts; An > 10%
Non-porphyritic quartz bostonite	0.014	Quartz; no phenocrysts; bostonitic texture
Quartz bostonite porphyry	0.007-0.014	Quartz; K feldspar phenocrysts; bostonitic texture
Syenitic bostonite	0.004-0.007	No quartz; alkali feldspar phenocrysts; bostonitic texture

Phair has postulated that uranium-rich solutions given off by a cooling quartz bostonite mass at depth became enriched by leaching more uranium from the rocks encountered enroute upward and were the probable source for the vein deposits of the Central City district.

A second, somewhat more typical example of uraniferous porphyry is that occurring in stock-like masses in the Yerington district, Lyon County, Nevada (King and Roberts, 1949). This is gray to pink, medium to fine-grained quartz monzonite porphyry, composed principally of orthoclase, plagioclase, and quartz phenocrysts in a felsitic matrix with moderate amounts of fine-grained biotite and hornblende. Assays range from 0.002 to 0.004 percent U_3O_8 and the rock has been mineralized by copper, for which parts of it are mined.

Summary

The foregoing examples of the presence and distribution of uranium in four distinct types have indicated the significant features, as we know them, for all uraniferous intrusive igneous rocks.

The principal uranium-bearing minerals--zircon, allanite, xenotime, sphene, and monazite--are more abundant in felsic than in mafic rocks. Hence the granites and syenites, and their textural equivalents, generally are considerably more uraniferous than other intrusives in a given magmatic series. Granodiorite, quartz, monzonite, and quartz diorite are all favorable host rocks for uraniferous vein deposits in many parts of the world, but imcomplete studies to date indicate that these rocks themselves are not as uraniferous as the average granite. Monzonite, diorite, and gabbro are even less so, although a few gabbro samples from the Adirondack Mountains contain on the order of 0.00X percent U (Narten and McKeown, 1952).

In summary, studies to date indicate that uranium may be held in igneous rocks (a) by isomorphous substitution in certain of the more common accessory minerals, (b) as the major constituent in some of the less common uranium mineral accessories, and (c) in the interstitial matter deposited in late stages of cooling magmas.

In the relatively common accessory minerals, uranium is capable of substituting in the crystal structure of zircon, allanite, monazite, apatite, and sphene. It also is present in the crystal structures of the less common minerals xenotime and pyrochlore.

Perhaps the most significant form in which uranium is held in igneous rocks, from the standpoint of the origin of other types of deposits, as well as potential economic concentrations in igneous rocks themselves, is in products of very late-stage crystallization from cooling magmas. Uranium held in such products may be in uranium minerals formed by the very "last gasps" of the end-product gases and fluids of a cooling magma, or it may be in an unstable, loosely bound form in the mineral interstices and intracrystalline fractures of the igneous rocks. Uranium minerals include uraninite, davidite, brannerite (including the Australian brannerite-like mineral), and the columbo-tantalates found largely in pegmatites. These minerals are generally not disseminated through the igneous rock bodies but are structurally controlled along shear zones or in pegmatitic bodies.

A somewhat specialized process of uranium concentration by the lamprophyric mechanism has been proposed by Emmons and others (1952). During a granitization process, including the formation of lamprophyric concentrations, he suggested that uranium may be transported as a halide and precipitated by decreasing pressure, as an oxide, in and around lamprophyric bodies.

Pegmatites

A wide variety of uranium-bearing minerals have been described from a large number of pegmatite deposits in all parts of the United States and in most of the well-known pegmatite districts of Canada (largely Ontario), Madagascar, Mozambique, India, Brazil, and other areas.

The most common primary uranium minerals in these pegmatites are uraninites; the refractory columbo-tantalates such as euxenite, samarskite, fergusonite and betafite; pyrochlore, and thucholite. Page (1950) has noted that potassium-rich pegmatites, or potassium-rich zones in zoned deposits, have been found to be the most likely hosts for uranium minerals, whereas sodium-rich or lithium-rich pegmatites or zones are somewhat less favorable.

Extrusive rocks

Flows

In general, the uranium content of extrusive igneous rock types has received little study. From the data at hand, however, the variation in uranium content in extrusives, like that of intrusives, seems directly proportional to the felsic constituents of the rock. Coats (TEI-390, p. 98) has made a preliminary report of field examinations and sampling of about 140 bodies of post-Cretaceous volcanic rocks throughout western United States. The rocks studied were mostly of glassy or partly glassy texture and nearly all of rhyolitic or dacitic composition. Uranium content in these rocks is generally in the order of 0.000X percent and only uncommonly as high as 0.00X percent.

In a suite of volcanic rocks from Mt. Lassen, California, as well as from scattered volcanics throughout the world, Adams (written communication, 1953) has noted an increase in uranium concentration with rising percentages of potassium and silica.

The uranium-bearing minerals in the extrusive rocks have not been identified except in isolated instances, but it is suspected that the uranium generally is contained in the same minerals in which it occurs in intrusive rocks or is held by adsorption on the clay minerals that are the common alteration products of extrusive rocks.

In the course of reconnaissance and prospecting for uranium deposits throughout the world, it has been widely observed that the more mafic extrusives, such as andesite, latite, and basalt are only weakly radioactive, although basalt acts as a host rock to uranium vein deposits in certain areas, as in northwestern Saskatchewan and the Northern Territory of Australia.

Tuff and volcanic debris

Tuffaceous volcanic rocks and volcanic debris in continental sediments have received special attention in several geologic studies in the United States relating to the origin of uranium deposits in continental sediments.

In the Colorado Plateau, Waters and Granger (1953) recognized volcanic debris, now altered to clay minerals, in the Salt Wash and Brushy Basin members of the Morrison formation and in the Shinarump and Chinle formations. Field studies and microscopic examination of the ores suggest a relationship between the ore minerals and montmorillonite clay formed by devitrification of volcanic glass. It is postulated that during devitrification of volcanic ash, ground waters may have leached alkalies, uranium, vanadium and other elements from the ash. Systematic study of the uranium content of the volcanic debris in the Colorado Plateau formations remains to be carried out.

The uranium content in the tuffaceous White River formation of Oligocene age in North and South Dakota has been called upon by Denson and others (*in* Vine and Moore, 1952) as the origin of uraniferous solutions that have deposited uranium in certain lignite beds underlying it. However, the content and distribution of uranium in the tuffaceous formations themselves is not well known. Analyses carried out to date indicate (Denson, 1954, oral communication) that the uranium content is remarkably uniform throughout the White River formation and ranges from 0.001 to 0.002 percent U. Little or nothing is known of the chemical or mineralogic state in which the uranium is held in the tuffs.

Summary

The lack of factual information concerning the manner in which uranium is held in extrusive rocks precludes any positive conclusions as to the details of its origin. However, the geochemical behavior of uranium in these rocks and the magmas from which they were formed is believed to be essentially the same as that in the intrusive rocks.

URANIUM IN VEIN DEPOSITS

Many of the richest and most productive uranium ore deposits of the world, as well as thousands of mineral occurrences, may be firmly classified as hydrothermal vein deposits. But within this general category, considerable variation exists in the physical and chemical nature and age of the host rock invaded, the mineral associates, the paragenesis, structural relationships, accompanying rock alteration effects, and the geologic age of the uranium minerals.

From a detailed consideration of typical vein deposits throughout the world (Everhart and Wright, 1953), it is possible to classify the deposits into three major types. These have definite characteristics in regard to the associated metallic and gangue minerals, the host rock invaded, structural habit, and geochemical history. The three major types are briefly tabulated in table 5.

Table 5

Characteristics of three major vein deposits of world

	Nickel-Cobalt-Native Silver veins	Silica-Iron-Lead veins	Iron-Titanium veins
Host rock	Metasediments, volcanics	Felsic intrusives	Granitic intrusives
Metallic minerals	Mineralogy complex; sulfides and sulfarsenides of Co, Ni, Cu, Pb, precious metals present	Mineralogy simple; minor galena and pyrite present.	Iron and titanium minerals; uranium contained in the mineral davidite.
Gangue minerals	Carbonates, lesser silica	Silica, fluorite; lesser carbonates.	Silica
Examples	Great Bear Lake, Canada	Marysvale, Utah	Radium Hill, South Australia
	Joachimsthal, Czechoslovakia	Urgeirica, Portugal	
	Shinkolobwe, Belgian Congo		

In order to present a composite outline of the geochemistry and presumed origin of uranium in hydrothermal vein deposits as a whole, the following paragraphs describe the uranium minerals; the known mineral associates, as a group; and the observed variations in paragenesis. There follows a discussion of the principal factors involved in the deposition of uranium in veins: temperature of the precipitating solutions, depth of the precipitation site and pressure relationships, chemical environment of precipitation, and structural control of ore deposition.

Uranium minerals in vein deposits

Uraninite (especially the variety pitchblende), davidite, brannerite, and coffinite are the four major primary uranium minerals in vein deposits of all types.

Uraninite, the natural primary black uranium oxide, is a complex mixture of oxides of uranium that may contain varying percentages of Th and rare earths incorporated into the isometric lattice. Uranium in valence states of both 4 and 6 is present. The uraninite may be coarsely or finely crystalline; it may occur either in the amorphous, botryoidal form known as massive pitchblende, or the finely divided, powdery form commonly referred to as "sooty pitchblende". The crystal chemistry and morphology of uraninite have received much detailed study (Kerr, and others, 1954; Ellsworth, 1932; Brooker and Nuffield, 1952), but much is yet to be learned about its chemical and crystalline structure habits in various chemical environments.

Davidite, an ill-defined mineral chemically, containing chiefly oxides of titanium and iron, plus variable amounts of rare earths of the cerium group, uranium, vanadium, and chromiun, is the principal uranium ore mineral in titanium-rich, high temperature vein deposits. It is dark brown to brownish-black, is sub-metallic in luster, and occurs in massive form intimately associated with the other vein minerals.

The newly discovered uranous hydroxy-silicate coffinite (Stieff and Stern, in preparation) has already been reported from a wide variety of pitchblende mines throughout the world and may be found to be second only to uraninite among primary uranium minerals.

Brannerite occurs in a few vein deposits throughout the world, notably the Bou Azzer mine, French Morocco (Everhart, personal observation) but is more common in pegmatites and as an accessory in granite. It is a black to brown vitreous mineral which is generally very fine-grained in vein deposits and disseminated deposits but occurs in stout, prismatic monoclinic crystals in the pegmatites.

Secondary uranium minerals--a host of hydrous oxides, phosphates, sulfates, arsenates, vanadates, etc.--may constitute alteration products of uraninite and other primary uranium minerals. In glaciated areas and cold climates, where oxidized surface zones are not well developed, such as the Canadian Shield, a minimun amount of secondary minerals is found. Also especially if pyrite is a major constituent of the ore, acid groundwaters may strip uranium minerals from the vadose zone (Phair and Levine, 1953). However, in some deeply oxidized zones, as in the granitic rocks of Portugal, various suites of these minerals, principally the phosphates, torbernite and autunite, may constitute the major part of the ore down to the water table. It is interesting to note that in deposits where both secondary uranium minerals and uraninite below them have been mined as ore, as in Portugal and Marysvale, Utah, there has been no significant change in grade. There appears to be no general secondary enrichment, or extensive impoverishment beyond a thin zone near the surface.

Mineral associates of uranium in vein deposits

Metallic minerals

The metallic minerals reported in association with uranium minerals in vein deposits are legion, and the list continues to grow. In the following paragraphs, the major metals in uraniferous veins are discussed in general order of abundance.

Iron in one of sevetal forms is a nearly universal and conspicuous associate of uranium in vein deposits. Pyrite or marcasite, of course, are common constituents of nearly every vein deposit and thus do not appear to be particularly diagnostic or significant with respect to uranium.

The iron oxides, however, are much more valuable as ore guides. Hematite, finely divided and disseminated through the vein matter and adjacent host rocks, has been described and emphasized as a diagnostic associate of uraninite in nearly every vein deposit described throughout the world (Everhart and Wright, 1953). Magnetite is a minor constituent of pitchblende veins at Marysvale, Utah (Kerr, and others 1952) and in Chile (Flores, 1942). Certain magnetite bodies (not necessarily veins) in the crystalline belt of New York and New Jersey, as well as in the Adirondack Mountains (McKeown and Klemic, TEI-390, p. 197-198; Kratchman, written communication, 1954), contain small concentrations of uraninite in them, although most of the large magnetite iron ore bodies of the world are not abnormally radioactive. Limonite and other hydrous iron oxides, derived from either iron-bearing sulfides or oxides, are commonly copious in the oxidized zones of uranium-bearing veins.

Copper is perhaps the second most common metallic associate of uranium in vein deposits. Nearly all of the ore-forming sulfides and sulfarsenides of copper have been reported--chalcopyrite, chalcocite, covellite, bornite, tetrahedrite, and enargite. The common secondary suites of copper minerals ordinarily found in gossans are also present in the oxidized zones of the deposits. Chalcopyrite is common in nearly all pitchblende vein deposits, whereas the others are largely restricted to the Ni-Co-Ag type described by Bastin (1939). Copper minerals seem restricted to uraninite ores and are not present in significant quantities in the davidite or brannerite-type of vein deposit.

The presence of cobalt minerals in uraninite ores was early recognized as a valuable aid in uranium exploration. Pitchblende is closely associated in many deposits--and in Morocco, brannerite too--with such cobalt-bearing sulfides and arsenides as smaltite, cobaltite, linnaeite, skutterudite, and, in the oxidized zone, erythrite. Principally this combination is present in the Ni-Co-Ag ore types noted above at such classic localities as Shinkolobwe in the Belgian Congo, the Joachimsthal district of Czechoslovakia and Germany, and the Great Bear Lake district of Northwest Territories, Canada (Everhart and Wright, 1953). The uraninite deposits of the Coeur d'Alene district, Idaho, were discovered as a result of the observed association of uranium oxide with Co and other diagnostic metals in this type of deposit (Thurlow and Wright, 1950).

Lead is the next most widespread and abundant metal associate of uranium in vein deposits. But because it is a very common metal in most hydrothermal veins and because hundreds of lead-bearing veins are singularly non-radioactive, lead is not in itself diagnostic of uranium. Galena is the only lead-bearing mineral that has been reported in significant quantity in uranium-bearing vein deposits although cerussite, anglesite, and pyromorphite are present in certain oxidized zones, particularly in the Goodsprings area of Nevada.

Nickel is a major constituent in the Co-Ni-Ag ore type. However, it is less widespread than Co in uraniferous vein throughout the world and is restricted to the one ore type. Nickel deposits other than those in association with Co and Ag in veins are generally non-radioactive. Common nickel minerals in the nickel-cobalt silver ore type are pentlandite and niccolite.

Silver is the third major associate in this ore type. It occurs in the same vein structure with uranium in this type of ore deposit in a variety of minerals--principally argentite, pyrargyrite, proustite, stephanite, polybasite, and native silver. The silver and uranium minerals, however, tend to occupy different positions in the zones that characterize these ore bodies and rarely occur together in the same specimen or, in quantity, even in the same stope.

Zinc is found in many uranium-bearing veins, but the association of the two metals does not appear to be particularly significant because zinc is common in vein deposits in general and because many rich zinc ores throughout the world are non-radioactive. Nevertheless, sphalerite is present in many of the ores containing uranium, copper, cobalt, lead, and silver.

Several molybdenum minerals have been identified in uranium-bearing veins--particularly in the silica-iron-lead type. Both molybdenite (MoS_2) and molybdite (MoO_3) have been described in these uranium ores in several districts. In the Marysvale district, Utah, ilsemannite, a molybdenum sulfide, and its oxidation product, jordisite, have also been observed in several of the veins, and in the Freedom No. 2 mine, the new mineral umohoite ($UO_2 \cdot MoO_4 \cdot 4H_2O$) has been described by Kerr, and others (1953). Furthermore, preliminary geochemical prospecting by Gilbert (personal communication) in the Marysvale area indicate that Mo anomalies in the rocks and soils of the Marysvale district serve as a useful guide to ore.

Native bismuth is an associate of pitchblende in a few ore deposits of the Co-Ni-Ag type, notably in the Great Bear Lake district of Canada and the Johanngeorgenstadt district of Czechoslovakia. It is not a widespread associate, however, and many of the notable concentrations of Bi in the world, especially those associated with mafic or ultramafic rocks, as in the Cobalt, Ontario district, are only weakly uraniferous.

Titanium is another somewhat localized associate of uranium in hydrothermal vein deposits. This association is restricted to the davidite-iron-titanium-uranium type and is best observed in the Radium Hill district of South Australia (Parkin and Glasson, 1954) and the Tete district, Mozambique, Africa (Davidson and Bennett, 1950). In this association, unlike the others discussed above, the Ti and U occur together in the same mineral, davidite. The titanium minerals ilmenite, rutile, and sphene are also common constituents in this type of "vein." The possibility exists that the Mozambique deposit is a magmatic segregation or late magmatic replacement in anorthosite, similar to the ilmenite deposits so commonly associated with anorthosite.

Vanadium is a common associate of uranium in uranium deposits occurring in continental sedimentary rocks. As discussed elsewhere in this paper, the mineral carnotite, a potassium-uranium vanadate, is one of the principal ore minerals in the deposits in sedimentary rocks. Carnotite has also been described as an alteration product in a few uranium-bearing veins in various parts of the world (e. g. pitchblende veins in French Morocco, uraniferous hydrocarbon veins at Placerville, Colorado, and davidite veins at Radium Hill, South Australia). Being both sporadic in distribution and low in relative content, vanadium cannot be considered as an important metallic associate in veins.

Native gold is a close and significant associate of uraninite in uranium deposits occurring in metasediments--particularly quartzite and silicified conglomerate, as in the Witwatersrand deposits of South Africa (C. F. Davidson, 1953) and in the Missisagi conglomerate deposits of the Blind River district, southwestern Ontario (Joubin, 1954). Gold-bearing vein deposits also are known to contain small pitchblende ore shoots at a few localities--notably the Central City-Quartz Hill district of the Front Range, Colorado. Auriferous veins in general have not been found to be abnormally radioactive, however, and gold is considered only as a sporadic and non-diagnostic associate of uranium.

Non-metallic minerals

The major non-metallic gangue minerals in uraniferous vein deposits fall generally into three groups--the silica minerals, the carbonates, and fluorite. Several other gangue minerals are prominent in certain localities but appear to have little general significance.

Crystalline alpha or beta quartz in one or more of a variety of colors, and ranging in form from microcrystalline to large single crystals, is present in nearly every known uranium-bearing vein deposit. At many localities the crystalline quartz adjacent to highly uraniferous minerals tends to be dark in color. In fact radiation damage is said to be the cause of some smoky quartz. In many of the uranium-bearing veins of the world, however, most of the copious quartz gangue is nearly colorless or white. Quartz is much more common in veins transecting igneous host rocks, in association with pyrite, galena, and uraninite or davidite than it is in metamorphosed sedimentary or volcanic host rocks, where uranium generally is associated with the complex Co-Ni-Ag ores.

Chalcedony and jasper are the dominant gangue minerals in many vein deposits--particularly those in Portugal, Joachimsthal, Czechoslovakia, Marysvale, Utah, and Cornwall, England. These minerals are especially susceptible to hematitic permeation, as discussed below.

Opaline silica is prominant in a few vein deposits--particularly those transecting granitic intrusive rocks, as at Marysvale, Utah, Wolsendorf, Germany, and Urgeirica, Portugal. Its presence apparently depends on the availability of excess water in the last hydrothermal fluids responsible for the deposition of the vein matter.

Nearly all the common carbonate minerals have been reported as gangue in a number of uranium-bearing veins throughout the world. For the most part, however, significant quantities of them are concentrated in veins transecting metasedimentary rocks, in association with complex suites of vein material. Dolomite, ankerite, and siderite are the most common; calcite is prominent only in a few deposits, principally in the Canadian Shield. Witherite and rhodochrosite are prominent in the Great Bear Lake deposits, Canada, but are not generally common elsewhere.

Dark-colored fluorite is one of the most characteristic of the gangue minerals in uraniferous veins, particularly those of relatively simple mineralogy in granitic intrusives. It is prominent in the veins of the Wolsendorf, Germany; Marysvale, Utah; and the Colorado Front Range districts and also occurs as a minor constituent of a majority of all vein deposits studied to date. There appears to be a direct correlation between the color of the fluorite and its proximity to uranium minerals--that in association with uranium is black or very dark purple and may be uranium-bearing too. Light green to white fluorite is universally non-radioactive and is not an associate in uranium veins. The fluorite veins of central Utah, the Jamestown district, Colorado, and the Wolsendorf district contain as much as 0.2 percent U in places; most of the uranium is in the form of uraninite, finely disseminated through the fluorite crystals.

Several other non-metallic minerals are prominent in certain deposits but appear to have little general diagnostic significance. Amorphous hydrocarbons, some identified as thucholite, are present in the Lake Athabaska district, Canada, in the Colorado Front Range, and a few other deposits. Barite is common in several localities. Chlorite is a prominent vein mineral in the Shinkolobwe deposits of the Belgian Congo and is present in several others. Talc is also prominent at Shinkolobwe. Actinolite, tourmaline, and diopside are all common vein minerals in the high-temperature uraniferous veins of

[illegible]

Paragenesis of uranium-bearing vein deposits

As a general rule primary uranium minerals in vein deposits occupy variable paragenetic positions. In many deposits they are among the earliest minerals to form and in others they are among the latest. In the deposits of Precambrian age, pitchblende is early in the mineral sequence (Everhart and Wright, 1951). In deposits of late Paleozoic and Mesozoic age it is variable in position and in deposits of late Mesozoic and early Tertiary age it is commonly late in the sequence.

The variable paragenetic position of the uranium minerals is believed to be a result of the varying chemical conditions under which the minerals are deposited. The rate and intensity of oxidation in the ore solutions appear to be the dominant influence as suggested in the preceding discussion of the uranium cycle in the chapter on the geochemistry of uranium.

Factors bearing on uranium deposition in vein deposits

Factors of significance in the process of uranium deposition in vein deposits include the temperature of the precipitating solutions, the depth of the precipitation site and pressure relationships, the chemical environment of precipitation, and structural control of the ore deposition.

The factual data presented in the foregoing paragraphs, together with laboratory work carried out to date, provide several strong clues to these important factors and in turn shed some light on the origin of uranium-bearing vein deposits.

Temperature

With the opening of the Shinkolobwe and Great Bear Lake deposits in the early days of uranium mining and geology, the Co-Ni-Ag-U type of deposit was the first to be studied thoroughly. Such deposits were recognized as being typically mesothermal according to the Lindgren classification (Lindgren, 1933). The temperature of deposition for such veins is generally regarded as falling in the range of 175° to 300°C. Subsequent studies of the silica-pyrite-galena type of uraniferous vein deposits, however, have indicated that at least the late-stage, "sooty" type of pitchblende, which has generally undergone considerable secondary oxidation, may represent deposits approaching the epithermal class, indicating precipitation ranging down to room temperature, (Miller and Kerr, 1954). At the same time, a consideration of uranium-bearing vein deposits in Chile (where such minerals as actinolite and tourmaline are associates) and in South Australia (with rutile and ilmenite) has indicated depositional temperature at least up to 500°C. In summary, field evidence suggests that uranium in veins may be deposited as an oxide at temperatures as low as room temperature and as high as several hundred degrees C, the upper limit not having been yet established. The davidite-type deposits appear to be formed at even higher temperatures and are gradational into pegmatite deposits.

In the laboratory, controlled synthesis of uranium oxide has provided data confirming the lower ranges of depositional temperature. Gruner (1952) demonstrated that pitchblende is precipitated from acid uranyl solutions at temperatures from 50° C to 215°C by either H_2S or organic reagents. S. M. Lang (1953) compiled current literature on the solid-state reactions of the uranium oxides that indicate precipitation over these temperature ranges. Miller and Kerr (1954) further confirmed Gruner's work by precipitating pitchblende from uranyl sulfate solutions with H_2S at temperatures ranging from 50°C to 233°C. Recently Gruner (personal communication) has precipitated pitchblende at 25°C.

Pressure and depth of precipitation

Typical mesothermal deposits, including the Co-Ni-Ag-U ores and many of the silica-pyrite-galena ore types, are believed (Lindgren, 1933) to form under pressures of 140 to 400 atmospheres at depths of 4,000 to 12,000 feet. Many of the more nearly epithermal types of uranium-bearing veins presumably were formed at considerably less pressure and shallower depths. In Gruner's syntheses (1952) of uranium oxide, only saturated vapor pressures of the solutions were maintained (in the experimental "bombs") for the respective temperatures. Likewise, Miller and Kerr (1954) sealed their solutions, saturated with a reductant, below a reducing atmosphere and heated them to various temperatures. The pressures of these experiments were thus the vapor pressure of the liquid and the pressure of the gas. They estimate that uranium oxide was synthesized at pressures from 0.1 to 29 atmospheres.

Field evidence indicates strongly that most uranium-bearing veins were formed at depths shallow enough, and at pressure low enough to provide open spaces along regular fissures. Most of the mineral concentrations have filled such open spaces although in a few localities replacement has occurred in carbonate-rich host rocks (as at Shinkolobwe) and to a much lesser extent in igneous intrusive rocks and quartzite.

Chemical environment of precipitation

It has been pointed out in the foregoing section on the geochemistry of uranium, that (1) the important valences of uranium in nature are 4 and 6; (2) U^{+4} is lithophilic and is stable in magmatic and metamorphic rocks; and (3) the valence state of uranium in solution during vein formation is not well known, but the uranium may be transported as U^{+6} and precipitated as UO_2 by a reduction reaction (Phair, 1952). Gruner (1953) also believes it probable that uranium initially is in the hexavalent state in nearly all solutions instrumental in its transfer, and that under oxidizing conditions it is in the solutions as the uranyl ion, UO_2^{++}. In natural solutions ranging in pH from 1 to 5, the uranyl ion is most commonly in association with sulfate ions. According to Miller and Kerr (1954), the uranyl ion, $\overset{+6}{U}O_2)^{+2}$, forms a significant couple in acid solution with the U^{+4} ion according to the equation (Latimer, 1952):

(1) $UO_2^{++} + 4H^+ + 2e^- = U^{+4} + 2H_2O, \quad E^o = 0.334$ volt

Given sufficient time the U^{+4} ion precipitates as pitchblende, UO_2, so the essential half-cell reaction is

(2) $UO_2^{++} + 2e = \overset{+4}{U}O_2$ (pitchblende), $E^o = 0.220$ volt

Confirming Gruner's work of 1952, pitchblende has been precipitated by Miller and Kerr from uranyl sulfate solutions by the use of hydrogen sulfide gas. It has been found that a catalyst is not necessary and the reaction is essentially

(3) $H_2S + (\overset{+6}{U}O_2)^{+2} + 4H^+ = S + \overset{+4}{U}O_2 + 2H_2O$

Pitchblende was also precipitated from uranyl sulfate solutions containing sodium sulfide. This reaction is similar to equation (3).

Sulfur dioxide readily reduces the uranyl ion according to the general equation

(4) $(\overset{+6}{U}O_2)^{+2} + SO_2 + 2H_2O = \overset{+4}{U}O_2 + H_2SO_4 + 2H^+$

Sulfur is not precipitated in this reaction since the SO_2 is being used as the oxidizing agent and goes to sulfate.

From these experiments, it is demonstrated that pitchblende is readily precipitated by H_2S and SO_2.

It is also well established (Katz and Rabinowitch, 1951) that several kinds of basic carbonate solutions, with a pH of 8.5 upward, hold uranium as complexed ions, particularly at temperatures above 150°C.

Thus, hydrothermal solutions that are even slightly acidic or basic may carry hexavalent uranium. Precipitation of primary uranium minerals may be caused solely by a decrease in temperature and/or pressure, or may be the result of chemical interaction with the host rock. Either mechanism may result in $(U^{+6}O_2)^{+2}$ reduction. The latter influence would seem to be of major importance in most hydrothermal deposits. The Co-Ni-Ag-U type of ore deposits, being characteristically rich in carbonates, may well represent the neutralization of alkali-rich solutions in metasedimentary and metavolcanic rocks, coupled with a critical threshold in temperature and pressure. The silicic davidite and the pyrite-galena-uranium types of deposits represent the precipitation of uranium from acidic solutions in reducing environments, also influenced by critical drops in temperature and pressure.

One of the most striking and persistent features of uranium veins is their common association with hematitic alteration. The association of hematite with pitchblende is so sufficiently consistent, that in nearly all of the districts described here, hematite staining is widely used by prospectors as a guide in the search for uranium deposits. In some deposits the alteration has particularly affected the gangue minerals--calcite, dolomite, and jasper. Elsewhere the wall rocks--granite, diabase, quartzite--are affected. In some deposits both gangue and wall rocks are altered. Uranium miners in the Erzgebirge long used reddish-brown platy vein dolomite as a guide to pitchblende; away from the pitchblende concentrations the dolomite is white. Wherever pitchblende is found in the Lake Athabaska district hematite is closely associated with it, both within the gangue material and within the country rock. Several of the Great Bear Lake veins are bordered by a band of reddish gangue.

The cause of such widely developed hematitic alteration is under investigation by a number of research workers. In a comparative study of the Colorado Front Range and Montreal River deposits, H. D. Wright (1954) noted that disseminated hematite is strongly developed in veins that carry limited pyrite and a predominance of calcite gangue. He suggests that the oxidizing action of carbon dioxide in mineralizing solutions and the small amount of sulfur available as a reducing agent may provide a partial explanation for the abundance of hematite. Under vein-forming conditions iron is a much more likely oxidizing agent than CO_2; perhaps the explanation lies in the reaction

$$2Fe^{++} + (U^{+6}O_2)^{+2} + 3H_2O = U^{+4}O_2 + Fe_2O_3 + 6H^{+}$$

which goes to completion at 25° C at pH values higher than about 4.0.

The work on hydrothermal alteration by Kerr and his associates (1953) in the Marysvale district, Utah, and that of Wright and Beiler (1953) in the Boulder batholith, Montana, have indicated the power of uraniferous hydrothermal solutions, in places, to soak several tens or even hundreds of feet into the granitic wall rock of the veins. This is reflected by an orderly zonal arrangement of mica and clay minerals and parallels in a general way the observations on hydrothermal effects in the Tintic district, Utah, by Lovering (1949) and in the Butte district by Sales and Meyer (1950). The same sort of evidence has been observed in Portugal by Everhart.

Structural control of ore deposition

Most of the deposits under consideration are characterized by relatively obvious structural control of uraninite deposition. Open space fissure filling is evidenced by such features as symmetrical banding of the vein matter, crystal lined vugs, open brecciated character of the veins, and the general lack of replacement. At Joachimsthal most production has been from the open "Midnight" veins which trend north across the schistosity. The "Morning" vein group which parallels the schistosity is largely lacking in pitchblende. Within the favorable "Midnight" group the open vertical portions of the veins are metalliferous, and in contrast the "flats", which are tight and strongly brecciated, are usually barren.

A similar control of mineralization by varying vein trends is indicated at Urgeirica. Most of the ore bodies here are within straight portions of the veins, where the initial controlling fissures were most open. In tight segments, along some bends, ore bodies are lacking. At Lake Athabaska many of the larger deposits are located along the St. Louis fault, which is one of the major persistent structures of the district. The fault itself is not consistently mineralized; rather, the ores are commonly associated with small-scale sympathetic fractures.

Only a few deposits show evidence of significant replacement. At Johanngeorgenstadt, for example, the wall rock is reported to be impregnated in places with pitchblende and can be mined for a width of several meters on each side of the vein proper.

Origin

Summing up the foregoing discussion, the following postulations for the emplacement of uranium minerals in vein deposits appear valid:

1. Because the more felsic magmas, and intrusive and extrusive rocks derived from them, are the most uraniferous known, the residual fluids forming hydrothermal solutions at the end of a granitic or syenitic magmatic cycle constitute a rich source for uranium.

2. These uraniferous solutions, under high pressure and temperature, seek out well-developed tensional, open-space fractures in the crust, as an access upward.

3. Uranium, in the uranyl ion, begins to encounter conditions favorable for precipitation in the higher-temperature hypothermal to mesothermal zones. If the solutions are also rich in titanium, iron, and silica, davidite-type ore deposits may be precipitated at this stage. The host is most commonly the parent granitic rock. If the solutions contain a complex assemblage of base metal ions, the Co-Ni-Ag type of ore may be deposited in the mesothermal zone. Metasedimentary and metavolcanic rocks appear to be the most favorable hosts for the precipitation of this type of assemblage. Fine-grained dissemination of hematite in and around the veins also typifies these deposits.

4. The simpler silica-iron-lead ore type appears to be deposited throughout a larger range of temperatures and pressures, approaching the epithermal zone at the lower end, and prefers felsic intrusives as a host rock. This type appears to be particularly susceptible to subsequent, near-surface oxidation effects, giving rise to the "sooty pitchblende" variety of uranium oxide and variable combinations of secondary phosphates, sulfates, arsenates, vanadates, and hydrous silicates and oxides. Such host rocks are also commonly affected by the alteration results of the hydrothermal solutions, as expressed by the zoning of clay, silica, chlorite, and other "alteration" minerals. Hence, caps of secondary minerals and alteration commonly characterize the deposits down to as much as 200 feet from the surface, and extensive physical exploration is necessary to ascertain the true primary nature of the deposit.

SANDSTONE-TYPE DEPOSITS

The sandstone-type deposits of the Colorado Plateau yield the largest production of uranium in this country, and similar deposits on the Witwatersrand of South Africa are the world's largest source of uranium. Moreover, many of the important recent discoveries of uranium in other areas are of this type. Although the genesis of these deposits has received well deserved consideration from many geologists, virtually all aspects of their origin have been and are now controversial. In fact, it is safe to say that the origin of these deposits is the most widely and hotly debated problem in the field of uranium geology.

Mode of occurrence

The most impressive common denominator of these deposits is that they generally occur in lenticular sandstones and conglomerates. Although they have many other similarities, their mode of occurrence is described here in terms of the two most important deposits, the Colorado Plateau and Witwatersrand.

Colorado Plateau

The ores of the Colorado Plateau have long been known as carnotite ores because of the prevalence of that mineral. Recent deeper drilling and mining, however, have shown that carnotite $(K(UO_2)_2(VO_4)_2 \cdot 1\text{-}3H_2O)$, tyuyammunite $(Ca(UO_2)_2(VO_4)_2 \cdot nH_2O)$, volborthite $(Cu_3(VO_4)_2 \cdot 3H_2O(?))$, and other high-valent hydrous oxides, carbonates, sulfates, arsenates, vanadates, and silicates are oxidation products of black ores that contain uraninite, coffinite, montroesite $((V, Fe)O(OH))$, chalcopyrite, pyrite, and several other low-valent oxides and sulfides (Rasor, 1952; Rosenzweig and others, 1954; Weeks and others, 1953; Weeks and Thompson, 1954; Garrels, 1953). A vanadium hydromica is common in the vanadium ores. Kaolinite is much more abundant in the ore-bearing parts of some of the sandstones than in adjacent barren beds (Williams, TEI 490, p. 47) and chlorite may be the predominant vanadium bearing silicate. Carbonized wood, asphaltic carbonaceous matter, and a harder form of uraniferous "carbon" that has been likened to thucholite (S. H. U. Bowie, oral communication, 1952) are also present; wood is the most abundant variety of carbonaceous matter and it is the exceptional deposit that does not have it or one of the other types of carbonaceous material. Quartz overgrowths are abundant on the sand grains, particularly along the edges of the ore bodies and in the wall rocks; within the ore many of the overgrowths are etched or ragged in outline (Waters and Granger, 1953).

The ores vary markedly in composition, particularly as regards metal content. Uranium, vanadium, copper, or silver may be the dominant metal, perhaps even to the exclusion of any but trace amounts of the others. The common types, however, are uranium-vanadium, copper, copper-uranium, and copper-silver ores (Riley and Shoemaker, 1952). Ores high in copper are generally low in vanadium and vice versa. Lead, zinc, silver, molybdenum, cobalt, nickel, arsenic, selenium, beryllium, barium, strontium, and rare earths also occur, though generally in minor amounts (Shoemaker, TEI-490, p. 69). The content of both major and minor metals displays regional trends in certain areas.

The ore minerals fill pore spaces in sandstones and conglomerates and also replace clay galls and logs as well as other wood fragments (Fischer, 1943). Most of the deposits are in tabular masses, elongated in the direction of the long axes of the sandstone or conglomerate lenses in which they occur, or in a direction parallel to the orientation of logs and other marks of current lineation. The host rocks are thus interpreted to be fossil stream channel deposits (Fischer, 1950). Most of the deposits occur in or near the thicker parts of the lenses, where mudstone partings or fine debris are present, and where logs and other types of carbonaceous matter are abundant (Weir, 1952; Stokes, 1952; Finch, 1953). The deposits often cut across the bedding, particularly where they form concretion-like structures known as "rolls." In the vicinity of ore, associated mudstone lenses are green or gray instead of red and, in the oxidized deposits, the sandstone has a freckled appearance instead of its usual uniform reddish brown color (Weir, 1952). In unoxidized deposits the sandstone near ore is light colored and contains disseminated grains of pyrite. Individual deposits range in length from a few to a few hundred feet in length and their ratio of length to width may range from nearly 1:1 to 10: 1 or more.

In stratigraphic distribution, the sandstone deposits of the Plateau are found in many formations ranging from those of Pennsylvanian to those of Tertiary age. Ore has been produced from about 20 formations over this span of beds, but the principal producers have been the Triassic Moenkopi, Shinarump, and Chinle formations, the Jurassic Entrada, Summerville and Todilto formations, and the Morrison formation (including the Salt Wash, Recapture, West Water Canyon, and Brushy Basin members) (Riley and Shoemaker, 1952; T. W. Mitcham, unpublished chart, 1954; Finch, 1955). Within any given area minable deposits generally are restricted to one favorable zone or layer a few or at most a few tens of feet in thickness, and they are widespread within it.

By and large most of the uranium deposits on the Plateau show no obvious relation to local structures other than those of sedimentary origin. In a few areas, however, particularly in the vicinity of the La Sal Mountains, copper, copper-silver, and some uranium-vanadium deposits are localized along faults, particularly faults of early Tertiary age associated with the collapse of salt anticlines (Shoemaker, written communication, 1951). In contrast to most of the deposits in sandstone and conglomerates, those in the Todilto limestone near Grants, New Mexico, seem to be concentrated along fractures (Bucher, 1953; Gilkey, 1953). Curiously, the deposits in the younger Westwater Canyon sandstone member of the Morrison formation in the same area also seem to be concentrated along and near fractures, though in other respects they resemble those in other formations in other areas. The Todilto deposits are often classed with sandstone deposits because of their geographic and stratigraphic position. They bear little resemblance to the sandstone deposits, however, except that the primary uranium mineral is pitchblende and the deposits, though apparently localized along fractures, are widespread at one stratigraphic horizon.

The regional distribution of the deposits has been correlated with both tectonic and sedimentary features. Within any given formation, the deposits are most prominent in areas where channel deposits are well sorted, but are intertongued or interbedded with mudstones (Craig and others, 1951; D. F. Davidson, 1953; Mullens and Freeman, 1954), or are near the margins of deposition of the formation (Mullens, TEI-390, p. 23; Finch, 1953). The host sediments have a high mean permeability, are characterized by large variations in permeability, and are only fair to poor in regional transmissive capacity (Jobin, TEI-490, p. 48). In some areas deposits are common in the vicinity of the soda-rich laccolithic intrusives (Shoemaker, written communication, 1951; Riley and Shoemaker, 1952; Reinhardt, 1952) and on the east side of the La Sal Mountains many deposits are closely associated with the Permian salt anticlines (Cater, 1954). As a result of these controls, singly or together, many of the most important deposits are clustered together in "mineral belts" that have considerable regional continuity. Of these, the Uravan mineral belt (Fischer and Hilpert, 1952), a crescent-shaped belt on the east and north side of the La Sal Mountains, is best defined but three others have been recognized recently in Utah and Arizona (Finch, 1953).

The distribution of metals also seems to form a regional pattern in western Colorado, despite the fact that the deposits occur in different formations (Riley and Shoemaker, 1952; Shoemaker, TEI-490, p. 68-78). Generally speaking, the deposits in the Entrada formation west and north of the San Juan Mountains are high vanadium ores, whose V_2O_5/U_3O_8 ratio ranges from 20 to 30. This ratio decreases westward to 3 or less in the Uravan mineral belt. Nearly all the copper-silver deposits lie between the Uravan mineral belt and the La Sal Mountains and small copper-gold deposits lie within the La Sal igneous complex itself. According to Shoemaker (written communication, 1954), present knowledge thus suggests the existence of a partially overlapping concentric zonal arrangement of copper-gold, copper-silver, and uranium-vanadium deposits around the east side of the La Sal Mountains.

Witwatersrand

The Witwatersrand ores consist mainly of pyrite, uraninite, thucholite, gold, sericite, chloritoid, and chlorite as well as minor amounts of cobalt, copper, nickel, lead, and zinc sulfides (Young, 1917; Reinecke, 1927, 1930; Davidson and Bowie, 1951; C. F. Davidson, 1953). These minerals are mainly in pore spaces in coarse sandstones and conglomerates that also contain abundant quartz overgrowths and considerable vein quartz in veinlets, seams, and irregular masses (Graton, 1930, p. 155-159). The gold is very fine-grained (visible gold is rare), crystalline, and closely associated with and in part dispersed in the pyrite, which is also fine-grained. Some gold is also closely associated with thucholite, a uraninite-hydrocarbon aggregate (Davidson and Bowie, 1951) that occurs in warty grains, thin botryoidal sheets, and veinlets (Graton, 1930, p. 143). Detrital heavy minerals are principally zircon and chromite (C. F. Davidson, 1953, p. 9), but a variety of others have been found in trace amounts.

The Precambrian Witwatersrand system is about 25, 000 feet in thickness, but ore is confined to a dozen or so thin conglomerates, mostly in the upper half of the system (McLean, 1954). Of these, only one or two are prominent ore-bearers in any given area (Reinecke, 1940, p. 120). Within these layers ore seems most abundant where the conglomerates are thickest and where the pebbles are coarsest and best sorted. The vertical sequence of sediments and of uranium in them is cyclical (Simpson, 1952, 1953a, 1953b). Shales alternate with quartzites in the lower part of the system and shaly or fine-grained quartzites alternate with conglomeratic zones in the upper part (Sharpe, 1950, p. 266-273). "At certain points quartzites tend to become coarser in texture and develop further through transition stages of grits and scattered pebble horizons into conglomerates. The cycle then reverses itself and the conglomerates pass upwards into quartzites. These cycles. . . are often associated with well defined cycles of uranium deposition which may open slowly, reach a full development of the conglomerates, and then slowly die away." (Simpson, 1953a, p. 42).

The ore-bearing horizons have considerable lateral continuity, but ore tends to be concentrated in elongated paystreaks as much as 4, 500 feet long and 1, 000 feet wide, but often much less. Vein quartz, quartz overgrowths, sericite, chloritoid, and chlorite are also often more abundant in the paystreaks than elsewhere (Reinecke, 1930, p. 100). The paystreaks are roughly parallel but tend to form a braided or arborescent pattern. Reinecke and Johnson (Reinecke, 1940, p. 127) have interpreted them as channels on a gigantic alluvial fan. Graton (1930, p. 16) and Young (1917), however, concluded that the deposits are marine and Sharpe (1950) that the conglomerates are shoreline deposits, formed along the margin of a large lake or sea.

The ores seem unrelated to fractures and faults, although a few faults are mineralized where they cross ore-bearing horizons and gold is not uncommon in pebble fractures. The abundance of vein quartz, quartz overgrowths, sericite, chloritoid, and chlorite in many places is determined by the location of faults, fractures and dikes (Reinecke, 1930, p. 100).

Thin quartz veinlets are not uncommon; some of them contain gold (Young, 1917) and one high in the system contains pitchblende (C. F. Davidson, 1953). Such phenomena, however, comprise a minor part of the Rand picture. A variety of igneous intrusives has been reported from the Rand. They range in composition from basic to acid to alkalic types, but the most common are altered diabase dikes. Few have any relation to ore.

Origin

The Witwatersrand ores have greater lateral continuity and are lower in uranium content than the Plateau ores; the ores also differ somewhat in the assemblage of dominant metals--chiefly the presence of gold and the absence or paucity of vanadium, copper, and silver in the Rand ores and the reverse with respect to the Plateau ores. Nevertheless, the deposits have many similarities and similar hypotheses of origin, or variants of them, have been presented for ores in both regions. The chief hypotheses are: 1) placer concentration of the chief ore metals, followed by recrystallization and some redistribution of them, possibly in conjunction with later introduction of sulfides (Bain, 1952; Mellor, 1916; Young, 1917, Reinecke, 1927); 2) precipitation from surface or ground-waters at or shortly after the time of deposition of the enclosing sediments, followed by recrystallization and some redistribution (Hess, 1914, Coffin, 1921; Fischer, 1937; Gruner, 1951; MacGregor, 1953); 3) derivation from volcanic tuffs or other sediments elsewhere in the sedimentary column by ground water action (Hillebrand and Ransome, 1905; Lindgren, 1913, p. 368; Butler, 1920, p. 156; Koeberlin, 1938; Proctor, 1953; Gruner, 1954); 4) derivation from petroleum or petroleum source beds (Gott and Erickson, 1952); and 5) precipitation from hypogene solutions derived from igneous activity but perhaps injected into circulating ground waters (Dodd, 1950; Rasor, 1952; Waters and Granger, 1953; Cater, 1954; Kerr and Lapham, 1954; Shoemaker, written communication, 1951; Graton, 1930; C. F. Davidson, 1953).

At the heart of the controversy are the facts that 1) the distribution of the ores is conspicuously related to sedimentary lithology and structure and less commonly or inconspicuously related to fractures and igneous rocks; 2) the ores in both districts occur in many beds over a wide stratigraphic range; 3) alteration of host or wall rocks is not pronounced; 4) vanadium, a prominent constituent of some of the Plateau ores, is not characteristic of hydrothermal ores--nor of placers or coarse clastic deposits in general; and 5) the assemblage of sulfides and low-valent oxides abundant in both the Plateau and Rand ores is not characteristic of placers or other syngenetic deposits in coarse clastics. Many other features, typical of syngenetic or of hydrothermal deposits, are absent or not present in the expected degree, so that the familar guide posts are lacking or are inconspicuous.

Space will not permit a detailed account here of all the points and counter points cited in the voluminous literature on this subject--the interested reader may refer to the citations above to learn more of the pros and cons of the various theories. The discussion here is restricted to the evidence and problems we consider most critical. Good intentions notwithstanding, the selection of evidence may well reflect bias. It is only fair to the reader, therefore, to identify our bias at the outset--we favor an outside, preferably hypogene, source for the ores.

Age of the ores compared to the host rock

The paragenetic relationships of the ore minerals in both districts clearly show that they were formed after the host rocks were deposited. Many believe, however, that the chief ore metals were introduced during or shortly after deposition of the host rocks, although most of those who favor a placer hypothesis agree that the sulfides were introduced later.

New and convincing evidence on the relative age of the Plateau ores has been presented recently by Stieff, Stern, and Milkey (1953). They show that the mean Pb^{206}/U age of many samples of Colorado Plateau ores, after correction for the common Pb present, is 71 million years. The mean ages of samples of Morrison, Entrada, and Shinarump ores are 72, 50, and 73 million years respectively. The most reliable individual determinations are those on uraninite ores from the Happy Jack and Shinarump No. 1 mines, in the Shinarump formation, which are 65 and 75 million years respectively. These ages are much younger and more uniform than would be expected if the ores were formed at the time of deposition of the host rocks, but they compare favorably to the 60.5 million years determined as the mean age of four pitchblende samples from hydrothermal veins in the Colorado Front Range. Stieff, Stern, and Milkey interpret their results to mean either that syngenetic uranium deposits were redistributed in late Cretaceous or early Tertiary time or that the uranium was introduced from depth at that time. The first alternative they regard as less probable because in such a redistribution the common lead found in the ores would have had to be transported and redeposited with the uranium and the previously formed radiogenic lead carried away or deposited elsewhere.

Liebenberg (1948, p. 20) interpreted rounded grains of thucholite in the Rand ores as detrital but Davidson and Bowie report that their shape can be matched exactly by hydrocarbon grains in the fissure veins. Isotope studies do not easily resolve the relative age of the ore and host rock in the Witwatersrand because the uraninite is very finely divided (and hence subject to radon leakage); it is difficult to separate the two generations of uraninite for age determinations; and the ages of the host rocks are known only roughly. Recent determinations reported by C. F. Davidson (1953) and Louw (1954) give ages of 1682 and 1850-1950 million years respectively_/. These ages are older than the Witwatersrand system was previously thought to be, though Davidson points out that, as the geology indicates, the system is still "younger than the pegmatites of the Archean of Southern Rhodesia (presumably coeval

---

_/ Davidson (1954) has since revised his figure to 465-816 million years and, L. R. Stieff (oral communication, 1955), believes correction for old radiogenic lead in the ore may significantly lower the ages computed by Louw.

with the Swaziland System) for which Ahrens has recently adduced an age of 2,100 million years". Louw considers the old age of the uraninite to indicate derivation from pre-existing terranes and depositions as placer grains with the coarse clastics of the Witwatersrand system. He gives no comparative data, however, on the age of the Witwatersrand system itself. Until the latter is established, the significance of the isotopic data will remain uncertain _/.

_/ It is possible that the minimum age of the system might be obtained by determination of the age of zircons and other accessory minerals by the Larsen method.

Source of the metals

Syngenetic sources.--The isotopic data on the Plateau ores limit the possible sources of the uranium to ones that could introduce it after the rocks were deposited. The conclusion that syngenetic sources of uranium--detrital uranium minerals or chemical or biochemical precipitates of uranium--may be ruled out of further consideration is supported by the facts that 1) uranium occurs in many horizons over a wide stratigraphic range; 2) the ores contain no appreciable quantities of heavy minerals--monazite, samarskite, brannerite, etc.--such as might be expected to compose a radioactive placer; 3) uraninite is, with one insignificant exception (Steacy, 1953), unknown as a placer mineral (C. F. Davidson, 1953); and 4) uranium, when it is concentrated by sedimentary processes, is associated with fine-grained carbonaceous shale or phosphorite, never with coarse clastic (idem). _/

_/ Perhaps it should be noted here that Bain (1952) has reported the occurrence of uranium-bearing jasperoid pebbles, believed to be derived from a Permian leptothermal uranium deposit. He regards these pebbles as the primary uranium carrier in the Shinarump ores. Part of the uranium in the pebbles is in uraniferous hydrocarbon that replaces jasperoid-- a relationship also reported in the Rand (Young, 1917, p. 60)--and because no other mineral has been reported it is possible, if not likely, that all the uranium is in this form. The pebbles are fossiliferous--not vein matter--and hardly deserve description as typical leptothermal jasperoid. Aside from the fact that Bain's conclusion is not supported by the isotopic data, more evidence seems required to show that the uranium has not entered the pebbles by replacement since, rather than before, their deposition.

These same facts, plus the occurrence of low-density thucholite with the gold--an anomaly hardly explainable if both were placer minerals (Graton, 1930, p. 145)--support a similar conclusion with respect to the Rand ores. In the absence of data on the relative age of ore and host rock, such a conclusion is perhaps less positive for the Rand ores than for those of the Plateau. Louw (1954) believes that the lack of uraninite in modern placers may not be significant as applied to the Rand ores for, according to H. C. Urey, the atmosphere prior to 700 to 800 million years may have been reducing. The pressure of primary Fe_2O_3 in sedimentary ores of Huronian age, however, makes Urey's postulation improbable.

The isotopic data bear mainly on the origin of uranium, of course, and it is possible that other metals were introduced at a different time. Admitting the lack of positive proof, we consider it probable that all the metals entered the rocks as a part of the same epoch of mineralization. This conclusion is most likely to be challenged with respect to the gold in the Rand ores. Our reasons for considering the gold epigenetic are those summarized by Graton, namely that bona fide detrital gold particles have been rarely, if ever, identified in the ore and the gold is less pure and much more fine-grained than ordinary detrital gold, so much so that it is virtually absent in recent alluvium in the district (Graton, 1930, p. 131). Recrystallization and redistribution would have tended to increase rather than decrease the grain size (idem, p. 179), so the gold likely was always finer-grained than would be expected for a placer accumulation. Although we consider the metals roughly contemporaneous in age, we recognize nevertheless that there may have been more than one epoch and one source of mineralization. The concept that the distribution of the metals is controlled by structural channelways, albeit sedimentary in origin, permits access by mineralizing solutions as long as the rocks are pervious. Present knowledge, however, does not indicate more than one period of mineralization, although Davidson suggests that the thucholite in the Rand ores has formed by polymerization of methane migrating through the rocks at a later epoch.

<u>Epigenetic sources.</u> --Three epigenetic sources have been suggested for the sandstone ores: 1) dispersed concentrations in tuffs or ordinary rocks in the sedimentary column; 2) migrating petroleum or solutions derived from petroleum source beds; or 3) hypogene solutions. Postulation of any of these sources assumes that the persistence of the ores at certain stratigraphic horizons and their relation to the texture and structure of the host rocks is mainly a function of the permeability and transmissability of the rocks. This assumption is in accord with the facts of the occurrence of both the Witwatersrand and the Colorado Plateau ores.

The isotopic data on the Plateau ores also cast light on their source. According to Stieff and Stern (oral communication, 1955; Stieff and others, 1953, p. 15) the uranium ores, the galena associated with the Plateau deposits, and lead in Tertiary vein deposits in the San Juan Mountains, the Colorado Front Range and the Tucson Mountains appear to be related in isotopic composition. All of these leads apparently contain one isotopically distinctive and member. They vary systematically in isotopic composition from this end member in a manner expectable by the addition of differing amounts of an old radiogenic lead. The added radiogenic lead has a high Pb^{207}/Pb^{206} ratio which gives a calculated age of approximately 750 million years. The averages of the Pb^{204}/Pb^{208} ratios of the leads from the separate regions overlap within one standard deviation suggesting that with the possible exception of the Colorado Front Range the thorium contents of the source areas did not exceed the concentration normally found in granitic rocks. From the presence of this lead in the Tertiary veins it seems most reasonable to assume that this source lay at depth, possibly in Precambrian, thorium-poor, uranium rich materials in the basement complex. The isotopic data make highly improbable syngenetic or penecontemporaneous derivation of the ore from the volcanic ash in the Triassic and Jurassic sediments because ores in these rocks do not show the differences between themselves expectable from the addition of radiogenic lead that would have formed in the ash prior to the removal of the uranium from the tuffs. The isotopic data alone, however, do not rule out the possibility that the ores might have been derived from a single source in the rocks above the deposits. Early Tertiary tuffs, for example, conceivably could have been derived from the same uranium-rich, thorium-poor magma postulated as the source of hypogene solutions and hence have yielded lead of like composition to leach solutions. The presence of the lead in the Tertiary veins and the fact that many of the sandstone deposits lie several thousand feet below the Tertiary make such a source improbable.

Although the isotopic data thus seem to point to a deep source for the uranium ores of the Plateau, they do not prove it conclusively.

The hypothesis that the metals might have been derived from dispersed sources within the sedimentary column has not been prominent in discussions of origin of the ores of the Witwatersrand, but it has been proposed by a number of geologists for the Plateau ores. Hillebrand showed that vanadium in small amounts is widely distributed in sandstones, limestones, and igneous rocks and Ransome postulated that the Plateau deposits simply represented a concentration of such dispersed vanadium under favorable conditions of solution and redeposition (Hillebrand and Ransome, 1905, p. 17). Butler (1920, p. 158) regarded the deposits "as having been formed by circulating waters that collected the metals disseminated through the sedimentary rocks and deposited on contact with carbonaceous matter, earlier sulphides, or other precipitating agents. The circulation in some places is believed to have been of artesian character and to have been controlled to a large extent by structural features." Butler adopted his view because he believed that all the areas in which important deposits were known were on the flanks or near the crests of folds or were associated with other structural features--a relationship Fischer (1937) thinks is not the rule--but that all had no obvious connection or association with igneous rocks.

Koeberlin (1938) and Proctor (1953) suggest that metals in the Colorado Plateau ores might have been derived from the weathering of volcanic ash. This hypothesis presumes that metal-bearing fluids are concentrated in the roof of batholiths and that the greater part of the metals are ejected into the atmosphere wherever and whenever the roof is broken by magmatic forces. Volcanic ash would therefore contain ore metals, though in low concentrations. Later weathering would release the metals to surface or ground waters, which then might redeposit them elsewhere. Koeberlin considers that the gold in volcanic ash in Chile; Hartsel, Colorado; and possibly Death Valley, California; and Snake River, Idaho; is concentrated in this manner and suggests that the metals in the sandstone ores of the Plateau are similar. Denson, Bachman, and Zeller (see Vine and Moore, 1952) present evidence that indicates such an origin for uranium in lignites in North and South Dakota. The presence of secondary uranium minerals in numerous tuffs in the western states lends credence to the hypothesis, at least as applied to some deposits. However, good chemical information indicating primary uranium concentrations in volcanic ash higher than those in rhyolites or granites is not available.

If the sedimentary column or large parts of it were available for circulating leach solutions, the volume of minor metals originally dispersed in the sediments in the Witwatersrand or the Plateau would be more than ample to form all of the ore deposits found, provided the metals could be concentrated. Gruner (1954) observes that 1 cubic mile of material averaging 0.0004 percent uranium would contain 40,000 tons of uranium; the total amount dispersed in the cubic miles of rock available would be many times greater than that found in the ore deposits. The hypothesis has the further attraction that the circulating waters would not be far out of equilibrium with the sediments and thus would not produce the marked alteration effects expected of hydrothermal solutions but not observed in the field.

Waters and Granger (1953, p. 20-22) consider that devitrification of ash may account for the presence of some of the quartz, alkalies, and metals, but they believe that most of the uranium released on devitrification of the ash would be adsorbed by montmorillonite and never get out of the source beds; they report that "over wide areas the volcanic sediments of the Brushy Basin and Chinle are thoroughly devitrified, but there are no ore deposits in the sandstones beneath." Gruner (1951) also objected to the leaching hypothesis on the grounds that the fine-grained sediments that might be the source of the minor metals are ordinarily not leached. Weeks (1953) finds no more than average radioactivity in montmorillonite in the Brushy Basin and no indication of the presence of water soluble uranium. The abnormally high amounts of uranium found in certain waters draining tuffaceous sediments in South Dakota and New Mexico show,, however, that the process does operate in nature, at least on a small scale.

Because the mechanics of lateral secretion on such a grade scale as that required to form deposits like those on the Colorado Plateau and the Witwatersrand have not been explored, the hypothesis probably deserves more consideration. The isotopic data, however, seem to make it an improbable explanation for the ores of the Colorado Plateau.

The dissemination of uranium throughout uraniferous "asphaltite" masses on the Plateau and elsewhere, suggesting that it may have been in the organic matrix while the latter was in a fluid state, the occurrence of "asphaltite" in oil-stained pore spaces, and the similarity of the assemblage of other metals in some asphaltites to that found in smaller concentrations in oil in nearby pools led Gott and

Erickson (1952; Erickson and others, 1954) to the conclusions that "asphaltite" is residual petroleum and that petroleum fluids may transport uranium to sites of ore deposition, particularly in sandstone-type deposits. Goldschmidt (1954, p. 497) postulates a similar source and history for vanadium and other metals in petroleums and asphalts. The thucholite in the Rand ores, however, has been explained as a polymerization of hydrocarbon gas resulting from its bombardment by alpha and beta radiations steaming from the uraninite, which it generally replaces (Liebenberg, 1948, p. 76; Davidson and Bowie, 1951). Davidson and Bowie (1951, p. 13) suggest that both a viscous and fluid hydrocarbon are formed on polymerization of the gas. The fluid phase dissolves and carries out some of the uranium, permitting the viscous phase to replace the uraninite. Though the uranium is dispersed in the viscous material, later, after cooling or ageing, some of it separates, forming discrete blobs or spheres of uraninite. This mechanism, though it involves some transportation of uranium by hydrocarbon fluids, seems to explain the uniform distribution of uranium in the thucholite without requiring the latter to have been a crude oil derived from petroleum source beds elsewhere. Davidson and Bowie point out that thucholite and related substances are generally found only in deposits where uranium is present in other minerals. The uraniferous asphaltite pellets recently found in the Panhandle and other gas fields in Texas and Oklahoma (Faul and others, 1952; Hill, 1954), however, are exceptions to this rule. Crude oils may contain a fraction of a part per billion to a few thousand parts per billion uranium (Erickson and others, 1954; Breger and Deul, TEI-490, p. 171), most of which seems to be in asphaltenes, but a few analyses of the Plateau oils indicate that the higher concentrations seem to be only in oil that has penetrated a uraniferous sandstone (Breger and Deul, idem). Oil is not common on the Plateau and asphalt is common only in a few areas (much "asphaltite" is proving to be woody material). For these reasons, as well as the fact that thucholite bears a replacement relationship to the early uraninite in the Rand, it seems unlikely that migrating petroleums are the source of much if any of the uranium on the Plateau or the Rand. It is entirely possible, however, that some of the uranium in both areas may have been transported short distances by fluid hydrocarbons.

Several lines of evidence have been cited to support a hydrothermal source for both the Plateau and Rand ores: 1) the Rand deposits contain ore minerals--pyrite, chalcopyrite, sphalerite, galena, pyrrhotite, arsenopyrite, cubanite, stibnite, cobaltite, coloradoite, niccolite, pentlandite, as well as gold, uraninite, and thucholite--known to be the mineral assemblage in hydrothermal deposits elsewhere (Graton, 1930, p. 73; Davidson and Bowie, 1951, p. 14; C. F. Davidson, 1953, p. 10); the Plateau ore mineral suite is similarly interpretable; 2) the gangue minerals in the Rand ores--quartz (as overgrowths but also in veins), sericite, and chlorite--are typical of this same hydrothermal association (Graton), and those on the Plateau (quartz overgrowths, carbonates, chlorite, and clay minerals) are not incompatible with it; 3) evidence of movement of mineralizing solutions--altered dikes, introduction of vein quartz and sulfides--are found along cross-cutting fractures and dikes in the Witwatersrand (Graton, 1930, p. 44); some of the ores on the Plateau, particularly those high in copper, are associated with faults (Shoemaker, written communication, 1954) or fractures (Bucher, 1953; Gilkey, 1953); 4) the content of uranium in both Plateau and Rand ores is similar to that found in many other hydrothermal ores and dissimilar to that in deposits of other origins (Davidson and Bowie, 1951, p. 14); 5) the ores in some parts of the Plateau are zonally arranged about the laccolithic intrusives (Reinhardt, 1952; Riley and Shoemaker, 1952; Shoemaker, written communication, 1954); 6) the ores in both areas occur in numerous horizons, widely separated stratigraphically; the host rocks on the Plateau are also widely separated in time (the span of time represented by the Rand ores has not been dated); 7) the ores of the Plateau, though shown by isotopic data to be genetically related, include vein copper deposits, limestone replacement ores, and the more abundant and typical sandstone ores; and 8) a hydrothermal source is most compatible with the isotopic data on the Plateau ores and not incompatible with isotopic data on the Rand ores.

Some of these features may be explainable in other ways, but one or another of them has been compelling enough to cause syngeneticists in both areas to admit that some of the deposits (see Fischer, 1937 on the copper ores of the Plateau) or some minerals in them (e. g. Liebenberg, p. 83) in both areas are hydrothermal. The arguments have not been accepted for other deposits or minerals mainly because (1) most of the ores show no direct relation to or control by structural or igneous features, whereas they are intimately related and plainly controlled by sedimentary features; (2) the host rocks are not as conspicuously altered as are most hydrothermal deposits; and (3) vanadium, an important component of some of the Plateau ores, is not an important mineral in other hydrothermal deposits. Those favoring a hypogene source admit the close relation to sedimentary features but believe that in the absence of fractures, solution movement would be controlled by the permeability of the bulk rock. They thus imagine the deposits to be bedded or "interstitial" quartz-sulfide veins, differing from hydrothermal veins only in that they occupy pore spaces in sandstones instead of fractures. The presence of "asphaltite" or thucholite in the deposits, whether derived from polymerization of a gas or a migrating petroleum, indicates that migrating fluids do have access to the ore-bearing formations and suggests that other solutions, whatever their source, might follow the same channelways to and in these beds.

The lack of conspicuous alternation may be more apparent than real. For one thing, some features of alteration are evident--the kaolin in the Triassic ores on the Plateau, for example (Williams, TEI-490, p. 47) and the widespread chlorite--and for another, quartz, the dominant mineral of the host rocks, is relatively resistant to hydrothermal alteration (Graton, 1930, p. 148).

The presence of vanadium in some of the Plateau ores is a more formidable argument against the hydrothermal theory. Wilson (1953) shows that vanadium, a lithophile element, ordinarily is concentrated in basic igneous rocks, particularly in titaniferous magnetites associated with norites and gabbros, and that this behavior, which is similar to that of chromium, accords well with known geochemical principles. Goldschmidt (1954, p. 491) reports, however, that I. and W. Noddack in their work on the geochemistry of rhenium record the presence of vanadium in practically every hydrothermal sulfide mineral in amounts up to several hundred ppm and Newhouse (1934) considers sulfide minerals a likely source of the vanadium in many of the oxidized lead deposits. Roscoelite is found in gold veins in the La Plata district, Colorado, where "it is highly regarded as an indication of good ore in many deposits" (Eckel and others, 1950, p. 74). As previously mentioned, carnotite is an alteration product of pitchblende veins in Morocco and of davidite veins at Radium Hill, Australia, suggesting that vanadium is a primary constituent of those deposits. It thus seems that vanadium can be transported by hypogene solutions, and it is possible that the vanadium in the Plateau ores was so derived. It is also possible that the vanadium or the bulk of it was derived from another source_/ within the sedimentary column, as has been suggested for the vanadium

---

_/ Syngenetic deposition of vanadium in these concentrations is unlikely because in weathering and sedimentary processes vanadium accumulates with residual or sedimentary iron or manganese deposits, or in marine carbonaceous shales--not with coarse clastics or even carbonaceous material of continental deposition.

Plainly the origin of the vanadium in the Plateau ores is a problem in its own right and it remains an open question. Nevertheless, the sum of other evidence, particularly the isotopic data, seems sufficient to us to favor a hypogene source for the uranium in the sandstone ores.

The source of the hypogene solutions on the Plateau is presumably the various laccoliths or their progenitors. The low degree of metamorphism surrounding the laccoliths (Gould, 1927, p. 103-104) suggests that they gave off only small volumes of solutions (Gruner and others, 1953, p. 38; Shoemaker, written communication, 1954). Shoemaker points out, however, that, although the zoning of the deposits does not imply a direct relation to the laccoliths, it may be related to regional variation of igneous processes at depth and be approximately a surface reflection of this variation brought about by solutions rising more or less vertically from a deep magmatic source. He remarks further that the uniformity of the laccoliths suggests a common derivation, possibly from a broad sheet-like body with lateral dimensions of the same order of magnitude as the Plateau.

The source of hydrothermal solutions on the Rand is more obscure. Although there are many basic dikes (as there are on the Plateau also) and alkalic granites intrude the Witwatersrand system at Vredfort, southwest of the Rand (Reinecke, 1927, p. 108), igneous rocks are not as widespread as on the Plateau. C. F. Davidson (1953, p. 13-14) has pointed out, however, that the Rand deposits, as well as those of the Plateau, the copper-cobalt-uranium ores of the Belgian Congo, and the uranium-copper deposits of Rum Jungle in Australia, are in a group of sediments that overlie a complex of Archean granites, which "have undergone domal uplift since the covering blanket of sediments was deposited, due presumably to 'younger' granites which are not always exposed.... May it not be that the ore deposits in each region represents a 'front' of mineralization which has emanated, through the older granites, from the younger magma below?"

In abandoning hypotheses for syngenetic sources of the ore metals, we nevertheless urge the reader not to lose sight of the fact that many exploration geologists in both districts who "know the ore best" believe it is syngenetic, for at the very least their belief attests to the close relation the ore bears to sedimentary rather than tectonic and igneous features. Thus A. M. MacGregor (1953) replied to C. F. Davidson's remarks (1953, p. 4) that the placer hypothesis for the Rand ores has become to the

South African geologists "a national article of faith" by observing that "this unfailing principle of sedimentary control has guided the underground development of the mines and has yielded dividends beyond compare in any other part of the world."

Transportation and deposition of the ore metals

The facts cited in the foregoing sections strongly suggest to us, despite the beliefs of the exploration geologists, that the sandstone ores of the Plateau and Rand are epigenetic and derived from a deep seated source. The subsequent discussion on the transportation and deposition of the ore metals is therefore so premised.

Because little is known as to how the ore metals were transported to the sites of deposition, or why they were deposited once they arrived there, it is perhaps best to begin with a list of pertinent questions on these subjects, as follows:

1. What were the physical and chemical properties of the ore bearing solutions--temperature, pH, redox potential, salinity, etc.? Were they liquid or gaseous?
2. By what means did they reach the favorable formations?
3. What physical or chemical factors defined the favorable formations?
4. How were they able to travel for long distances (perhaps miles) within the the favorable formations?
5. To what extent was deposition of the ore metals influenced by changes in the physical properties of the solutions--pressure, for example--and to what extent was it influenced by the composition of the "wall-rock"--organic matter, for example?
6. What accounts for the zonal distribution of metals in some areas? Why are they not zonally distributed everywhere?

Most of these questions will go unanswered here but it is worthwhile to present available interpretations (with particular reference to the Colorado Plateau), even though they are largely speculative.

From the time of emplacement of the ores in late Cretaceous or early Tertiary (Stieff and others 1953), there is little doubt that the formations that became mineralized were saturated with water. Consequently, because the ores commonly occur in the lower part of the formations, on top of impermeable layers, as in the Shinarump deposits in Arizona (Dodd, 1950); or "float" in the middle of an apparently homogeneous rock, as in the deposits at Rifle, Colorado (Fischer, 1943), the implication is strong that the ore-transporting medium had a density approximately that of the pore waters. If so, it would either be a liquid or a dense gas with the general properties of a liquid. This is further borne out by the generally tabular and concordant nature of the ore bodies, which tend to parallel the general bedding and to ignore cross beds. Ore is controlled by crossbedding locally, but generally not on an ore-body scale. Such a density requirement, unfortunately for simplicity of interpretation, is not incompatible with the properties of such a gas as CO_2 (Garrels and Richter, 1955) even at depths of as little as a few thousand feet.

As usual, our knowledge of the solvent properties of water or oil or dense CO_2 at elevated temperatures and pressures is so scant that there is little basis for choice of medium from such information. The introduced elements of the ores--such as uranium, vanadium, copper, iron, molybdenum, sulfur, selenium, and nickel--are strikingly similar to the trace element suite of petroleum, and this coincidence has been one of the chief arguments of the advocates of the petroleum transport school. Such a suite, however, might also be consistent with another non-polar solvent, such as dense gaseous CO_2. Furthermore, the same suite, with the exception of vanadium, characterizes vein deposits of generally accepted hydrothermal origin.

There are no good criteria for the temperature of deposition. If a late Cretaceous age is accepted, the deposits must have formed under a cover of one to two miles, which would lead to a minimum temperature of 70°-120° C, assuming a normal geothermal gradient. Whereas the fineness of grain of the ores is in itself suggestive of low temperatures, this same fineness has precluded to date any satisfactory temperature determinations by use of fluid inclusions or decrepitation techniques. The argument can be raised that the fineness of grain stems chiefly from the absence of more than intergranular openings, but polished sections of the ores reveal intricate intergrowths of the ore minerals, even within the confines of a single interstice in a medium-grained sandstone. Also the structure and texture of the ore occurrence in the Todilto limestone resemble very strikingly those of the low temperature zinc deposits in the Knox dolomite in Tennessee (cf. Bailey and Cameron, 1951, for temperature of formation of Tennessee zinc deposit). Many of the deposits show the development of chlorite and kaolinite, which accompany a removal of ferric oxide ("bleaching") from the sandstones--an effect not incompatible with a low temperature mildly acid alteration.

These considerations, while not conclusive, point, together with the ore mineral assemblage, to temperatures probably of the order of 100°-120° C. The pressures, again assuming a late Cretaceous or early Tertiary age, with a corresponding depth of formation of one to two miles, would be in the range from about 200 atmospheres (hydrostatic load) to 800 atmospheres (lithostatic load).

The primary ore minerals show unequivocally a reduced or reducing environment of deposition. Two chief schools of thought have emerged concerning the mechanism of precipitation. One school holds that the elements were transported in their higher valence state and were precipitated by a reduction mechanism. The other school believes they were carried in the lower valence state and precipitated by reaction without reduction. The argument for the first view is based largely upon the greater solubility of oxidized uranium and vanadium compounds in aqueous solutions under most conditions deemed "natural," plus the undisputed widespread replacement of fossil wood by pitchblende. Several major difficulties are present: first, the amount of reducing material originally in the sediments required to reduce vanadium from V^{+5} to V^{+3}, and uranium from U^{+6} to U^{+4}, is very large. In essence, where now a sandstone is cemented by ore, it must have been before saturated with a very effective reducing agent. A ton of 2 percent vanadium ore, for example, would require about 180 equivalents of reductant, and many extensive ore bodies occur in sandstones apparently free from carbonaceous matter. Second, the "bleached zone" that is commonly much more extensive than ore, suggests that the effect of the transporting fluids has been a neutral or reducing one (removal of Fe_2O_3), rather than the oxidizing effect of a medium in which uranium and vanadium could be carried in their higher valences.

On the other hand, to carry uranium and vanadium in their reduced state in an aqueous solution requires a chemistry with which we are not cognizant, if indeed it exists. The acidity necessary to prevent U^{+4} and V^{+3} from precipitating as insoluble oxides is great; to dissolve more than a few parts per million of uranium from pitchblende, without oxidizing it, a pH of about 3 or less is necessary. Such a low pH should have much more severe effects on the rock minerals than have been observed. If we ascribe the apparent quantitative difficulties of transport under reducing conditions to our ignorance, it is not impossible that a "compromise" hypothesis is nearer to the truth. In a strongly reduced solution, the chief ionic species in equilibrium (except at very low pH values) are V^{+3}, Fe^{+2}, and $(U^{+6}O_2)^{+2}$. Therefore montroseite and pyrite could be precipitated without a reduction step, whereas pitchblende could not. Under such an hypothesis, the quantity of reducing agent required is small; perhaps fossil wood is sufficiently abundant.

A non aqueous medium, such as oil or dense CO_2, might have certain advantages as an ore medium. If the metals were dissolved in their lower valence state, the primary uranium and vanadium oxides could precipitate by hydrolysis at the interface between the medium and the pore waters.

The preceding discussion contains few, if any, aspects that are not suggestive of similar discussions for almost any ore body. In general it can be said that our ignorance is not greater concerning the nature of the transporting agent for uranium, vanadium, and their associated elements, than it is for that in which the ore elements are carried in less controversial deposits.

The means by which the ore solution reached the favorable formations is difficult to prove. Because of the relationship that mineral deposits bear to early Tertiary faults on collapsed salt domes in the Sinbad Valley-Fischer Valley area, Shoemaker (written communication, 1954) considered these faults the entry-way to the favorable beds in that area. Bucher (1953) believes that deep fractures are the entry-way to the Todilto limestone in the Grant's district, and Graton (1930) thinks that fractures and altered dikes provide evidence of the path followed by mineralizing solutions in the Rand ores. With a few exceptions, evidence, in the form of conspicuous vein matter or alteration, for such cross-cutting channel ways is lacking but so is it lacking along channels within the favorable formations themselves, away from the ore deposits, where most of the lateral secretionists and modified placerists will agree such solutions must have traveled.

There is no doubt that one of the necessary factors for mineralization of a given formation is a relatively high permeability. However, the mineralized layers are not unique or unusual in this characteristic, and some other feature must be operative in addition. In general ore-bearing beds lie beneath thick impermeable shales, and it may be that mineralization is determined by the development of a near-horizontal flow in the sandstones caused by limited egress through the shales above. Whereas release of fluids, in a deeply buried group of water saturated rocks, may be chiefly dominantly vertically along fractures, lateral movement may take place through permeable rocks beneath blanketing shales.

The occurrence of the ores at or near the margins of permeable rocks, in trash pockets, at bends in channels, and in lenticular beds in general indicates that facies lenticularity is probably also a prerequisite for an ore bearing formation. The part lenticularity plays is not clear. Perhaps it keeps the solution from dispersing so widely that no minable or even any visible concentrations would result (Graton, 1930, p. 83). Stated differently, it may confine a large part of the flow to contact with zones favorable for the precipitation of the metals.

Although the majority of favorable beds on the Plateau are permeable sandstones, the Todilto limestone is a conspicuous exception. In this connection Gruner (1951, p. 18) suggests that if copper and uranium were carried in hydrothermal acid solutions they should have been deposited when the solution reached neutrality --a condition that would have been effected on the Plateau when the solutions passed through the Pennsylvanian or Triassic limestones that underlie the ore bearing formation. The question of why the metals did not replace lower limestones instead of rising to permeate higher sandstones, cannot be answered any more definitely than the same question asked with reference to many lead-zinc and copper replacement deposits which also overlie other limestones. Because ore is found in formations overlying the

Todilto in the Grants area, however, it is likely that part of the mineralizing solution passed through the limestone there. Thus, deposition in the impermeable Todilto probably took place mainly by replacement, working back into the limestone from fractures; this process likely did not proceed fast enough to handle the incoming flow, some, perhaps the major part, of which therefore passed on to higher horizons. This also may have happened elsewhere on the Plateau. In fact, if the ores had a hypogene source, we may expect to find other vein or replacement deposits along cross-cutting structures in Pennsylvanian limestones and carbonaceous beds. Incidentally, whereas we expect and find a close spatial relationship between fractures and ore in limestones, it is unlikely that many close spatial relationships will ever be found between individual fractures and ore in permeable sandstone, simply because the solutions would have moved freely from the fracture into the sandstone.

The ability of solutions to travel long distances, as in artesian aquifers, is well known but it is hard to understand how ore-bearing solutions were able to travel miles or even scores of miles without depositing their dissolved load. If this took place, it is fundamentally because the solutions were chemically stable. This must mean that the temperature of the solutions was little if any above that indicated by the geothermal gradient at those depths and that neither temperature nor pressure was an important factor in the precipitation or solution of the uranium, vanadium, and the other metals associated with them. Chemical factors, therefore, likely were more responsible for the precipitation of the uranium and vanadium. Before discussing these further, however, it should be mentioned that Shoemaker (written communication, 1954) has mentioned the possibility that, because many of the copper-silver deposits in the Sinbad Valley-Fischer Valley area are found along the margins of the Paradox intrusions and in diverse rock types and structures, the precipitation of copper was triggered by "loss of pressure as the solutions left the Paradox intrusions and entered more openly fractured sandstones." Even though the main controls in the precipitation of the uranium-vanadium ores seem to be chemical rather than physical, it is possible that the regional variation in the uranium-vanadium ratio may reflect a slight temperature or pressure control on the stability of these metals in solution.

One other factor, time, probably had an important influence on the accumulation of ore deposits. As previously mentioned, we think it likely that the ore solutions were not used up in replacement deposits because this process did not act quickly enough to handle the flow of solutions coming through. By the same token, it seems likely that the reason the deposits are found at or close to the margins of permeable and impermeable zones is that the lower velocity of fluids in these areas afforded opportunity for precipitates to form, accumulate, and replace carbonaceous matter and clay.

Conclusions

The sum total of the facts of the occurrence of the deposits on the Colorado Plateau and Witwatersrand suggests to us that they were formed from deep-seated solutions, probably originating from igneous rocks that, for the most part, did not reach the surface. These solutions rose along fractures to permeable beds, which they then followed. Some minerals, notably copper, were deposited rather quickly after the solutions reached these beds, perhaps as a result of decrease in pressure, but others were carried in solution to areas where the transmissibility of the channel decreased and where chemical factors caused their precipitation. We believe that this interpretation fits the facts of the occurrence of similar deposits in other important areas, such as the Black Hills area of South Dakota and Wyoming, and the newly discovered deposits in the Blind River area of southwestern Ontario.

Doubtless many will not agree with this interpretation but if it or a substantial part of it is correct, it offers clues to the location of as yet undiscovered deposits, not only in known ore-bearing formations and districts, but in others not as yet known to contain uranium. For example, it seems worth while to us to search for new deposits in continental sediments, particularly fluviatile or piedmont deposits, overlying or surrounding intrusives, especially alkalic ones. In known districts, like the Plateau and Rand, it seems justifiable to search for vein or replacement deposits in older carbonate and carbonaceous rocks and to search for ore in other formations above and particularly below those known to contain ore. The economics of exploration and mining in sandstone districts might well justify some blind deep drilling with the discovery of additional ore-bearing formations as its goal, but such exploration would be more fruitful and less costly if guided by a knowledge of sedimentary facies. For example, Craig and orhers (1951) have shown that the Salt Wash member of the Morrison in western Colorado passes, in a north-easterly direction, from a coarse conglomeratic facies to a channel sandstone-floodplain siltstone facies to lacustrine clays and evaporites at the toe of the fan or piedmont. Sharpe (1950) has shown a cyclical arrangement or repetition of the sediments in the Rand area. Sedimentary and tectonic principles demand that favorable beds have unfavorable time equivalents, and vice versa, and that they be repeated vertically, owing to a migration of environments with time as a result of epeirogenic movements in the source area or depositional area or both. The oldest transmissable sandstone seems the most promising in any given area but younger ones deserve to be prospected too, as experience in both the Rand and Plateau shows.

Although further studies on the geochemistry and mineralogy of the ores are sure to yield important information that will aid in the discovery of additional deposits, in our opinion keen analysis of relationships between sedimentary facies, regional structures, and igneous masses is likely to contribute most to the future discovery of new ore-bearing sandstone formations and districts.

URANIFEROUS COAL AND ASSOCIATED CARBONACEOUS SHALE

Mode of occurrence

Coals and associated carbonaceous shale beds are generally non-uraniferous. In recent years, however, several coals and carbonaceous shales have been found in the western United States that contain 0.005 to about 0.1 percent uranium and in the summer of 1954 important minable deposits containing 0.2 percent uranium or more were found in northwestern South Dakota and adjacent areas (Gill, TEI-490, p. 149-155). Uraniferous coal has also been reported recently from Rio Turbio, Argentina (Lexow and Maneschi, 1950); at Freital, near Dresden, Germany (Davidson and Ponsford, 1954); and uraniferous alluvial sandy clay and intercalated peat in the Vinaninkarena basin, Madagascar, have been mined intermittently for many years (Turner, 1928).

Secondary uranium minerals, such as autunite, meta-autunite, metatyuyamunite (Gill, idem), a hydrous uranium oxide, probably becqueralite (Stugard and others, 1952, p. 21), and uranocircite (Turner, 1928) are found in some of the higher grade deposits. Lower grade deposits generally contain no visible uranium minerals nor any minerals of which uranium is an essential constituent. Breger and Deul (1952) have shown by heavy liquid separations of uraniferous lignite from the Mendenhall mine in the Slim Buttes area, Harding County, South Dakota that most of the uranium is associated with the organic matter rather than in the inorganic impurities. The uranium there is not held by ion exchange but it is easily leached from the coal with 1 normal HCl, as are other metals. Other tests suggest that the uranium is in organo-uranium complexes or ionic organic uranium compounds which are soluble at a pH of less than 2.18. Bates and Spackman (written communication) found that the same lignite is made up of "vitrinite-like" materials. "Vitrinite" and "semi-fusinite" appear to parallel one another in distribution and relative abundance and fusinite and "gum" seem to bear an inverse relationship to them. Beta-gamma measurements show some correlation with the abundance of fusinite and "gum" and show an inverse relationship to the observed mineral matter. These results were also confirmed by autoradiograph studies (Koppe and others, written communication, 1953), which showed that nuclear tracks are commonly associated with the organic constituents of the lignite. Dispersed tracks have been seen emanating from "vitrinite" and "gum" but none from resinite. A few have been seen over areas dominated by inorganic constituents (Breger and Deul, 1952; Koppe and other, idem).

Uranium is fairly uniformly distributed in individual specimens (Gott and others, 1952, p. 34) of low-grade coals, but the uranium content of individual beds is irregular, highly so in certain areas. Although no general correlation has been found between the uranium content and any inherent chemical or physical property, the highest uranium contents (say more than 0.05 percent uranium in average content) are generally found in carbonaceous shale and high ash lignite beds, rather than fine quality, low ash coals. Thus, of the many coals tested in the United States, none now being mined for fuel value alone have been found to contain 0.01 percent or more. The only two weakly uraniferous coals that might be possible to mine for their fuel value alone are the lignites in the Paleocene Ft. Union formation in the Dakotas (Denson and others, in Vine and Moore, 1952; Gott and others, 1952; Gill and others, TEI-330, p. 123-138; Gill, TEI-390, p. 131; Moore, TEI-390, p. 123) and the subbituminous coals in the

Eocene Wasatch formation in the Red Desert area of Wyoming (Gott and other, 1952; Masursky, TEI-330, p. 140; Masursky and Pipiringos TEI-390, p. 139-143); both contain about 0.01 to 0.03 percent uranium in the ash (individual samples may be much higher, of course), but it appears that the higher of the two is the lignite in the Dakota field, which also contains slightly more ash. The sandy or bony lignites now being mined for uranium in South Dakota; the carbonaceous shale beds in the Pliocene Salt Lake formation, Goose Creek, Idaho field (Duncan, 1953c; Mapel and Hail, TEI-390, p. 135-139); the Lower Cretaceous Bear River formation at Fall Creek, Idaho (Vine and Moore, 1952); the Cretaceous Dakota formation near Gallup, New Mexico (Mirsky, 1953); the Pennsylvanian Paradox formation in San Miguel County, Colorado (Baltz, TEI-390, p. 119); and subbituminous coal in the Upper Cretaceous Mesaverde group, La Ventana Mesa, New Mexico (Bachman and Read, 1951); and in Tertiary beds in Churchill County, Nevada (Gott and others, 1952), are examples of high ash coals or carbonaceous shales (in some cases up to 50-80% ash;) that contain 0.05 percent uranium or more, at least in local areas. Nearly all of the deposits in the United States are in beds of Cretaceous or Tertiary age, and of subbituminous or lower rank. Scores of coals have been tested in the central and eastern states, but none of consequence has been found to contain as much as 0.005 percent uranium.

In their studies of the lignites in Harding and Perkins Counties, South Dakota, Denson, Bachman, and Zeller found that in most places only the first lignite bed immediately below the Oligocene White River formation, which unconformably overlies the coal-bearing strata there, is appreciably uraniferous. Traced laterally, a given bed, uraniferous where it is the first bed below the unconformity at the base of the White River, is found to be non-uraniferous down dip where it is overlain by another lignite higher in the section. (See also Gill, TEI-390, p. 131) Moreover, the uranium content of a given layer is highest at the top. Concentrations of uranium may be found in lower beds adjacent to faults or through-going joints, or where they are in contact with a pervious sandstone layer. In the Red Desert area, the coal-bearing beds intertongue with Eocene Wasatch stream-deposited sandstone on the northeast and lacustrine Green River shale to the southwest; the highest uranium contents are generally found in the area where the coal intertongues with the Wasatch, though high values are also found where the beds are in contact with high gravels of possible Miocene age (Masursky, TEI-390, p. 141). The sequence of the sediments is cyclical--sandstone, then coal, then shale--and the coal generally has a higher uranium content at the bottom of the bed adjacent to the permeable sandstone.

Origin

The irregular distribution of uranium in the lignite and carbonaceous shale beds and the regional variations in the uranium content of individual beds found by Denson and others indicate that the uranium in its present position was introduced into the lignites after their deposition. The even distribution of the uranium in some of the lignites in North Dakota, and the apparent absence of concentrations on fractures there, however, suggested to Gott and others (1952, p. 34), that the uranium was present before coalification.

The source of the uranium is more debatable and, chances are, is different from place to place. It is well known that certain land plants concentrate uranium and certain associated elements (Beath, 1943; Lexow and others, 1948; Cannon, 1952), enough so to be of value in prospecting for ore deposits. However, it appears that significant concentrations of uranium--1 ppm or more in the ash--are found only where plants are growing on mineralized ground (Cannon, 1952, p. 743). Even there it is exceptional to find uranium contents in uranium-absorbing plants of 100 ppm in the ash, an amount (0.01 percent) that is rather common in the ash of uraniferous lignites and carbonaceous shales. It appears unlikely, therefore, that the uranium in coals and lignites is concentrated by living plants, even assuming later redistribution and reconcentration of uranium.

Because of the relationships already described, Denson, Bachman, and Zeller concluded that the uranium in the Dakota lignites was derived from uraniferous tuffaceous materials in the White River formation. The presence of uraniferous bones in the White River, as well as the comparatively high amounts of uranium in ground waters draining from the White River formation support this view. Thus, whereas ordinary waters contain less than 1 ppb of uranium, several hundred ppb of uranium have been found in springs in the White River formation and other areas of tuffaceous rocks. The coals in the Red Desert appear to have derived their uranium from uraniferous waters percolating through the Wasatch formation, which is locally overlain by tuffaceous rocks. The deposits in the La Ventana area are not now in contact with tuffs; but, because they were once overlain by the Bandolier tuff and because coatings of secondary uranium minerals are found on joints in the overlying sandstone, it seems likely that the uranium there also came from tuffaceous rocks (Bachman and Read, 1951). Although the uranium in the Madagascar peat is thought to come from the decomposition of nearby titano-niobates (Turner, 1928, p. 83), --minerals ordinarily rather resistant to weathering--the alluvium of which the peats are a part also contains rhyolitic pumice.

From these and other occurrences it seems not unlikely that some devitrifying tuffs yield uranium, as Koeberlin postulated (1938), that is later taken up by carbonaceous shales and lignites under favorable conditions of ground water movement. It is possible also, that other sources besides tuff--decaying granitic or arkosic rocks or hydrothermal solutions--might be the source of uranium found in lignites and carbonaceous shales. Thus, the uranium in a coal bed cut by a shear zone at the Old Leyden mine at the foot of the Colorado Front Range probably was derived from hydrothermal solutions (L. R. Page, oral communication, 1952), a view strengthened by the recent discovery of high-grade pitchblende vein deposits near by (Everhart, 1954).

The emplacement of the uranium in the lignite doubtless took place by chemical reaction or adsorption. Moore (1954) found that subbituminous coal, lignite, and peat irreversibly removed more than 98 percent of the uranium from a solution containing 196 ppm of uranium (in the form of UO_2SO_4) to which they were exposed for 12 days. Under the same conditions wood adsorbed 40 percent of the uranium, a bituminous coal 17 percent, an anthracite 34 percent, graphite 28 percent, charcoal 31 percent, canneloid coal 80 percent, phosphate rock 63 percent, bentonite 28 percent, oil shale 21 percent, calcite 16 percent, gilsonite 10 percent, and silica flour 0 percent. On the basis of these results Moore concluded that the uranium is not held by surface adsorption phenomena but is more likely precipitated as a metallo-organic compound. Breger and Deul (1952), after noting that the pH of several lignites from the western states was less than 6.5 (the Mendenhall lignite was the most acid, with a pH of 3) observed that "...certain alkaline uranyl carbonates and alkaline-earth carbonates are extremely soluble in water.... These compounds are sensitive to acids and break up with the release of carbon dioxide. It is considered possible, therefore, that a uranium-bearing solution came into contact with a lignite, a zone of low pH, with the subsequent decomposition of complex soluble salts, such as $Na_4(UO_2)(CO_3)_3$ or $Na_6(UO_2)_2(CO_3)_5$ or $Mg_2(UO_2)(CO_3)_3$. In the presence of the acid (HA), the following reaction would be expected:

$Na_4(UO_2)(CO_3)_3 + 6HA \longrightarrow 4NaA + UO_2A_2 + 3CO_2 + 3H_2O$. In the case of lignite the acid, represented by HA, is unknown in structure and, for the sake of balancing the above equation, is assumed to be monobasic. If this acid were an organic acid, then it is quite conceivable that a compound, such as UO_2A_2 might be insoluble above pH 2.18. This process might, therefore, account for the introduction of the uranium and its retention in coal."

It thus appears that, by one process or another, coaly materials can remove uranium from percolating solutions. The full story, however, is not yet established. For example, certain lignite beds in the vicinity of uraniferous tuffs are not appreciably uraniferous (Duncan, 1953b; 1953c, p. 14) and variations in the uranium content of others are not easily explainable. Some anomalies may prove to result from variations in the pH or other chemical properties of the lignite beds. Others may result from the lack or variation in degree of access of uraniferous solutions to the lignite beds. For example, Breger and Deul (1952) were unable to pass water through a column of -50 mesh coal, even under a pressure of 15 psi of nitrogen, unless diatomaceous earth was mixed with the coal to increase its porosity. As Gott and others assumed for other reasons, this may mean that introduction of uranium-bearing solutions had to take place when the coal was more pervious, but in any case it emphasizes the importance of permeability as a factor controlling mineralization of coal and other carbonaceous sediments. This may be one reason why uranium is concentrated at the top or base of many beds, and it is possible too that it is the reason why high-ash carbonaceous sediments are more uraniferous than those of low ash content.

URANIFEROUS MARINE SEDIMENTARY ROCKS

As with other elements, traces of uranium may be found in almost any marine sedimentary rocks, particularly fine-grained ones, but concentrations of more than 0.002 percent uranium are generally confined to phosphorites and carbonaceous black shales. The uranium content of other marine rocks appears to be largely related to the amount of colloidal matter they contain (Beers, 1945, p. 15) and particularly to the amount of carbonaceous matter. Thus, Burton and Sullivan (1951, p. 881) found a straight line relationship between the average radioactivity of limestone, sandstone, and shale, as determined by Bell, and the carbon content of the same rock types, as determined by Trask.

The phosphorites and black shales are closely related, both stratigraphically and genetically, but they will be discussed separately in the following pages.

Black shales

Uraniferous marine black shales, like the Upper Cambrian alum shale of Sweden (Munthe, and others, 1928; Westergard, 1944a, 1944b), the Devonian and Mississippian Chattanooga shale of Tennessee (Conant, 1952; Swanson, 1953), and the shale in the Pennsylvanian Hartville formation in Wyoming (Duncan, 1953a), contain 0.005 to 0.02 percent uranium and minor amounts of other metals such as vanadium, nickel, molybdenum, and zinc. Not all black shales or even the bituminous ones are appreciably uraniferous, but those that are have many features in common (McKelvey and Nelson, 1950, p. 38), as outlined below.

Mode of occurrence

The uraniferous black shales are mainly of the sapropelic, rather than the humic variety--rich in sulfides, distillable hydrocarbons, and finely comminuted carbonaceous matter, and generally unfossiliferous except for species of plankton and nekton. Most uraniferous shales contain 0.5 to 3 percent P_2O_5 and thus are more phosphatic than other shales. Although the shale beds may contain carbonate lenses, such as are conspicuous in parts of the alum shale of Sweden, the uraniferous shales themselves contain almost no detectable carbonates. In the Chattanooga shale, for example, the uranium content drops off sharply in slightly calcareous shale beds.

The uranium in black shale is in acid-soluble form (McKelvey and Nelson, 1950, p. 39; Brown and Keller, 1952), but its mineral occurrence has not been established definitely. Whitehead (1952, p. 196-198) reports that in the Miocene nodular shale of California and the Pennsylvanian Cherokee shale in Oklahoma the net beta count increases with increasing phosphorus and carbon content (between which there is also a direct relation). Alpha-track studies of thin sections of these shales and of the Woodford shale show that the ratio of the number of alpha particles originating in inorganic material to these originating in organic material is 2.4 to 1. These studies therefore suggest that uranium may be held both in phosphate and organic matter. Beers (1945), p. 11) has shown that in the Sunbury and Antrim shales, which are partial correlatives of the Chattanooga, the uranium content increases directly with increasing percentage of carbon, and a similar relationship has been found in other formations (Burton and Sullivan, 1951, p. 884). Because many forms of so-called amorphous carbon are graphitic in character, Fredrickson (1948) thinks it possible that the $(U^{+6}O_2)^{+2}$ ion "is adsorbed between the graphite layers of carbonaceous material, forming a strong structure due to the stable UO_2^{++} ion holding the two layers together".

The largest amounts of uranium (as much as 0.5 percent) in the alum shale of Sweden are in lenses of dark bitumen called "kolm." Although the megascopic lenses of kolm do not contain an appreciable proportion of the total uranium in the alum shale, the uranium content of the alum shale increases as the total equivalent thickness of kolm increases (Josef Eklund, oral communication, 1952). Two types of hydrocarbons have been separated from the shale matrix by flotation--one a yellowish kerogen, which is believed to be the source of most of the distillable hydrocarbons, the other a dark substance resembling kolm in appearance. Because increase in visible kolm might reflect increase in microscopic kolm pellets it is possible that the uranium in the alum shale is carried mainly in fine-grained kolm pellets. This is pure speculation at this point, however, for as far as we know, the composition of the microscopic pellets has not been studied, nor has their areal variation in abundance.

The uranium content generally increases with the pyrite content, but the pyrite itself contains little uranium. Autoradiograph studies (Bates and others, 1954), however, show that much of the uranium in the Chattanooga is in organic matter- pyrite complexes. The tracks do not point to resolvable particles of matter different in color, refractive index, opacity or other physical properties from the brown organic matter in which they are often found. This, together with the fact that the tracks usually occur singly rather than in radiating groups, indicates that the uranium is not present in a distinct uranium mineral.

Although most evidence thus seems to indicate that the uranium is adsorbed by carbonaceous matter or is held in an organo-uranium compound, perhaps similar to that in petroleum and uraniferous asphaltite (Erickson and others, 1954). Brown and Keller (1952) found that the uranium in a black shale in the Mississippian Spergen limestone in Missouri is not soluble in common organic solvents, though it is soluble in dilute acids. Moreover, the uranium appears to be fixed in the fine clay fraction and not in the black organic matter, judged on the basis of size separations, the composition of which was determined by x-ray diffraction and differential thermal analysis. Small amounts of uranium or radioactivity have been reported elsewhere from non-carbonaceous clays (Russell, 1945, p. 1472-1478; Hoogteijling and Sizoo, 1948, p. 362) and gibbsite (Fredrickson, 1948), and Beers (1945, p. 15) reports experiments showing that certain clay minerals adsorb large amounts of uranium. It is evident from these various investigations that uranium may occur in several forms in black shales but the absence of appreciable amounts or uranium in natural non-carbonaceous shales or clays, together with the widespread association of uranium and carbonaceous matter in the shales and their demonstrated capacity to adsorb uranium (Tolmachev, 1943), strongly suggests that the uranium in most black shales is held by one or another type of organic matter.

Many black shale formations are of wide extent and the uranium content of individual layers in all of them persists for miles with little change. The richest parts of the alum shale in Sweden, however, are in the middle or upper part of the shale sequence, in or closely adjacent to that part of the sequence that contains maximum amounts of distillable oil, total organic matter, pyrite, and kolm; areally, the richest parts are in tongues, interpreted as embayments in the Upper Cambrian sea, that thin and pass laterally into cherty carbonate rocks (Josef Eklund, oral communication, 1952). The most uraniferous shale yet found in this country, a shale in the Pennsylvanian Hartville formation in Wyoming and Nebraska known only in the subsurface, passes laterally into carbonate rocks of the Hartville formation before it reaches the surface a few miles to the west in the Hartville uplift; uranium in the Hartville thus was also apparently concentrated near the margin of the black shale sea. The thickness of the alum shale, as well as its total uranium content and equivalent thickness of kolm, increases toward the center of the tongues or basins. The uranium content of the Chattanooga shale decreases from Tennessee northward to Michigan as the thickness of formations of similar age increases, but Russell (1945, p. 1489) believes that the uranium content in the same formation increases as the thickness increases westward. Glebov (1941) reports that the thicker the series of Dictyonema shales in Esthonia, the greater is the radioactivity of separate layers. In spite of this relation between uranium content and thickness within some of the shale formations, the uraniferous black shales as a group are thin for the period of time their accumulation represents. Thus both the alum and Chattanooga shales are less than 100 feet in thickness over most of their extent, yet respectively they represent most of Upper Cambrian and Upper Devonian times.

Origin

In vertical sequences, the uraniferous black shales are associated with phosphatic rocks, particularly nodular phosphorites, as well as with chert, carbonate rock, glauconite, and sandstone. Curiously, however, the black shales in this same rock family are not appreciably uraniferous where thick, high-grade phosphorite beds are present. Thus in the great phosphorite formations of the world, most of the uranium is present in the phosphorites themselves, rather than in the associated shales.

Because of the great lateral continuity of the uranium content of individual layers of the marine black shales, no one has seriously questioned the common opinion that the bulk of the uranium and associated metals were introduced at the time of the deposition of the enclosing sediments. In view of the capacity of colloidal and carbonaceous materials to adsorb uranium and other metals, however, it is entirely possible that black shales adsorb uranium from circulating waters as long after their deposition as they maintain appreciable permeability. The slow rate of accumulation of these sediments means that they are exposed to sea water for a longer than normal period and therefore have opportunity to adsorb uranium after they have come to rest on the bottom. In addition, Beers and Heroy (1951, p. 66) have pointed out that much formation water must be expelled from the black shales on their compaction (3, 7, and 15 volumes if their water content at the time of deposition was 80, 90, or 95 percent, respectively--contents that studies of similar modern sediments show to be reasonable); any uranium these formation waters contain might be taken out as they pass through favorable layers. Uranium in waters draining through overlying beds might be adsorbed also (Glebov, 1941), though in view of the fact that this would not take place until after compaction and perhaps lithification, uranium derived in this way might be concentrated along joints, a phenomenon rarely observed in these formations, rather than uniformly distributed in certain layers.

As a corollary of the accepted belief in the syngenetic deposition of uranium in the black shales, no one doubts that the bulk of the uranium is derived directly or indirectly from the sea water, which contains $1.0-1.8 \times 10^{-6}$ grams of uranium per liter (Koczy, 1950). The question might be raised, however, as to whether the uranium has been locally derived or brought to the site of deposition through oceanic circulation. Both Glebov (1941) and Strøm (1948) have postulated that the uranium is derived from adjacent granitic terranes, presumably during periods when chemical weathering is the dominant process of erosion. This is a reasonable assumption if the basins of deposition are restricted embayments, such as the Norwegian fiords on which Strøm's observations were based, and it may explain the uranium content of the alum shale, the most uraniferous parts of which apparently were deposited in embayments not far from a granitic terrane (Eklund, oral communication, 1952).

As previously mentioned, however, most black shales are of wide extent and are associated with the phosphorite family of sediments. In lateral sequence shoreward the facies of this association consist typically of black shale, phosphorite, chert, carbonate rock, glauconitic sandstone, sandstone, red beds and evaporites (McKelvey and others, 1953; Sheldon, 1954); this is also the vertical sequence deposited by a regressing sea and in reverse order it is the sequence formed by a transgressing sea. The rocks in this association are found on a shelving bottom where cold waters rich in phosphate, nitrate, and possibly other substances whose solubility is influenced by pH, upwell from oceanic depths (Kazakov, 1937). As these waters are warmed, some of the dissolved substances become insoluble and are chemically precipitated or removed from the sea by organisms. The nutrients carried by these waters fertilize the upper waters of the sea, producing tremendous blooms of plankton (Brongersma-Sanders, 1948). Growth of populations proceeds more rapidly than the decay and resorption of individuals after death, so that an anerobic sapropel develops on the sea bottom, even in the open ocean (Brongersma-Sanders, 1951). Landward from the zone of phosphate-shale deposition, aerobic conditions exist on the bottom, as evidenced by the presence of fossiliferous limestone and clean quartz sandstone, and redbeds and evaporites may form along the coast. The latter form primarily as a result of the arid coastal climate, caused by the cold upwelling waters. The upwelling waters are plainly the source of the major elements found in this family of sediments, and it seems likely that they are the source of the minor ones, too. Moreover, the arid coastal conditions are the antithesis of those that might be expected to yield large volumes of minor metals in solution to the sea.

The fiord and shelf environments are perhaps end members of the series of environments in which black shales may form and much more study of facies relations and paleogeography of black shale seas will be necessary to define the environments in which the uraniferous black shales are deposited. Although most if not all of the uraniferous shales have been deposited in the shelf environment, the data at present available suggest that the most uraniferous parts of them were deposited in embayments or near their margins of deposition.

The manner of, and conditions favoring precipitation of uranium in the black shales are difficult to decipher, particularly because it is possible, even likely, that the uranium in the black shales now is in a form or association different from that at the time of deposition. Deposition may have taken place in either or both of two ways: 1) chemical adsorption by organic matter (living or dead) or apatite; or 2) direct precipitation. Some marine algae concentrate minor metals (Lexow, and others, 1948; Black and Mitchell, 1952), and dead plankton is reported to be an effective adsorbent for uranium (Steel, E. W. and Gloyna, E. F., written communication, 1953) and other metals (Harvey, 1945; Krauskopf, 1952). The adsorption of uranium by apatite is, as will be discussed more fully later, the method believed to be important in the precipitation of uranium in the phosphorites, and it is possible that it may account for the precipitation of uranium in some of the black shales.

The presence of uranium in rocks containing the largest amounts of organic matter and pyrite in the shale sequence and its apparent concentration in embayments like those in the alum shale, suggests that the precipitation of uranium may be controlled by redox potential. According to Goldschmidt (1954, p. 566), precipitation of uranium in black shales "might result from a reduction of sexivalent uranium to the quadrivalent stage by the action of hydrogen sulfide in stagnant bottom waters....We may therefore expect accumulation of the solute uranium from sea water by re-precipitation in areas where strongly reducing conditions prevail." The general solubility relationships of U^{+4} and U^{+6} already described confirm this view, but the absence of any uranium mineral in the black shales suggests that uranium did not precipitate as a definite uranium compound, even under reducing conditions. Although it thus seems more likely that the uranium was adsorbed by organic matter or other colloidal materials, conditions that favored the chemical precipitation of uranium would also have favored its removal from solution by chemical adsorption. The latter, as its name implies, is a chemical process, governed by laws similar to those that govern chemical precipitation. For example, according to the Paneth-Fajans-Hahn rule, "a cation will be adsorbed by a salt of low solubility when it forms with the anion of the adsorbing salt a compound, the solubility of which in the solvent is small;" the amount precipitated increases more or less with decreasing solubility of the compound formed (Hevesey and Paneth, 1926, p. 163; see also Koltoff and Sandell, 1952, p. 122-137). Reducing conditions, therefore, may well be a prerequisite for the removal of uranium from the sea by adsorption as well as by direct precipitation, if such ever occurs.

Anyone who has worked with black shales or studied the results of their uranium analyses cannot help asking and being baffled by the question as to why one shale layer contains a much different concentration than another when both appear closely similar if not identical in composition. The answer to this question may lie in Eh-pH control. The close relation between maximum amounts of uranium, oil, total organic matter and sulfides in the alum shale suggests that appreciable deposition of uranium takes place only when the pH and Eh lie within narrow limits--limits that may be approached closely enough in the deposition of ordinary black shales to permit the formation of sulfides and the preservation of organic matter, but are reached only rarely. Perhaps the amount of uranium in the sea at the time of deposition, or the length of time the shale constituents were exposed to the seawater before burial also influenced the amount of uranium present in individual beds. Other factors also might account for the variation in uranium content of the black shales but these factors are unknown now.

It seems likely that the uranium in the hydrocarbons in the black shales enters those compounds after deposition. Smith (1954), in reporting his discovery of oil in many recent sediments, adopts F. C. Whitmore's earlier hypothesis that "the generation of petroleum is very largely a process of selection and concentration of hydrocarbons originally synthesized by the metabolism of marine (or even terrestrial) plants." Collection and concentration of the hydrocarbons probably begin shortly after burial and minor metals are probably dissolved at this stage (Erickson, and others, 1954); Goldschmidt, 1954, p. 497). Uranium, as well as other metals, seems concentrated in the heavier fractions of petroleum; Erickson and his coworkers (1954) have suggested that the reason more uranium is not found in petroleum is that it remains in the reservoir rocks with heavier fractions, i. e. asphaltite, etc. It may remain in the source beds for the same reason. In the Billingen and Falbygden area of Sweden, where a diabase sill lies not far above the alum shale, the distillable hydrocarbon content of the shales is much reduced; veinlets of petroleum coke are found in the overlying beds and although these contain 3.5-8.9 percent V_2O_5 in their ash, they contain no uranium (Munthe and others, 1928). The uranium and kolm content of the shale has not been affected in these areas. This occurrence suggests that not only does a natural fractionation of hydrocarbons take place but that it is accompanied by a fractionation of associated or dissolved metals.

Phosphorites

Uranium was first discovered in phosphatic rocks in 1908 by Strutt. His investigations, as well as extensive ones undertaken since 1944 (McKelvey and Nelson, 1950; Davidson and Atkin, 1953), show that marine phosphorites, phosphatic nodules in black shales, and many fossil bones commonly contain 0.005 to 0.03 percent uranium; specimens, particularly of bone, may contain 0.1 percent or more. Many of the phosphatic rocks are closely associated with black shales, as already mentioned, but there are significant differences in both their mode of occurrence and origin.

Mode of occurrence

The uranium content of phosphorites generally increases as the phosphate content increases but deposits or beds richest in phosphates are not necessarily richest in uranium and, in the Permian Phosphoria formation, the most uraniferous samples known, which contain as much as 0.065 percent U (Thompson, 1953), are not the most phosphatic. With few exceptions, however, amounts of more than 0.01 percent uranium are not found in rocks containing less than 25 percent P_2O_5. As in the shales, the uranium content bears an inverse relationship to CO_2 content; in the Phosphoria formation the uranium content generally falls off sharply as the CO_2 content rises above 2 percent, regardless of the P_2O_5 content, and phosphatic nodules in limestone are generally non-uraniferous (McKelvey and Nelson, 1950, p. 41; Davidson and Atkin, 1953, p. 27). At one locality in the Phosphoria formation, Thompson (1953, p. 48) reports a positive correlation between uranium and organic matter, though the product of the percent organic matter and percent P_2O_5 shows a better correlation with uranium than with either separately. Elsewhere she finds an inverse relation between uranium and organic matter. The Florida phosphates contain almost no organic matter, although the highest uranium content there is found in black pebbles that also contain sulfides, a rarity elsewhere in the formation.

Contrary to indications provided by earlier studies (McKelvey and Nelson, 1950, p. 48), weathered rocks in the Phosphoria formation appear to contain less uranium than fresh rocks--two thirds or even half as much in fact. Highly weathered rocks in the Florida field (Cathcart and others, 1953), in Senegal (Guntz and Arene, 1953; Capdecomme, 1953), and Nigeria (Davidson and Atkin, 1953, p. 21) consist only of a residuum of quartz sand and minus 200 mesh material that consists largely of aluminum-bearing phosphates, such as wavellite and crandallite (pseudowavellite). These aluminum-bearing phosphates contain about the same amount of uranium as that in the calcium fluorophosphates, and locally they may contain as much as 0.1 percent or more.

The phosphatic nodules in black shales show the same rough correlation between the P_2O_5 and uranium content as is found in the phosphorites (Runnels and others, 1953). Phosphatic nodules on the present sea bottom off the coast of California contain about the same quantity of uranium as older phosphorites (Emory and Dietz, 1950). The uranium content of fossil bones and teeth seems to increase with increasing age (Jaffee and Sherwood, 1951), though there is also a tendency for the more radioactive specimens to occur in deposits of a sandy or gravelly nature (Davidson and Atkin, 1953, p. 24). Fossil vertebrate bones are uraniferous in many localities and on the Colorado Plateau and elsewhere they are commonly partly replaced with carnotite or other uranium minerals. Among unmineralized phosphatic materials, the values of 0.55 and 0.19 percent eU_3O_8 reported by Davidson and Atkin (1953, p. 24-25) in fish remains in the Old

Red sandstone and in a fossil fish tooth from the Carolina phosphate deposits are of interest in showing how much uranium can occur in phosphatic materials in nature without forming a discrete mineral phase. Bones in phosphorites may also contain appreciable contents of uranium. Thus, Altschuler (1952) reports that the most uraniferous sample of phosphate rock examined by him from Khouribga, Morocco, contained 0.022 percent uranium, compared to an average of about 0.014 in other samples, and contained more bone fragments than other specimens. Separate analyses of the bone fragments showed that they contain 0.08 percent uranium. On the other hand, beds in the Phosphoria formation that consist almost wholly of fish scales and other organic remains are, as a group, less uraniferous than other phosphatic materials. Neuman and others (1949a, p. 332) have shown that glycol-ashed bone can adsorb as much as 4.8 percent uranium; unashed, fresh bone can adsorb only about 1/7 as much and furnace-ashed bone does not adsorb any.

Guano contains almost no uranium; limestone phosphatized by leaching of guano deposits, such as those on some of the Pacific Islands, and residual deposits derived from the weathering of phosphatic limestones, such as the "brown-rock" deposits of Tennessee, contain less than 0.01 percent uranium (Davidson and Atkin, 1953, p. 19; McKelvey and Nelson, 1950, p. 41).

Although traces of secondary uranium minerals have been found in the Moroccan (Arambourg and Orcel, 1951), Florida (Altschuler and Boudreau, 1949), and Phosphoria phosphorites, and conspicuous amounts are often observed in bones, discrete uranium minerals are ordinarily not present in the phosphatic materials. The uranium is in acid-soluble form. In fact, the amount of uranium that can be dissolved from phosphate rock with acid is generally proportional to the amount of phosphate dissolved. For this reason, as well as from autoradiographic evidence (Altschuler 1954), it is judged to be in the phosphate mineral, which is carbonate fluorapatite (Altschuler and others, 1953). In an excellent series of experiments, in which fresh bone and bone ash were treated with various concentrations of buffered bicarbonate solutions of uranyl acetate, Neuman and his co-workers (1949a, 1949b, and 1949c) demonstrated that one mole of UO_2^{++} substitutes for two moles of Ca^{++} on the surface of bone (Neuman and others, 1949a, p. 332; 1949b, p. 339), rendering two moles of surface phosphate non-exchangeable. They interpreted this to mean "that uranium combines with two adjacent phosphate groups in the mineral surface, structurally analogous to uranyl pyrophosphates" (1949c, p. 347). The conclusion that uranium substitutes for calcium in phosphorite apatite is supported by the fact that the uranium is tetravalent and that the uranium and calcium contents parallel one another in sections of leached phosphorite (Altschuler, and others, 1954). Uranium also probably substitutes for calcium in crandallite and is not present at all in wavellite; all the uranium in wavellite deposits is apparently carried by small amounts of crandallite (Altschuler, oral communication, 1955).

Although the uranium in phosphorites is not in readily exchangeable form, the presence of secondary minerals in the Phorphoria formation, below zones of advanced weathering where the uranium content of phosphate rocks is less than normal and the phosphate content is higher than normal, shows that some differential leaching takes place in nature.

The distribution of most phosphorites and phosphatic nodules is closely related to the black shales and, with the exception of the Florida deposits, need not be discussed fully here. Suffice it to say that the formations are of wide extent and that the uranium content of individual layers persists for many miles; small local variations in uranium content are often found, but many of these seem ascribable to weathering. In the Phosphoria formation, and possibly in others, too, the uranium content decreases shoreward and drops off rapidly where carbonate facies become prominent.

The Pliocene Bone Valley formation of Florida contains no black shale or chert facies and bears little resemblance in other ways to the marine phosphorite formations. The lower part of the formation, known as the "matrix," consists of pellets and pebbles of carbonate-fluorapatite in an unconsolidated matrix of clay (mainly montmorillonite) and quartz sand. Upward the content of quartz increases, the rocks become vesicular, and crandallite and kaolin are present along with the apatite and montmorillonite (Altschuler and Boudreau, 1949; Altschuler, TEI-330, p. 172); still higher, apatite and montmorillonite disappear and in the highest part wavellite is the main phosphatic mineral but is present mainly in the minus 200 mesh fraction. The upper part is known as the leached zone or the aluminum phosphate zone. The Bone Valley formation rests on a karst surface of the Miocene Hawthorn formation, which consists mainly of phosphatic limestone and sandy clay (Cathcart and others, 1953). Regionally, fine-grained phosphatic pellets in the matrix generally are found on Hawthorn formation lows and coarser phosphorite on Hawthorn highs (D. F. Davidson, 1952a, 1952b). The matrix tends to be thicker over the major highs on the limestone. The leached zone is thin or absent there, apparently having been eroded away (Cathcart, oral communication, 1954). The phosphate content of the phosphatic pellets in the matrix ranges from 30 to 36 percent; it generally varies inversely with grain size and increases upward within the matrix. On a regional basis, the phosphate content is lowest in the central, higher part of the field, where coarse pebble predominates and is highest in the peripheral, lower parts of the field where fine pebble predominates. The uranium content is higher in the coarse, less phosphatic pebble (especially the dark pebble) than in the fine pebble, and is therefore highest in the central part of the field (Ketner, 1952). The phosphatic pellets of the Hawthorn are considerably less uraniferous than those in the Bone Valley. The most uraniferous part of the formation seems to be the lower part of the leached zone where crandallite and kaolin are present along with apatite and montmorillonite (Altschuler, TEI-330, p. 172).

The Bone Valley formation has been variously interpreted as a residual deposit formed on the Hawthorn, showing progressive stages of weathering and leaching from a phosphatic limestone to a quartz sand; as a formation consisting of residuum reworked by marine waters; and as a formation consisting locally of unreworked residuum in the lower part but overlain by reworked materials, the whole later subjected again to subtropical weathering which proceeded to an advanced stage (Cathcart and others, 1953). The latter hypothesis seems most reasonable.

Origin

Like the black shales, most of the uranium in the phosphorites and phosphatic nodules probably was derived from sea water at or shortly after the time the rocks were deposited. To a much greater degree than in the shales, however, some of the uranium may have been derived from later solutions or redissolved and redeposited by them. This will be treated more fully after the manner of precipitation has been discussed.

Deposition of uranium in phosphatic materials seems to have taken place by one of the processes generally described as chemical adsorption. As previously mentioned, Moore (1954) found that phosphate rock removed 63 percent of the uranium present in a solution of UO_2SO_4 containing 196 ppm of uranium; and Neuman and others (1949a, 1949b, and 1949c), working with more dilute solutions also demonstrated that bone (which consists of hydroxyapatite) can adsorb as much as 4.8 percent uranium from a bicarbonate buffered solution of uranyl acetate, replacing calcium at the surface of the apatite crystal. Other experiments (idem, 1949c) show that the precipitation of uranium in bone ash decreases with increase in calcium and increase in bicarbonate ions in solution and with increasing pH, from 6.5 to 8.0. These results indicate "that a direct competition exists between calcium and uranium for the combining sites on the bone phase...[and] between carbonate ion (which forms a relatively undissociated complex with uranyl ion) and the surface phosphate groups for uranium. The reduced uranium adsorption observed at elevated pH is somewhat more complicated but, in part, may be viewed as a competition between surface phosphate groups and hydroxyl ions." The studies of Neuman and his associates spell out the mechanism of the precipitation of uranium in bone with a clarity and finality seldom achieved, in geology at least. They also indicate one mechanism by which uranium may be deposited in the phosphorites and they point to the factors that explain the observed inverse relation between uranium and carbonate in the rocks. Inasmuch as the uranium in the phosphorites is in tetravalent form a reduction reaction must be involved in its precipitation.

The question has been asked (Davidson and Atkin, 1953, p. 28) as to why the uraniferous phosphates contain only small amounts of uranium, particularly in view of the fact that bone can take up several percent. Possibly the amount of uranium available limits the uranium content of some materials, particularly bones in non-marine deposits, but in the phosphorites it is likely that the answer lies in the fact that uranium must compete with several other ions that occupy the same position in the cell (notably calcium, but also strontium and rare earths), all of which are more abundant in seawater than is uranium.

The variation in the uranium content of different but similar phosphorite layers and of the content of individual layers poses a question just as it does with the black shales, but it is easier to answer. Variations in the uranium content of the seawater at the time of deposition, or in its pH, bicarbonate ion concentration, etc., or in the length of time the phosphorite pellets are exposed to the sea before burial may account for some of the variations as they may in the shales. The largest variations, however, probably result from the fact that the phosphorite beds are more permeable and may therefore pick up uranium from, or lose it to, percolating solutions after burial. The presence of uranium in phosphatic limestones formed by the leaching of non-uraniferous guano and the increase of uranium in bone with increasing age and increasing permeability of the enclosing rocks demonstrates the tendency of phosphatic materials to pick up uranium after their deposition (Davidson and Atkin, 1953). Neuman and others (1948, p. 708) have shown that the amount, place, and time of deposition of uranium in rats is a function of vascularity, a property directly analogous to permeability in rocks. The lower uranium content of the fish-scale beds in the Phosphoria formation may result from the fact that these beds are dense--crystalline in appearance, in fact--and therefore had less chance to pick up uranium from later solutions than did the pelletal beds.

The distribution of uranium in the Florida field demonstrates some of these relationships very well. The lack of appreciable uranium in the phosphatic particles of the Hawthorn is probably a result of the presence of excess calcium and bicarbonate ions in the sea at the time of their deposition. Reworking of the residual phosphatic materials, following a period of weathering, in a marine environment re-exposed the pellets to the sea, giving them a chance to adsorb more uranium. Following the return to continental conditions, leaching by acid surface waters gradually dissolved the more soluble constituents, carrying some of them away and permitting others to recombine in more stable minerals. The variations in phosphate content of the pebble fraction are largely a function of residual enrichment--the smaller particles are leached of soluble constituents, such as carbonates, more readily and completely than the larger ones. Uranium is not completely removed from the apatite but some is leached out, so that higher concentrations are found in the coarse pebble, particularly in the black ones that also contain sulfides. Some of the dissolved uranium is readsorbed, particularly in the zone below that of most advanced weathering, where soft, spongy, partly decayed apatite is present, giving a zone of secondary enrichment (Altschuler, TEI-330, p. 172). Some of the uranium, however, recombines with other elements to form minerals of the wavellite group. With a history as complex as this, variations in the uranium content of the phosphatic materials become readily understandable.

The questions as to why uranium is present in the phosphorites and not in the associated black shales in the great phosphorite formations cannot be answered definitely on the basis of present information. It may mean that uranium bears a greater affinity for phosphate than it does for organic matter--expressed either at the time of deposition or during the later migration of solutions, including formation water.

SUMMARY

In summarizing the origin of uranium deposits it may be most fruitful to single out the sources, the modes and avenues of transportation, and the causes of precipitation that lead to concentration of uranium in nature, rather than discussing again the origin of specific deposits. Such a summary will not only emphasize those features of the behavior of uranium that bear most on the search for new deposits, but it may also provide a cross-section of ore-forming processes in general.

In igneous rocks, uranium follows pegmatite-forming metals and concentrates with them in silicia and silica-alkalic igneous rocks and pegmatites. Some of it also concentrates with chalcophile elements in late-stage solutions that are carried away from the magma and deposited in hydrothermal vein, replacement, and cavity-filling deposits. Deposits formed by primary, igneous processes thus include those found in certain igneous rocks, in pegmatites, in volcanic ash, and in veins and related deposits.

Of these primary deposits, the igneous rocks and volcanic ash obviously contain the largest quantities of uranium, and they are perhaps the most important sources of uranium in deposits concentrated by continental surface and ground waters. They, as well as more concentrated and more dispersed sources, contribute uranium to the ocean reservoir, which is the direct source for uranium in marine sedimentary rocks.

Uranium may be transported by many different solutions but those that contain the highest concentrations and are thus ones from which uranium deposits might be precipitated directly, are hypogene solutions (aqueous solutions and perhaps CO_2 also), certain ground and spring waters, petroleum, and ocean water. The uranium content of the hypogene solutions is not known but in ocean waters it is 1-2 parts per billion and in the anomalously uraniferous petroleums, ground and surface waters it ranges from one to a few tens or scores ppb (water or oil directly associated with ore may contain a few hundred ppb). The aqueous solutions may be either acid or alkaline; the alkaline solutions generally contain more than a few hundred parts per million of total dissolved solids and are high in either bicarbonate or sulfate or both. The form of uranium in these solutions has not been much explored but it seems likely that it is a metallo-organic compound in petroleum--perhaps a U^{+4} asphaltene--and a U^{+6} (or UO_2^{++}) carbonate or sulfate in aqueous solutions.

The avenues of transportation of uranium-bearing solutions are, of course, of great significance in the localization of ore deposits. The avenues that carry the solutions from which epigenetic deposits are formed are the usual ones--joints and fractures in crystalline igneous, metamorphic, and sedimentary rocks, and pore spaces in pervious sedimentary rocks. The occurrence of large uranium deposits in sandstones and lignites serves to emphasize the importance of aquifers in channeling ore solutions through sedimentary rocks and in localizing their precipitates.

As with many other metals, uranium may be precipitated in two general ways: 1) direct chemical precipitation as a uranium mineral and 2) chemical adsorption or isomorphous substitution in inorganic or organic substances. The precipitation of uranium by either of these processes is influenced, of course, by the concentration of uranium in the solution. Precipitation seems to be effected as much as anything, however, by reduction of U^{+6} to U^{+4}. This is attested to by the widespread association of uranium with sulfides and carbonaceous matter. In the deposits in which uranium is not associated with either sulfides or carbonaceous matter or both--mainly igneous rocks, pegmatites, phosphorites, and certain secondary deposits in the vicinity of oxidized veins, etc.--the precipitation is brought about by the presence of elements that form complex stable compounds with uranium. The most stable of these compounds are those in which uranium is tetravalent--the titanates and niobates, for example--but hexavalent uranium forms moderately stable compounds with phosphates, vanadates, and arsenates. Precipitation of uranium by chemical adsorption or isomorphous substitution is favored where uranium forms a relatively stable compound with the anions involved, where it can displace an ion of similar radius and valence, and where the solution carries few ions that can compete successfully with uranium for the lattice position.

ACKNOWLEDGMENTS

This paper was prepared as part of a program conducted by the Division of Raw Materials of the U. S. Atomic Energy Commission and by the U. S. Geological Survey on the Commission's behalf. Because the paper is mainly a review of the observations of others, the list of references is also a list of acknowledgments. In addition, we are indebted to F. C. Armstrong, J. H. Eric, H. L. James, and George Phair for information and suggestions that aided in the presentation and interpretation of the data.

Although we share responsibility for the plan of the paper and for any gross errors it may contain, Garrels has been chiefly responsible for the section on the geochemistry of uranium and the chemistry of deposition of the sandstone ores, Everhart for the sections on uranium in igneous rocks, pegmatites, and veins, and McKelvey for the other parts.

BIBLIOGRAPHY

Altschuler, Z. S., Cisney, E. A., and Barlow, I. H., 1953, X-ray evidence of the nature of carbonate-apatite: 19th Internat., Geol. Cong. Algiers, Comptes, Rendus., sec. 11, p. 9.

__________, Clarke, R. S., Jr., and Young, E. J., 1954, Uranium in apatite (abs.): Geol. Soc. America Bull., v. 65, p. 1225.

Arambourg, C., and Orcel, J., 1951, Observations préliminaires sur la présence d'un vanadate d'urane dans les gisements de phosphates du Maroc: Acad. des Sci. Paris, Comptes. Rendus., v. 233, p. 1635.

Bailey, S. W., and Cameron, E. N., 1951, Temperatures of formation of bottom-run lead-zinc deposits in the Upper Mississippi Valley: Econ. Geology, v. 46, p. 626-651.

Bain, G. W., 1950, Geology of fissionable materials: Econ. Geology, v. 45, p. 273-323.

__________, 1952, Uranium in the Dirty Devil Shinarump channel deposit: U. S. Atomic Energy Comm. RMO-66, Tech. Inf. Service, Oak Ridge, Tenn.

Bastin, E. S., 1939, The nickel-cobalt-native silver ore type: Econ. Geology, v. 34, p. 1-40.

Bates, T. F., Strahl, E. O., Short, N. M., Silverman, E. N., and Camilli, E., 1954, Mineralogy and petrography of the Chattanooga shale: Geol. Soc. America Bull., v. 65, p. 1230.

Beath, O. A., 1943, Toxic vegetation growing on the Salt Wash member of the Morrison formation: Am. Jour. Botany, v. 30, p. 698-707.

Beer, K. E., 1951, The petrology of some of the riebeckite-granites of Nigeria: Geol. Survey of Great Britain, Rept. no. 116.

Beers, R. F., 1945, Radioactivity and organic content of some Paleozoic shales: Am. Assoc. Petrol. Geol. Bull., v. 29, p. 1-22.

Billings, M. P., and Keevil, N. B., 1946, Petrography and radioactivity of four Paleozoic magma series in New Hampshire: Geol. Soc. America Bull., v. 57, p. 797-828.

Black, W. A. P., and Mitchell, R. L., 1952, Trace elements in the common brown algae and in sea water: Jour. Marine Biol. Assoc. of the United Kingdom. v. 30, p. 575-584.

Brongersma-Sanders, M., 1948, The importance of upwelling water to vertebrate paleontology and oil geology: Verhandelingen der Koninklijke Nederlandsche Akademie van Wetenschappen, Afd. Natuurkunde, Tweede Sectie, Deel XLV, no. 4

__________, 1951, On conditions favouring the preservation of chlorophyll in marine sediments: World Pet. Cong., The Hague, 1951, Proc., v. 1, p. 401-413.

Brooker, E. J., and Nuffield, E. W., 1952, Pitchblende from Lake Athabaska, Canada, 4. of Studies of radioactive compounds: Am. Mineralogist, v. 37, p. 363-385.

Brown, H., Blake, W. J., Chodas, A. A., Kowalkowski, R., McKinney, C. R., Neuerburg, G. J., Silver, L. T., and Uchiyama, A., 1953, Leaching studies of interstitial material in igneous rocks: Geol. Soc. America Bull., v., 64, no. 12, p. 1400-1401.

Brown, J. H., Jr., and Keller, W. D., 1952, Uranium in the clay of a black radioactive shale: Science, v. 116, no. 3023, p. 632-633.

Brown, R. D., Bunger, W. B., Marshall, W. L., and Secoy, C. H., 1952, The electrical conductivity of uranyl sulfate and uranyl fluoride in aqueous solution: U. S. Atomic Energy Comm. AECD-3488 (rev.), Tech. Inf. Service, Oak Ridge, Tenn.

Bucher, W. H., 1953, Fracture studies in the Zuni and Lucero Uplifts, New Mexico: U. S. Atomic Energy Comm. RME-3042, Tech. Inf. Service, Oak Ridge, Tenn.

Burton, V. L., and Sullivan, G. R. 1951, Carbon content and radioactivity of marine rocks: Am. Geophys. Union Trans., v. 32, p. 881-884.

Butler, B. S., 1920, The ore deposits of Utah: U. S. Geol. Survey Prof. Paper 111, p. 154-158.

Cannon, H. L., 1952, The effect of uranium-vanadium deposits on the vegetation of the Colorado Plateau: Am. Jour. Sci., v. 250, no. 10, p. 735-770.

Capdecomme, L., 1953, Etude mineralogique des gites de phosphates alumineux de la region de Thiès (Sénégal): 19th Int. Geol. Cong. Algiers, Comptes. Rendus., v. XI, p. 103-118.

Cater, F. W., Jr., 1954, Geology of the Bull Canyon quadrangle, Colorado: U. S. Geol. Survey Geol. Quadrangle Map ser., GQ 33.

Cathcart, J. B., Blade, L. V., Davidson, D. F., and Ketner, K. B., 1953, The geology of the Florida land-pebble phosphate deposits: 19th Int. Geol. Cong., Algiers, Comptes. Rendus., v. 11, p. 77-91.

Coffin, R. C., 1921, Radium, uranium, and vanadium deposits of southwestern Colorado: Colo. Geol. Survey Bull. 16.

Conant, L. C., 1952, Origin of the Chattanooga shale: Nuc. Sci. Abs., v. 6, no. 20, p. 709-710.

Connick, R. E., and Hugus, Z. Z., 1952, The participation of orbitals in bonding in uranium and transuranium elements: Am. Chem. Soc. Jour., v. 74, p. 6012.

Craig, L. C., Holmes, C. N., Cadigan, R. A., Freeman, V. L., Mullens, T. E., and Weir, G. W., 1951, Preliminary report on the stratigraphy of the Morrison and related formations of the Colorado Plateau region: U. S. Geol. Survey TEI-180, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.; U. S. Geol. Survey Bull. 1009-E.

Davidson, C. F., 1953, The gold-uranium ores of the Witwatersrand: Min. Mag., v. 88, p. 73-85.

__________, 1954, Discussion: Inst. Min. Metallurgy Bull., Feb., p. 247.

__________, and Atkin, D., 1953, On the occurrence of uranium in phosphate rock: 19th Int. Geol. Cong., Algiers, Comptes. Rendus., v. XI, p. 13-31.

Davidson, C. F., and Bennett, J. A. E., 1950, The uranium deposits of the Tete district, Mozambique: Mineral. Mag., v. 29, p. 291-303.

Davidson, C. F., and Bowie, S. H. U., 1951, On thucholite and related hydrocarbon-uraninite complexes, with a note on the origin of the Witwatersrand gold ores: Geol. Survey of Great Britain Bull. 3, p. 1-19.

Davidson, C. F., and Ponsford, D. R. A., 1954, On the occurrence of uranium in coals: Min. Mag., v. 91, p. 265-273.

Davidson, D. F., 1952a, Grain size distribution in the surface sands, and the economic phosphate deposits of the land-pebble phosphate district, Florida: U. S. Geol. Survey TEM-362, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1952b, Relation of the "topography" of the Hawthorn formation to size of phosphate particles in the deposits, and to present topography in the northern part of the land-pebble district: U. S. Geol. Survey TEM-337, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1953, Distribution of coarse- and fine-grained rocks in the Wasatch formation and their relationship to uranium deposits, Powder River Basin, Wyoming: U. S. Geol. Survey TEM-676, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Dodd, P. H., 1950, Happy Jack Mine, White Canyon, Utah: U. S. Atomic Energy Comm. RMO-660, Tech. Inf. Service, Oak Ridge, Tenn.

Duncan, D. C., 1953a, Reconnaissance investigations for uranium in black shale deposits of the western states during 1951 and 1952: U. S. Geol. Survey TEI-381, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1953b, A uranium-bearing rhyolitic tuff deposit near Coaldale, Esmeralda County, Nevada: U. S. Geol. Survey Circ. 291.

__________, 1953c, Results of reconnaissance for uranium in non-marine carbonaceous rocks in parts of California, Idaho, Nevada, Oregon, Utah, and Washington during 1951 and 1952: U. S. Geol. Survey TEM-444A, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Eckel, E. B., Williams, J. S., Galbraith, F. W., and others, 1950, Geology and ore deposits of the La Plata district, Colorado: U. S. Geol. Survey Prof. Paper 219.

Ellsworth, H. V., 1932, Rare element minerals of Canada: Geol. Survey of Canada, Econ. Geology ser. 11, 272 p.

Emmons, R. C., Reynolds, C. D., and Saunders, D. F., 1952, Genetic and radioactivity features of selected lamprophyres in Selected petrogenic relationships of plagioclase: Geol. Soc. America Mem. 52, p. 89-100.

Emory, K. O., and Dietz, R. A., 1950, Submarine phosphorite deposits off California and Mexico: Calif. Jour. Mines and Geology, v. 46, p. 7-15.

Erickson, R. L., Myers, A. T., and Horr, C. A., 1954, Association of uranium and other metals with crude oil, asphalt, and petroliferous rock: Am. Assoc. Petrol. Geol. Bull., v. 38, no. 10, p. 2200-2218.

Evans, R. D., and Goodman, Clark, 1941, Radioactivity of rocks: Geol. Soc. America Bull., v. 52, p. 459-490.

Everhart, D. L., 1954, Uranium: Eng. Min. Jour., v. 155, no. 2, p. 84-86.

Everhart, D. L., and Wright, R. J., 1951, The paragenesis of pitchblende-bearing veins: Denison Univ., Jour. Sci. Lab., v. 42, Art. 6, p. 66-74.

__________, 1953, The geologic character of typical pitchblende veins: Econ. Geology, v. 48, p. 77-96.

Faul, H., Gott, G. B., Manger, G. E., Mytton, J. W., and Sakakura, A. Y., 1952, Radon and helium in natural gas: 19th Int. Geol. Cong., Algiers, Rés. des communications, p. 59.

Finch, W. I., 1953, Geologic aspects of the resource appraisal of uranium deposits in pre-Morrison formations of the Colorado Plateau: U. S. Geol. Survey TEI-328A, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1955, Preliminary geologic map showing the distribution of uranium deposits and principal ore-bearing formations of the Colorado Plateau region: U. S. Geol. Survey Mineral Inv. Field Studies Map 16.

Fischer, R. P., 1937, Sedimentary deposits of copper, vanadium-uranium, and silver in southwestern United States: Econ. Geology, v. 32, p. 906-951.

__________, 1943, Vanadium deposits of Colorado and Utah, a preliminary report: U. S. Geol Survey Bull. 936-P, p. 363-394.

__________, 1950, Uranium-bearing sandstone deposits of the Colorado Plateau: Econ. Geology, v. 45, p. 1-11.

__________, and Hilpert, L. S., 1952, Geology of the Uravan mineral belt: U. S. Geol. Survey Bull. 988A, p. 1-13.

Flores, Hector, 1942, Geologia de los yacimientos de cobre y oro de Chile: Anales Primer Congreso Pan Americano de Ing. Minas y Geol., v. 3, pt. 2, Santiago, Chile.

Fredrickson, A. F., 1948, Some mechanisms for the fixation of uranium in certain sediments: Science, v. 108, p. 184.

Garrels, R. M., 1953, Some thermodynamic relations among the vanadium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: Am. Mineralogist, v. 38, p. 1251-1265.

__________, 1954, Mineral species as functions of pH and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulphide ore deposits: Geochimica et Cosmochimica Acta, v. 5, no. 4, p. 153-168.

Gilkey, A. K., 1953, Fracture pattern of the Zuni uplift: U. S. Atomic Energy Comm. RME-3050, Tech. Inf. Service, Oak Ridge, Tenn.

Glebov, S. M., 1941, Radioaktivnost diktionemovykh slantzer: Leningradski gornyi Institut, Leningrad, Zapaski, v. XIV, p. 1-12.

Goldschmidt, V. M., (Edited by Alex Muir), 1954, Geochemistry: Oxford, at the Clarendon Press.

Gott, G. B., and Erickson, R. L., 1952, Reconnaissance of uranium and copper deposits in parts of New Mexico, Colorado, Utah, Idaho, and Wyoming: U. S. Geol. Survey Circ. 219, 16 p.

Gott, G. B., Wyant, D. C., and Beroni, E. P., 1952, Uranium in black shales, lignites, and limestones in the United States: U. S. Geol. Survey Circ. 220, p. iii, 31-35.

Gould, L. M., 1927, The geology of La Sal Mountains of Utah: Mich. Acad. Sci. Papers, v. 7, p. 55-106.

Graton, L. C., 1930, Hydrothermal origin of the Rand gold deposits: Econ. Geology, v. 25, suppl. to no. 3.

Green, Jack, 1953, Geochemical table of the elements for 1953: Geol. Soc. America Bull., v. 64, p. 1001-1012.

Gruner, J. W., 1951, Origin of the uranium deposits in the Shinarump formation, a preliminary study: U. S. Atomic Energy Comm. RMO-837, Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1952, New data of syntheses of uranium minerals: U. S. Atomic Energy Comm. RMO-983, Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1953, Interim report: uranium-bearing carbonaceous and asphaltic materials of the Colorado Plateau: U. S. Atomic Energy Comm. RME-3022, Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1954, The origin of the uranium deposits on the Colorado Plateau and adjacent regions: Mines Mag., v. 44, no. 3, p. 53-56.

__________, Gardiner, L., and Smith, D. K., Jr., 1953, University of Minnesota annual report for July 1, 1952, to March 31, 1953: Pt. I, Field work for 1952 p. 6-13; Pt. II, Uranium-bearing carbonaceous and asphaltic materials of the Colorado Plateau, p. 14-19; Pt. III, Syntheses of uranium minerals, p. 20-27; Pt. IV, The changes from red to gray shales and silts in uranium-bearing areas, p. 28-36; Pt. V, Primary and secondary sources of uranium in the Colorado Plateau, p. 36-40; Pt. VI, syngenetic versus hydrothermal hypothesis for the origin of the uranium deposits of the Colorado Plateau, p. 41-58: U. S. Atomic Energy Comm. RME-3044, Tech. Inf. Service, Oak Ridge, Tenn.

Guntz, A. A., and Arene, M., 1953, Sur la présence de l'uranium dans les phosphates africains: 19th Int. Geol. Cong., Comptes. Rendus., Algiers, v. 11, p. 11.

Harvey, H. W., 1945, Recent advances in the chemistry and biology of sea water: Cambridge Univ. Press.

Hess, F. L., 1914, A hypothesis for the origin of the carnotites of Colorado and Utah: Econ. Geology, v. 9, p. 675-688.

Hevesey, G. von, and Paneth, F. A., 1926, A manual of radioactivity: Oxford Univ. Press, London.

Hill, J. W., 1954, Uraniferous asphaltic materials of southwestern Oklahoma: Geol. Soc. America Bull., v. 65, p. 1377.

Hillebrand, W. F., and Ransome, F. L., 1905, On carnotite and associated vanadiferous minerals in western Colorado: U. S. Geol. Survey Bull. 262, p. 9-31.

Holland, H. D., and Kulp, J. L., 1954, The transport and deposition of uranium, ionium and radium in rivers, oceans, and ocean sediments: Geochimica et Cosmochimica Acta, v. 5, no. 5, p. 197-213.

Hoogteijling, P. J., and Sizoo, G. J., 1948, Radioactivity and mineral composition of soil: Physica, v. 14, no. 6, p. 357-366.

Hurley, Patrick M., 1950, Distribution of radioactivity in granites and possible relation to helium age measurement: Geol. Soc. America Bull., v. 61, p. 1-8.

Jaffe, E. B., and Sherwood, A. M., 1951, Physical and chemical comparison of modern and fossil tooth and bone material: U. S. Geol. Survey TEM-149, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Joubin, F. R., 1954, Uranium deposits of the Algoma district, Ontario: Canadian Inst. of Mining and Metallurgy Trans., v. LVII, p. 431-437.

Katz, J. J., and Rabinowitch, E., 1951, The chemistry of uranium: McGraw-Hill Book Co.

Kazakov, A. V., 1937, The phosphorite facies and the genesis of phosphorites, in Geological Investigations of Agricultural Ores: Sci. Inst. Fertilizers and Insecto-Fungicides Trans. no. 142 (published for the 17th Geol. Cong.) Leningrad, p. 8-21.

Keevil, N. B., 1944, Thorium-uranium ratios in rocks and minerals: Am. Jour. Sci., v. 242, no. 6, p. 309-321.

Kerr, P. F., Brophy, G., Dahl, H. M., Green, J., and Woolard, L. E., 1952, A geologic guide to the Marysvale area: U. S. Atomic Energy Comm. RMO-924, Tech. Inf. Service, Oak Ridge, Tenn.

Kerr, P. F., Croft, W. J., Miller, L. J., and Sciacca, T. P., 1954, Columbia University annual report for June 30, 1953 to April 1, 1954 (pt. 2): U. S. Atomic Energy Comm. RME-3096, Tech. Inf. Service, Oak Ridge, Tenn.

Kerr, P. F., Hamilton, P. K., Brophy, G. P., Simpson, W. L., Cohen, Wm., Dahl, H., and Green, J., 1953, Columbia University annual report for June 30, 1952 to April 1, 1953: U. S. Atomic Energy Comm. RME-3046, Tech. Inf. Service, Oak Ridge, Tenn.

Kerr, P. F., and Lapham, D. M., 1954, Report on a nodule from Temple Mountain, Utah: U. S. Atomic Energy Comm. RME-3096 (pt. 1), Tech. Inf. Service, Oak Ridge, Tenn.

Ketner, K. B., 1952, Correlation between uranium and P_2O_5 in a coarse pebble phosphate deposit, Florida: Abs. in U. S. Geol. Survey TEI-270, p. 30, Tech. Inf. Service, Oak Ridge, Tenn.

King, D., 1954, Northeast uranium exploration, explanatory notes to accompany mineral map of the Crocker Well area: Geol. Survey of South Australia, Rept. no. G-S 11, C-W 15.

Koczy, Gerta, 1950, Weitere Uranbestimmunger an Meerwasserproben: Akad. Wiss. Wien, Math.-nautrwiss. Kl., Sitzungher, Abt. IIa, 158 Band, 1-5, Heft, p. 113-122.

Koeberlin, F. R., 1938, Discussion of "Sedimentary deposits of copper, vanadium-uranium, and silver in southwestern United States" by R. P. Fischer: Econ. Geology, v. 33, p. 458-461.

Koltoff, I. M., and Sandell, E. B., 1952, Textbook of quantitative inorganic analysis: Macmillan, New York.

Krauskopf, K. B., 1952, Control of trace-element concentrations in sea waters (abs): Geol. Soc. America Bull., v. 63, no. 12, pt. 2, p. 1336, Dec. 1952.

Lang, A. H., 1952, Canadian deposits of uranium and thorium (Interim account): Canada Geol. Survey, Econ. Geology ser. no. 16, 173 p.

Lang, S. M., 1953, Solid state reactions of the uranium oxides: Nat. Bur. of Standards Circ. 535.

Latimer, W. M., 1952, Oxidation potentials: Prentice-Hall, Inc.

Lexow, S. G., and Maneschi, E. P. P., 1950, Germanium in the coal of Rio Turbio: Anales assoc. quim. Argentina, v. 38, p. 225-229, 1950 (in Spanish); see also Nuc. Sci. Abs., v. 5, p. 203, 1951.

Lexow, S. G., Maneschi, E. P. P., and Sa, A. M., 1948, Preliminary note on the presence of uranium in living things in Argentina: Anales assoc. quim. Argentina, v. 36, p. 203-207, (in Spanish); see also Nuc. Sci. Abs., v. 3, p. 76, 1949.

Liebenberg, W. R., 1948, Rare minerals in the banket of the Witwatersrand system: Dissertation, Pretoria Univ., Pretoria, Transvaal; U. S. Atomic Energy Comm. NP-3992, Tech. Inf. Service, Oak Ridge, Tenn.

Lindgren, W., 1913, Mineral deposits: McGraw-Hill.

__________, 1933, Mineral deposits (4th Ed.): McGraw-Hill Book Co.

Louw, J. D., 1954, Geological age determinations on Witwatersrand uraninites using the lead isotope method: Geol. Soc. S. Africa, advance proof, p. 1-19.

Lovering, T. S., 1949, Rock alteration as a guide to ore, East Tintic District, Utah: Econ. Geology Mon. no. 1.

MacGregor, A. M., 1953, Discussion of "The gold-uranium ores of the Witwatersrand" by C. F. Davidson: Min. Mag., v. 88, p. 281-282.

Mackay, R. A., and Beer, K. E., 1952, The albite-riebeckite-granites of Nigeria: Geol. Survey of Great Britain, Rept. GSM/AED, 95, publ. H. M. S. O., 25 p.

Mawdsley, J. B., 1952, Uraninite-bearing deposits, Charlebois Lake area, northwestern Saskatchewan: Canadian Min. Metall. Bull., no. 482, p. 366-375; abs. in Geol. Soc. America Bull., v. 64, p. 1550, 1953.

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

McKelvey, V. E., Swanson, R. W., and Sheldon, R. P., 1953, The Permian phosphorite deposits of western United States: 19th Int. Geol. Cong., Algiers, Comptes. Rendus., sec. 11, p. 45-64.

McLean, C. S., 1954, The uranium industry of South Africa: Chem. Met. and Min. Soc. South Africa, Jour., v. 54, no. 10, p. 345-356.

Mellor, E. T., 1916, The conglomerates of the Witwatersrand: Trans. Inst. Min. Metall., v. 25, p. 226-348.

Miller, L. J., and Kerr, P. F., 1954, Progress report on the chemical environment of pitchblende: U. S. Atomic Energy Comm. RME-3096 (pt. 2), p. 72-99, Tech. Inf. Service, Oak Ridge, Tenn.

Mirsky, A., 1953, Preliminary report on uranium mineralization in the Dakota sandstone, Zuni Uplift, New Mexico: U. S. Atomic Energy Comm. RME-47, Tech. Inf. Service, Oak Ridge, Tenn.

Moore, G. W., 1954, Extraction of uranium from cold water solutions by coal and other materials: Econ. Geology, v. 49, p. 652-658.

Munthe, H., Westergard, A. H., and Lundquist, G., 1928, Beskrivining till Karbladet Skovde (description relating to the Skovde map sheet): Sveriges geologiska undersökning, Stockholm, Ser. As Kartblad i skalan 1:50,000 med Beskrivningar, no. 121.

Murata, K. J., Cisney, E. A., Stieff, L. R., and Zworykin, E. V., 1951, Hydration and base exchange properties of carnotite, tyuyamunite and related compounds (abs.): Am. Mineralogist, v. 36, p. 323.

Narten, P. F., and McKeown, F. A., 1952, Reconnaissance of radioactive rock of the Hudson Valley and Adirondack Mountains, New York: U. S. Geol. Survey TEI-70, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Neuman, W. F., Neuman, M. W., and Mulryan, B. J., 1948, The deposition of uranium in bone, I. Animal studies: Jour. Biol. Chem., v. 175, p. 705-709.

Neuman, W. F., Neuman, M. W., Main, E. R., and Mulryan, B. J., 1949a, The deposition of uranium in bone, IV. Adsorption studies in vitro: Jour. of Biol. Chem., v. 179, p. 325-333.

__________, 1949b, The deposition of uranium in bone, V. Ion exchange studies: Jour. of Biol. Chem., v. 179, p. 335-340.

__________, 1949c, The deposition of uranium in bone, VI. Ion competition studies: Jour. of Biol. Chem., v. 179, p. 341-348.

Neumann, H., 1948, On hydrothermal differentiation: Econ. Geology, v. 43, p. 77-83.

Newhouse, W. H., 1934, The source of vanadium, molybdenum, tungsten, and chromium in oxidized lead deposits: Am. Mineralogist, v. 19, p. 209-220.

Nininger, R. D., 1954, Minerals for atomic energy: D. van Nostrand Co., Inc., New York.

Page, L. R., 1950, Uranium in pegmatites: Econ. Geology, v. 45, p. 12-34.

Parkin, L. W., and Glasson, K. R., 1954, Geology of the Radium Hill uranium area, South Australia: Econ. Geology, v. 49, p. 815-825.

Phair, George, 1952, Radioactive Tertiary porphyries in the Central City District, Colorado, and their bearing upon pitchblende deposition: U. S. Geol. Survey TEI-247, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.; Nuc. Sci. Abs., v. 6, p. 776.

__________, and Levine, H., 1953, Notes on the differential leaching of uranium, radium, and lead from pitchblende in H_2SO_4 solutions: Econ. Geology, v. 48, p. 358-369.

Picciotto, E. E., 1950, Distribution de la radioactivité dans les roches eruptives: Bull. de la Soc. Belge de Geol. de Paleontol. et d'Hydrol., v. 59, p. 170-199.

Proctor, P. D., 1953, Geology of the Silver Reef (Harrisburg) mining district, Washington County, Utah: Utah Geol. and Min. Soc. Bull. 44.

Rankama, K., and Sahama, T. G., 1950, Geochemistry: Univ. of Chicago Press.

Rasor, C. A., 1952, Uraninite from the Grey Dawn mine, San Juan County, Utah: Science, v. 116, no. 3004, p. 89-90.

Reinecke, L., 1927, The location of payable ore-bodies in the gold-bearing reefs of the Witwatersrand: Trans. Geol. Soc. of S. Africa, v. 30, p. 89-119.

__________, 1930, Origin of the Witwatersrand system: Trans. Geol. Soc. S. Africa, v. 33, p. 111-133.

__________, 1940, Gold in the Witwatersrand system, *in* Mineral resources of South Africa: South Africa Geol. Survey, p. 110-163.

Reinhardt, E. V., 1952, The distribution of uranium-vanadium deposits in the Colorado Plateau relative to Tertiary intrusive masses: U. S. Atomic Energy Comm. RMO-816, Tech. Inf. Service, Oak Ridge, Tenn.

Rosenzweig, A., Gruner, J. W., and Gardiner, L., 1954, Widespread occurrence and character of uraninite in the Triassic and Jurassic sediments of the Colorado Plateau: Econ. Geology, v. 49, p. 351-361.

Runnels, R. T., Schleicher, J. A., and Van Nortwick, H. S., 1953, Composition of some uranium-bearing phosphate nodules from Kansas shales: Kansas Geol. Survey Bull. 102, p. 93-104.

Russell, W. L., 1945, Relation of radioactivity, organic content, and sedimentation: Am. Assoc. Petrol. Geol., Bull., v. 29, p. 1470-1493.

Sales, R. H., and Meyer, Charles, 1950, Interpretation of wall-rock alteration at Butte, Montana: Colorado School of Mines Quart., v. 45, p. 261-273.

Schwellnus, C. M., 1946, Vanadium deposits in the Otavi Mountains, Southwest Africa: Trans. Geol. Soc. S. Africa, v. 48, p. 49-74.

Seaborg, G. T., and Katz, J. J., 1954, The actinide elements: McGraw-Hill Co.

Seaborg, G. T., and Levine, C. A., 1951, The occurrence of plutonium in nature: Jour. Am. Chem. Soc., v. 73, p. 3278-3283.

Senftle, F. E., and Keevil, N. B., 1947, Thorium-uranium ratios in the theory of genesis of lead ores: Am. Geophys. Union Trans., v. 28, no. 5, p. 732-738.

Sharpe, J. W. N., 1950, The economic auriferous bankets of the upper Witwatersrand beds and their relationship to sedimentation features: Trans. Geol. Soc. S. Africa, v. 52, p. 265-288.

Simpson, D. J., 1952, Some results of radiometric logging in the boreholes of the Orange Free State gold fields and neighboring areas: Trans. Geol. Soc. S. Africa, v. 54, p. 99-133.

__________, 1953a, Correlation by means of radioactivity logging in the Witwatersrand System in the Klerksdorp area: Trans. Geol. Soc. S. Africa, v. 55, p. 33-52.

__________, 1953b, Correlation of the sediments of the Witwatersrand System in the West Witwatersrand, Klerksdorp and Orange Free State areas by radioactivity borehole logging: Trans. Geol. Soc. S. Africa, v. 55, p. 135-154.

Smith, P. V., 1954, Studies on origin of petroleum: Occurrence of hydrocarbons in recent sediments: Am. Assoc. Petrol. Geol. Bull., v. 38, p. 377-404.

Steacy, H. R., 1953, An occurrence of uraninite in a black sand: Am. Min., v. 38, p. 549.

Stieff, L. R., Stern. T. W., and Milkey, R. G., 1953, A preliminary determination of the age of some uranium ores of the Colorado Plateau by the lead-uranium method: U. S. Geol. Survey Circ. 271.

Stokes, W. L., 1952, Uranium-vanadium deposits of the Thompsons area, Grand County, Utah, with emphasis on the origin of carnotite ores: Utah Geol. and Mineralog. Survey Bull. 46, 51 p.

Strøm, K. M., 1948, A concentration of uranium in black muds: Nature, v. 162, p. 922.

Strutt, R. J., 1908, Helium and radioactivity in rare and common minerals: Royal Soc. London Proc., ser. A, v. 80, p. 572-594.

Stugard, F., Jr., Wyant, D. G., and Gude, A. J., 3rd., 1952, Secondary uranium deposits in the United States <u>in</u> Selected papers on uranium deposits in the United States: U. S. Geol. Survey Circ. 220, p. 19-25.

Sullivan, C. J., and Matheson, R. S., 1952, Uranium-copper deposits, Rum Jungle, Australia: Econ. Geology, v. 47, p. 751-758.

Swanson, V. E., 1953, Uranium in the Chattanooga shale (abs.): Geol. Soc. America Bull., v. 64, p. 1481.

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

Thurlow, E. E., and Wright, R. J., 1950, Uraninite in the Coeur d'Alene district, Idaho: Econ. Geology, v. 45, p. 395-404.

Tilton, G. R., Patterson, C., Brown, H., Ingram, M., Hayden, R., Hess, D., and Larsen, E. S., Jr., 1954, The isotopic composition and distribution of lead, uranium, and thorium in a pre-Cambrian granite: U. S. Atomic Energy Comm., AECU-2840, Tech. Inf. Service, Oak Ridge, Tenn.

Tolmachev, U. M., 1943, Adsorption of uranyl salts by solid adsorbants: U. S. S. R. Acad. Sci. Bull. no. 1, p. 28-34.

Tomkieff, I., 1946, The geochemistry of uranium: Science Progress, v. 34, p. 696.

Turner, H. W., 1928, Review of the radioactive minerals of Madagascar: Econ. Geology, v. 23, p. 62-84.

U. S. Geological Survey, 1953a, Search for and geology of radioactive deposits, Semiannual progress report December 1, 1952 - May 31, 1953: TEI-330, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1953b, Search for and geology of radioactive deposits, Semiannual progress report June 1 - November 30, 1953: TEI-390, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1954a, Geologic investigations of radioactive deposits, Semiannual progress report, December 1, 1953 to May 31, 1954: TEI-440, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, 1954b, Geologic investigations of radioactive deposits, Semiannual progress report, June 1 to November 30, 1954: TEI-490, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

Vine, J. D., and Moore, G. W., 1952, Uranium-bearing coal and carbonaceous rocks in the Fall Creek area, Bonneville County, Idaho: U. S. Geol. Survey Circ. 212.

Waters, A. C., and Granger, H. C., 1953, Volcanic debris in uraniferous sandstones, and its possible bearing on the origin and precipitation of uranium: U. S. Geol. Survey Circ. 224.

Weeks, A. D., 1953, Mineralogic study of some Jurassic and Cretaceous claystones and siltstones from Western Colorado and Eastern Utah: U. S. Geol. Survey TEI-285, U. S. Atomic Energy Comm., Tech. Inf. Service, Oak Ridge, Tenn.

__________, Cisney, E. A., and Sherwood, A. M., 1953, Montroseite, a new vanadium oxide from the Colorado Plateaus: Am. Mineralogist, v. 38, p. 1235-1242.

Weeks, A. D., and Thompson, M. E., 1954, Identification and occurrence of uranium and vanadium minerals from the Colorado Plateaus: U. S. Geol. Survey Bull. 1009B, p. 13-62.

Weir, D. B., 1952, Geologic guides to prospecting for carnotite deposits on Colorado Plateau: U. S. Geol. Survey Bull. 988B, p. 15-27.

Westergard, A. H., 1944a, Borrningar genom Skanes alunskiffer 1941-1942: Sveriges geol. undersökning, ser. C, no. 459.

__________, 1944b, Borrningar genom alunskifferlagret pa oland och i Ostergotland 1943: Sveriges geol. undersökning, ser. C, no. 463.

Whitehead, W. L., 1952, Studies of the effect of radioactivity in the transformation of marine organic materials into petroleum hydrocarbons: _in_ Am. Petroleum Inst. Fundamental research on occurrence and recovery of petroleum, 1950-1951, p. 192-201.

Wilson, H. D. B., 1953, Geology and geochemistry of base metal deposits: Econ. Geology, v. 48, p. 370-407.

Wright, H. D., 1954, Mineralogy of a uraninite deposit at Caribou, Colorado: Econ. Geology, v. 49, p. 129-174.

__________, and Beiler, B. H., 1953, An investigation of the mineralogy of uranium-bearing deposits in the Boulder batholith, Montana: U. S. Atomic Energy Comm., RME-3041, Tech. Inf. Service, Oak Ridge, Tenn.

Wyant, D. C., Beroni, E. P., and Granger, H. C., 1952, Some uranium deposits in sandstone: U. S. Geol. Survey Circ. 220, p. 26-30.

Young, R. B., 1917, The banket: Gurney and Jackson, London.

UNPUBLISHED REFERENCES

Altschuler, Z. S., 1952, The petrography and uranium content of phosphates from Morocco: U. S. Geol. Survey Trace Elements Memo. Rept. 238.

__________, and Boudreau, C. E., 1949, A mineralogical and chemical study of the leached zone of the Bone Valley formation of Florida, a progress report: U. S. Geol. Survey Trace Elements Inv. Rept. 102.

Bachman, G. O., and Read, C. B., 1951, Results of recent reconnaissance investigations of uranium in coal, black shale, and related deposits in Sandoval and Rio Arriba Counties, New Mexico: U. S. Geol. Survey Trace Elements Memo. Rept. 309.

Beers and Heroy, 1951, The radioactivity of black shales: U. S. Atomic Energy Comm. Rept. RMO-865.

Breger, I. A., and Deul, M., 1952, Status of investigations on the geochemistry and mineralogy of uraniferous lignites: U. S. Geol. Survey Trace Elements Inv. Rept. 284.

Bullwinkel, E. D., 1954, The chemistry of uranium in carbonate solutions: U. S. Atomic Energy Comm. Topical Rept. RMO-2614.

Coats, Robert R., 1952, Preliminary report of reconnaissance for uraniferous granitic rocks in Montana, Idaho, Oregon, Washington, and California: U. S. Geol. Survey Trace Elements Memo. Rept. 343.

Garrels, R. M., and Richter, D. H., 1955, Is carbon dioxide an ore-forming fluid under shallow earth conditions?: U. S. Geol. Survey Trace Elements Inv. Rept. 472.

King, R. U., and Roberts, W. A., 1949, Yerington property, Anaconda Copper Mining Company, Lyon County, Nevada: U. S. Geol. Survey Special Rept. of Field Examination No. 11, July 1949.

Mullens, T. E., and Freeman, V. L., 1954, Lithofacies of the Salt Wash member of the Morrison formation: U. S. Geol. Survey Trace Elements Inv. Rept. 341.

Riley, L. B., and Shoemaker, E. M., 1952, Distribution of ore deposits and spectrographic analyses of some rocks and ores on the Colorado Plateau: U. S. Geol. Survey Trace Elements Inv. Rept. 278.

Sheldon, R. P., 1954, Physical stratigraphy of the Phosphoria formation in northwestern Wyoming: U. S. Geol. Survey Bull., in press.