Geochemistry of Uranium in Phosphorites and Black Shales of the Phosphoria Formation

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GEOLOGICAL SURVEY BULLETIN 1084-D

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

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By RICHARD P. SHELDON

CONTRIBUTIONS TO GEOCHEMISTRY

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GEOCHEMISTRY OF URANIUM IN PHOSPHORITES AND BLACK SHALES OF THE PHOSPHORIA FORMATION

By Richard P. Sheldon

ABSTRACT

Uranium in the Phosphoria formation of Permian age in the western phosphate field occurs mostly in phosphorite and partly in black shale. However, some of the phosphorites and most of the black shales of the formation are practically nonuraniferous. These anomalies in uranium content can be related to the petrography and composition of the rocks.

A basic premise to this study is that the immediate source of the uranium in the Phosphoria formation was the ocean. The facts that the quantity of uranium in the formation is large and widely distributed and that comparable Recent marine phosphorites are uraniferous support this premise. The chemistry of uranium in the ocean has been little studied, but several deductions can be made from the known thermodynamic data and the chemical data of uranium in aqueous solutions. Garrels (1955) has shown that the pH and the Eh control the oxidation state of uranium in natural water, and a survey of the literature reveals that the increasing pH favors the formation of complex ions made up of a uranyl ion and anions present in the sea, such as PO_4^{-3}, CO_3^{-2}, OH^-, and SO_4^{-2}. The formation of uranyl sulfate complexes is favored by high Eh.

The phosphatic rocks of the formation are classified according to the Eh and pH of their depositional environment, and their uranium contents are compared by means of a distribution-free statistical test. This analysis shows that the phosphatic sediments that were deposited in an environment of low Eh are relatively rich in uranium, whereas phosphatic sediments deposited in an environment of high Eh are relatively poor in uranium. The pH of the environment where apatite is stable apparently has no effect on the concentration of uranium. Two hypotheses for the occurrence of uranium in apatite are reviewed: (a) the substitution of U(IV) for calcium in the apatite lattice, and (b) the adsorption of the uranyl ion on the surfaces of apatite crystallites. No clear-cut choice between these two modes of occurrence can be made with the present data, as both U(IV) and U(VI) are known to occur in the Phosphoria formation. Multiple regression analyses show that uranium is positively correlated with both P_2O_5 and fluorine present in the apatite in quantities exceeding that of lattice requirements. This correlation seems to be best explained by adsorption of both excess fluorine and uranium on the surfaces of apatite crystallites. The size of apatite crystallites was investigated by X-ray diffraction techniques; the results suggest, but do not prove, that apatite rich in excess fluorine and uranium is made up of the smallest crystals.

These data suggest that uranium is probably deposited in apatite in one or both of two ways:

1. Low Eh of the depositional environment causes the highest concentration of the U^{+4} ion and thereby more U(IV) is substituted for calcium in the apatite lattice; or
2. A low Eh of the depositional environment allows the accumulation of organic matter, which inhibits growth of apatite crystallites, allowing more uranyl ion to be adsorbed on crystallite surfaces.

Few data are available on the mode of occurrence of uranium in black shale, but, from chemical and stratigraphic considerations, it seems possible that the uranium is deposited as disseminated UO_2 in a reducing acid depositional environment.

INTRODUCTION

Marine phosphorite formations the world over contain small amounts of uranium. In a general way the amount of uranium of these phosphorites varies directly with the phosphate content, but the correlation is not perfect. Significant differences of uranium content for a given quantity of phosphate have been found from formation to formation over the world (Altschuler and others, 1958) and within the Phosphoria formation of Permian age in the Idaho-Wyoming-Montana-Utah phosphate field (McKelvey and Carswell, 1956). Similarly, the uranium contents of black shale formations differ. Some, such as the Chattanooga shale of Devonian and Mississippian age of the central United States, contain relatively high concentrations of uranium, whereas others contain negligible quantities. Similarly, most of the black shale of the Phosphoria formation contains almost no uranium, but several zones of limited extent have a quantity of uranium comparable to that in the Chattanooga shale.

These differences of uranium content are difficult to analyze for several reasons. First, the uranium in the phosphatic rocks and black shales occurs in small amounts and the host rocks are very fine grained. Uranium minerals, if present, generally cannot be seen or separated, and host minerals of the uranium cannot be cleanly separated from other minerals. Hence, indirect methods, such as statistical correlation of chemical analyses, autoradiographs, and the like, must be used to study the distribution of uranium. Second, uranium can be fairly easily leached or enriched in phosphatic rocks by weathering processes, so that genetic studies based on samples collected from outcrops are subject to error. Third, apatite, the host mineral for most of the uranium, is a complex mineral, subject to many ionic substitutions of trace elements. In marine rocks it is commonly so finely crystalline that surface chemical effects can easily play an important part in determining the composition of the apatite. The distinction between such structural or surficial phenomena of the crystals is extremely difficult to make. Finally, apatite, like the carbonate minerals, is easily subject to recrystallization, solution, and redeposition during diagenesis of the rocks; hence, chemical differences due to differing depositional environments may be erased by diagenetic processes.

The present study of the geochemistry of uranium in the Phosphoria formation is based on a genetic classification of the uranium-bearing rocks. It was found earlier from a study of the physical stratigraphy of the Phosphoria formation in Wyoming that the sequence of facies of the black shales and phosphatic rocks was caused by the increase of pH and Eh of the depositional environment from the deeper water sediments in western Wyoming to the shallow water sediments in central Wyoming (Sheldon, 1957, p. 146–152). Because the uranium content of the phosphatic rocks decreases eastward (McKelvey and Carswell, 1956, p. 484), it seems possible that the physical-chemical depositional environment may be a control in uranium concentration. To test this hypothesis, the physical chemistry of uranium in the ocean is reviewed to determine the effect of pH and Eh of the sea water on the state of uranium. The uraniferous rocks are classified according to the likely pH and Eh of the depositional environment (Krumbein and Garrels, 1952), and variations of their uranium content are analyzed by statistical methods. This study shows that the Eh of the depositional environment plays a part in the concentration of uranium, but the mechanism of concentration is still in doubt.

ACKNOWLEDGMENTS

Many members of the U.S. Geological Survey have been very helpful in the criticism of this report; among these, Z. S. Altschuler has been a particularly excellent and constructive critic. Dr. Lincoln E. Moses, of Stanford University, has very kindly advised me at many stages of the statistical analyses in this paper. The work is part of a program conducted by the U.S. Geological Survey on behalf of the Division of Raw Materials of the U.S. Atomic Energy Commission.

SOURCE OF URANIUM IN THE PHOSPHORIA FORMATION

A basic premise of this paper is that the uranium in the Phosphoria formation was mainly extracted from the sea water during the deposition of the major constituents of the rocks. Two arguments support this assumption.

Perhaps the most convincing argument concerning the source of uranium is the amount and distribution of uranium in the Phosphoria. On the assumptions that the average ratio of uranium to P_2O_5 is 0.4×10^{-3} (the mean of a fairly large sample of rocks from western Wyoming) and that the Phosphoria formation contained 1.7×10^{12} metric tons of P_2O_5 before Cenozoic erosion occurred (Mc-

Kelvey and others, 1953, p. 56), the Phosphoria formation contained about 0.7×10^9 metric tons of uranium. This amount is of the same order of magnitude as that in the ocean today, as will be discussed below. This uranium is distributed in phosphatic material of the formation over an area of about 135,000 square miles in the Western United States (McKelvey and Carswell, 1956, p. 483). It would seem highly improbable that connate water, a possible source of the uranium, could supply this quantity; or that magmatic water, another possible source, could be distributed uniformly in the formation over the whole area.

Altschuler, Clarke, and Young (1958, p. 56) report that nodules dredged from the sea floor off California contain as much as 0.012 percent uranium, which is comparable to the uranium content of phosphorite from the Phosphoria formation. There is no doubt that the uranium in the nodules was derived from the ocean.

URANIUM IN THE OCEAN

A beginning to the understanding of the distribution and chemistry of uranium in the ocean has been made by recent investigations. Oceanographic studies indicate that uranium has a distribution somewhat comparable to that of phosphorus, silica, and several other variable constituents of sea water. The chemistry of uranium in sea water has not been directly investigated, but several deductions can be made from thermodynamic calculations and from knowledge of the behavior of uranium in aqueous solutions.

AMOUNT AND DISTRIBUTION

The average content of uranium in the oceans is about 3.3×10^{-6} grams U per liter, according to Rona and others (1956, p. 699). F. F. Koczy (1956, p. 95), using a less accurate method of determination, found that the content of uranium in surface waters of the oceans is fairly constant over the world. His average content was about 1.1×10^{-6} grams U per liter. With depth this content increases and at about 1,000 meters reaches a maximum of about 1.4×10^{-6} grams U per liter. With greater depth the content falls and near the sea bottom amounts to about 1.2×10^{-6} grams U per liter (Koczy, 1950). Thus, the distribution of uranium in the ocean seems to follow that of such components as phosphate, nitrate, and silica, which also reach maximum contents at about 1,000 meters, and either decrease or remain constant in value with greater depth (Sverdrup and others, 1942, p. 241–245). However, Koczy and others (1957, p. 86) report a correlation between uranium content and salinity in the Baltic Sea. On the assumption that the ocean contains on the average 3.3×10^{-6} grams U per liter (Rona and others, 1956, p. 699) in a volume of

137×10^7 km^3 (Sverdrup and others, 1942, p. 15, 220), the total amount of uranium in the ocean would be about 4.6×10^9 metric tons, or only about 7 times the assumed original content of uranium in the Phosphoria.

CHEMISTRY

Garrels (1955, p. 1009) has analyzed existing thermodynamic data and shows that uranium in natural solutions will be present as either the U^{+4} ion or the UO_2^{+2} ion, and that the ratio between the activities of these ions is controlled by pH and Eh of the solution and is given by the expression:

$$Eh = -E^\circ + 0.03 \log \frac{a_{UO_2}{}^{+2} a^4{}_{H}{}^{+}}{a_U{}^{+}}$$

which can be rewritten as

$$Eh = -E^\circ + 0.03 \log \frac{a_{UO_2}{}^{+}}{a_U{}^{+4}} - 0.12 \text{ pH}$$

where E^0 is equal to -0.334 volts (Latimer, 1952, p. 301). Thus, the ratio UO_2^{+2}/U^{+4} will decrease with decreasing Eh and pH. In water at 20°C, at pH of 7.5 to 8.4 and Eh of 0.2 to 0.4, the uranyl ion will be from about 10^{25} to about 10^{37} times as abundant as the tetravalent uranium ion. In an environment of $pH = 6$, $Eh = -0.3$, the uranyl ion will be about 100 times as abundant as the tetravalent uranium ion.

As a further complication the uranyl ion can combine with the sulfate, carbonate, phosphate, and arsenate anions to form a number of uranyl complex ions (Seaborg and Katz, 1954, p. 169). The uranyl ion also hydrolizes to form further polynuclear complex ions (Ahrland, and others, 1954). U(IV) also forms a carbonate complex ion (McClaine and others, 1956). Some of the complex ions so far reported in the literature, and which possibly form in sea water, are given in table 1. The equilibrium constants for the formation of some of these ions are given in table 2.

TABLE 1.—*Complex ions and molecules of uranium*

Complex ion	Remarks	Reference
$[UO_2(CO_3)_2(H_2O)_2]^{-2}$		McClaine and others, 1956.
$[UO_2(CO_3)_3]^{-4}$		Do.
$U\ (CO_3)_5{}^{-6}$	Formula uncertain	Do.
$UO_2(SO_4)_2{}^{-2}$		Arhland, 1951.
$UO_2(SO_4)_3{}^{-4}$		Do.
UO_2SO_4		Do.
$UO_2(OUO_2)_n{}^{+2}$	Can be written as $UO_2((OH)_2UO_2)_n{}^{+2}$.	Ahrland and others, 1954.
Uranyl pyrophosphate complex ion.		Neuman and others, 1949b.

TABLE 2.—*Equilibrium constants of uranyl complex ions in aqueous solutions*

Equilibrium constants	Temperature °C	Reference
$\frac{[UO_2(CO_3)_2(H_2O)_2^{-2}]}{[UO_2^{+2}][CO_3^{-2}]^2} \approx 4 \times 10^{14}$	25	McClaine and others, 1956.
$\frac{[UO_2(CO_3)_3^{-4}]}{[UO_2^{+2}][CO_3^{-2}]^3} \approx 2 \times 10^{18}$	25	Do.
$\frac{[UO_2(SO_4)]}{[UO_2^{+2}][SO_4^{-2}]} \approx 50$	20	Ahrland, 1951.
$\frac{[UO_2(SO_4)_2^{-2}]}{[UO_2^{+2}][SO_4^{-2}]^2} \approx 350$	20	Do.
$\frac{[UO_2(SO_4)_3^{-4}]}{[UO_2^{+2}][SO_4^{-2}]^3} \approx 2500$	20	Do.
$\frac{[(UO_2)_2O^{+2}][H^+]^2}{[UO_2^{+2}]^2} = 10^{-6.05 \pm 0.1}$	20	Ahrland and others, 1954.
$\frac{[UO_2(OUO_2)_{n+1}{}^{+2}][H^+]^2}{[UO_2^{+2}][UO_2(OUO_2)_n{}^{+2}]} = 10^{-6.35 \pm 0.1}$	20	Do.
Dissociation constant of uranyl pyrophosphate complex ion $= 5 \times 10^{-8}$.	--------	Neuman and others, 1949b.

Knowledge of the chemistry of uranium complex ions is far from complete; therefore, it seems inappropriate in this paper to attempt any mathematical analysis of these data. However, several important qualitative deductions can be made. First, these uranyl complex ions have different degrees of dissociation. Seaborg and Katz (1954, p. 166) report that the more basic the anion or the more readily it combines with the hydrogen ion, the less the degree of dissociation of the uranyl complex ion or salt. This generalization is well shown for all the anions listed in table 2. If these anions are listed in order by decreasing basicity or by increasing dissociation constants of their corresponding acids (calculated for their last hydrogen dissociation), they are: OH^-, CO_3^{-2}, $P_2O_7^{-4}$, and SO_4^{-2}. Listed in order of increasing dissociation constants of their complex uranyl ions, they are: hydrolized uranyl ions (the equilibrium equation must be recalculated for $UO_2((OH)_2UO_2)^{+2}$), uranyl carbonate ions, uranyl pyrophosphate ions, and uranyl sulfate ions. Second, the proportion of the uranyl ion tied up in such complex ions will depend on the concentrations of the various anions. These anion concentrations are dependent on both the total phosphate, carbonate, and sulfate concentrations, and the pH of the water. With decreasing pH, increasing proportions of the anions combine with H^+, resulting in a decrease in the concentration of the anion. Thus, with decreasing pH the ratio of the uranyl ion to the uranyl complex ion will increase, that is, the concentration of the uranyl ion will increase. In a similar way, the ratio of U^{+4} to U(IV) carbonate complex ion will increase with decreasing pH. In addition to a pH dependence, the concentration of SO_4^{-2} is dependent on the Eh. At low Eh values, sulfide rather than sulfate is more likely to occur; thus, a lowering of the Eh of a solution would cause an increase in the proportion of the uranyl ion to the uranyl sulfate complex ion.

URANIUM IN THE PHOSPHORIA FORMATION

The mineralogic occurrence of uranium in the Phosphoria is obscure. The rocks contain uranium in amounts up to 0.06 percent (Thompson, 1953, p. 56), but, in general, the more uraniferous rocks contain only about 0.01 to 0.02 percent uranium. As in similar marine deposits (McKelvey and others, 1955, p. 514), the Phosphoria contains only two types of significantly uraniferous rocks, phosphorite and carbonaceous black shale.

RADIOACTIVE EQUILIBRIUM OF URANIUM IN THE PHOSPHORIA FORMATION

Before discussing the distribution and mode of occurrence of uranium in the Phosphoria it is important to examine briefly possible secondary effects that may have added or removed uranium from the rocks. The absence or unimportance of such secondary effects are a premise of the study that follows.

Although uranium has not been selectively leached from phosphorites in laboratory experiments, it has in nature. Some evidence that uranium has been leached from the Phosphoria formation near the surface has been presented by McKelvey and Carswell (1956, p. 485–486). More definite evidence of such leaching has been presented for some Florida phosphate rocks (Altschuler and others, 1958, p. 57). Moreover, Altschuler and his coworkers have shown that uranium has been enriched in other Florida phosphate rock.

Leaching of uranium from phosphate rock possibly can be detected by determining if uranium is out of radioactive equilibrium with its daughter products (Phair and Levine, 1953, p. 360). If the chemically determined uranium (U) is equal to the radiometrically determined uranium (eU), the uranium may be assumed to be in radioactive equilibrium with its daughter products. To test this equivalence, U and eU of each sample analyzed from western Wyoming are plotted on a scatter diagram in figure 12. A regression analysis (Hald, 1955, p. 522–584; table 3 below) shows that the slope is not significantly different from 1.0, and that the *y*–intercept, or the value of $\hat{U}$ at $eU=0$, is significantly different from zero. The line of the regression equation is plotted on figure 12. This relationship shows,

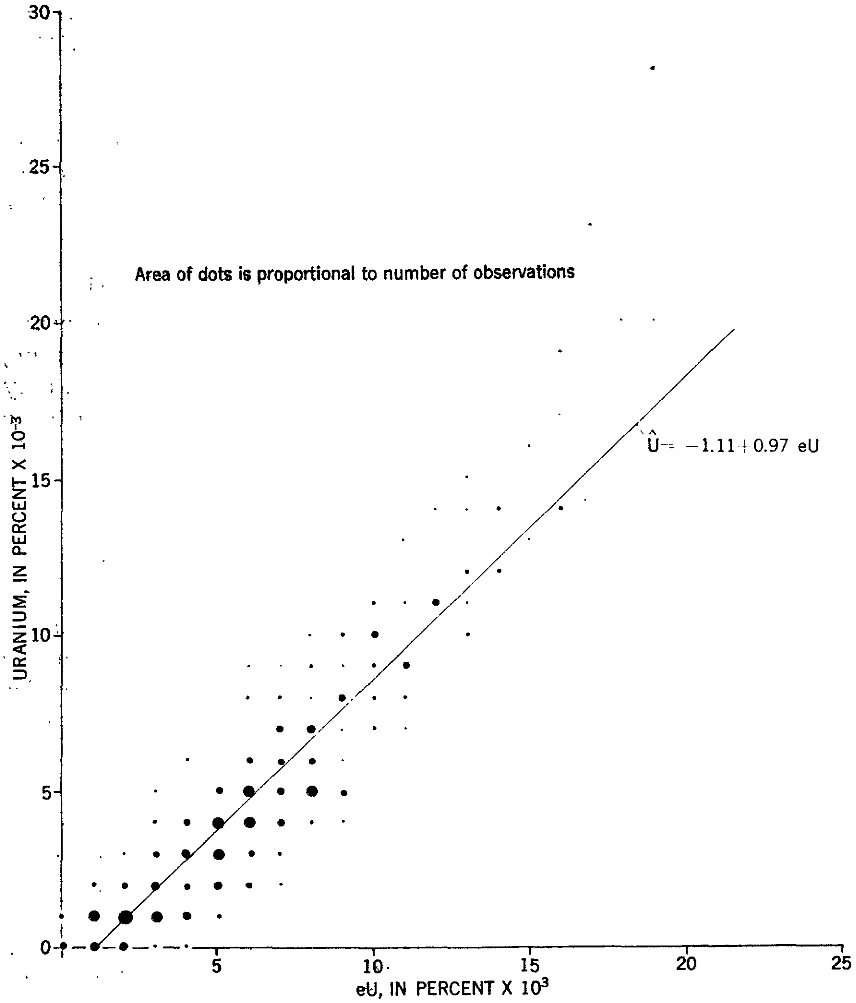

FIGURE 12.—Scatter diagram showing relation between uranium (U) and eU in Permian rocks of western Wyoming.

then, that the average value of U is somewhat less than the corresponding value of eU. The reason for this cannot be determined without further investigation; but it may be that the values of either the eU or U determinations are slightly biased, or perhaps a small amount of radioactive material other than uranium and its daughter products is in the rocks. It does not seem likely that leaching could cause the difference, because it would be difficult to explain how a constant amount of uranium was leached regardless of the amount of uranium in the rocks. Several of the samples fall far below the regression line so that eU is much higher than U, and it seems likely that uranium has been leached from these rocks. The bulk of the rocks, however, are in radioactive equilibrium, so that recent surface leaching of the uranium in the rocks studied in this report has not been so extensive that it affects conclusions about the original distribution of uranium.

TABLE 3.—*Regression analysis. Relation between the percentage of radiometrically determined uranium* (eU)×10³ *and the percentage of chemically determined uranium* (U)×10³ *in Wyoming phosphatic rocks of Permian age*

[Symbols used are: *n*, the number of observations; *S*, the sum; *SS*, the sum of squares; *SSD*, the sum of the squares of the deviations from the mean; *SPD*, the sum of the products of the deviations; *f*, the degrees of freedom; s^2, the variance]

	eU	U
n	386	
S	2,316	1,821
SS	19,618	15,369
S^2/n	13,896	8,591
SSD	5,832	6,778
SPD^2/SSD_{eU}		5,520
$SSD_{U/eU}$		1,258
f		384
s^2		3.276
s		1.810
S/n	6.00	4.72

$SP=16{,}600$ $\quad S_{eU}S_{U}/n=10{,}926$ $\quad SPD=5{,}674$ $\quad b=0.972$

$$\hat{U}=4.72+0.972(eU-6.0)=-1.11+0.972eU$$

$s^2_a=0.0085$ $\quad s_a=0.0921$

$s^2_b=0.00056$ $\quad s_b=0.0237$

Tests (t):

$b=1.0$

$$t=\frac{1.0-0.972}{0.0237}=1.181,\quad f=384$$

$t_{(0.05,\, f=384)}=1.97$

Because t is less than $t_{(0.05,\, f=384)}$, the hypothesis that $b=1.0$ is accepted at 0.05 probability level.

$a=5.83$

$$t=\frac{5.83-4.72}{0.0921}=12.0,\quad f=384$$

$t_{(0.05,\, 384)}=1.97$

Because t is greater than $t_{(0.05,\, 384)}$, the hypothesis that $a=5.83$ is rejected. Thus, the value of U at eU=0, is not 0, with a probability of less than 5 percent being wrong.

It is possible, however, that diagenetic processes or weathering occurring as late as early Tertiary time caused changes in uranium content, because enough time has elapsed for radioactive equilibrium to have been re-established. An example of older weathering may be seen at the exposure in Laketown Canyon, Utah, where the Meade Peak phosphatic shale member of the Phosphoria formation lies just below a widespread Eocene(?) erosion surface and is so leached that virtually no organic matter remains in the rocks, and in all probability uranium was leached from the rocks. The analyses of U and eU (T. M. Cheney, R. A. Smart, R. G. Waring, and M. A. Warner, written communication, 1953), however, show that the uranium is now in radioactive equilibrium with its daughter products.

URANIUM IN APATITE

The uranium in phosphorites of the Phosphoria formation is associated with carbonate-fluorapatite. Two lines of evidence support this conclusion. First, uranium in a general way varies directly with the apatite content of the rocks as determined from the P_2O_5 analyses (McKelvey and Carswell, 1956, p. 485). Second, uranium cannot be beneficiated in phosphorite by usual methods of ore beneficiation or by infrasizing, elutriation, or flotation in liquids of appropriate specific gravity, and the amount of uranium dissolved on acid treatment of phosphorities is proportional to the amount of phosphate dissolved (Igelsrud and others, 1948, p. 27–29).

This conclusion that the uranium in phosphorites is combined with apatite is basic to the arguments that follow. It will be shown that phosphorites rich in organic matter contain more uranium than phosphorites lean in organic matter. One might conclude from this that the organic matter rather than the apatite contains the extra uranium. Studies by Thompson (1953) rule out this possibility. She found that for groups of "close" [1] samples from five phosphorite beds, the rocks richest in uranium were also richest in organic matter. Yet the statistical correlation of uranium with P_2O_5 was best, and with organic matter it was worst in rocks with the greatest uranium content. The exact opposite results would be expected if a large part of the uranium in the most uraniferous beds were combined with organic matter. Her results are somewhat clouded by differing ranges of P_2O_5 values within each group; but her conclusion stated above is valid even if the two groups with slight range in P_2O_5 are discarded.

RELATION BETWEEN SEDIMENTARY ENVIRONMENT AND URANIUM CONTENT

The Permian rocks of Wyoming may be classified according to the probable pH and Eh of their depositional environment as follows: (a) rocks that contain benthonic fossils, such as phosphatic brachiopods and gastropods, or are light colored (color value$>$5) are assumed to have been deposited in an oxidizing environment (Eh$>$0); (b) rocks that are dark colored (color value$<$4), contain authigenic pyrite, and have none of the attributes of (*a*) above, are assumed to have been deposited in a reducing environment (Eh$<$0); (c) rocks that contain less than 20 percent carbonate are assumed to have been deposited in an environment with a lower pH than (d) rocks that contain carbonate in excess of 20 percent. The justification for the classification of depositional environments with respect to pH and Eh has been presented by Krumbein and Garrels (1952), and the application of their concept to the Permian rocks of western Wyoming has been given by Sheldon (1957). It is beyond the scope of this paper to discuss these arguments in detail, but several comments should be made.

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[1] Thompson (1953, p. 45) defines a "close" sample as "one of a large number of small contiguous samples taken across a single unit where all the samples together represent the entire unit."

The color of the rocks is a rough index of the quantity of organic matter in the rock (Patnode, 1941); the darker the rock the greater the amount of organic matter. Those rocks with intermediate color values of 4 and 5 have been excluded from this analysis; therefore,only the dark and light rocks are discussed. There is little doubt that the organic matter in the dark rocks was deposited in the original sediment (McKelvey and others, 1953, p. 59–60), so that the abundance of organic matter indicates a reducing environment. The absence of organic matter and the fossil evidence of oxygen-consuming animals on the sea floor, on the other hand, indicate an oxidizing environment.

The pH of the depositional environment influences the deposition of apatite and carbonate; in the ocean today carbonate cannot precipitate unless the pH is above about 7.8 (Krumbein and Garrels, 1952, p. 19), whereas apatite is stable at pH values over 7.0 (Kazakov, 1950) and can precipitate at a lower pH than carbonate (Krumbein and Garrels, 1952, p. 9; Rubey, *in* McKelvey and others, 1953, p. 59). Thus, noncarbonatic phosphorites are deposited in an environment with lower pH than phosphatic carbonate rocks. Furthermore, when carbonate and apatite coprecipitate, the ratio is very high in favor of carbonate (Krumbein and Garrels, 1952, p. 9); this conclusion is supported by the fact that rocks in the Phosphoria formation with a composition intermediate between carbonate rock and phosphorite are very rare (R. A. Gulbrandsen, oral communication, 1956). Thus, rocks with less than 20 percent carbonate include mostly noncarbonatic phosphorites, and rocks with more than 20 percent carbonate include the rare rocks of intermediate apatite-carbonate composition and the slightly phosphatic carbonate rocks. It then seems likely that, even though there are exceptions, the pH of the depositional environment of the rocks containing more than 20 percent carbonate was higher than that of the rocks containing less than 20 percent.

Finally, the precision of the class divisions of Eh=0 and pH=7.0 is low indeed. The experimental and theoretical data used by Krumbein and Garrels (1952) was for a temperature of 25°C, whereas the temperatures prevailing in areas of phosphate deposition in modern seas are much lower. Also, the high ionic strength of the ocean makes the application of thermodynamic data only approximate.

For the analysis of the relation between uranium content and the depositional environment 146 beds were selected. Only those beds that were analyzed for P_2O_5, eU, and U could be used, and, of these, beds that consisted of 2 or more subunits of differing rock types were discarded. Also, those rocks whose chemical U and eU differed by more than 0.002 percent were discarded to eliminate as nearly as possible any effects of leaching or enrichment of uranium. The 146 beds were divided into 4 classes according to the Eh and pH of the depositional environment: (a) Eh >0 and pH <7.8, (b) Eh <0 and pH <7.8, (c) Eh >0 and pH >7.8, and (d) Eh <0 and pH >7.8. The chemical uranium is plotted against P_2O_5 for each of these groups in figure 13, and the rocks of differing Eh and pH depositional environments are contrasted in figure 14*A* and *B*, respectively.

It is readily apparent that, for a given amount of phosphate, there is more uranium in the rocks deposited in a reducing environment than in an oxidizing one (fig. 14*A*). Although less apparent, the pH of the environment seems to have had little effect on the amount of uranium relative to phosphate (fig. 14*B*). Because some doubt may arise as to the validity of this judgment, the data were analyzed statistically. A distribution-free test was used.

A regression analysis would be more discriminating, but it did not seem warranted because the variance of U given P_2O_5 (assumed to be independent variable) seems to depend on the value of the P_2O_5. Several transformations of the variables were tried, but none appeared to stablize this variance for all groups. This distribution-free test used is as follows:

The question investigated was whether the uranium content, allowing for P_2O_5, is systematically higher or lower in (1) rocks deposited in an oxidizing environment than in (2) rocks deposited in a reducing environment. It is hypothesized that so far as the relation of U to P_2O_5 is concerned both types of rock may be regarded as equivalent; a line is then fitted to the combined data. The method of fitting is that of Brown and Mood (Mood, 1950, p. 406–408). A rock yielding a point above the line is regarded as being relatively rich in uranium (in this sample) and any rock yielding a point below the line as being relatively deficient in uranium. If, indeed, rocks of types 1 and 2 are from a common population, then the fraction of "high" type 1 and "high" type 2 should be about equal.

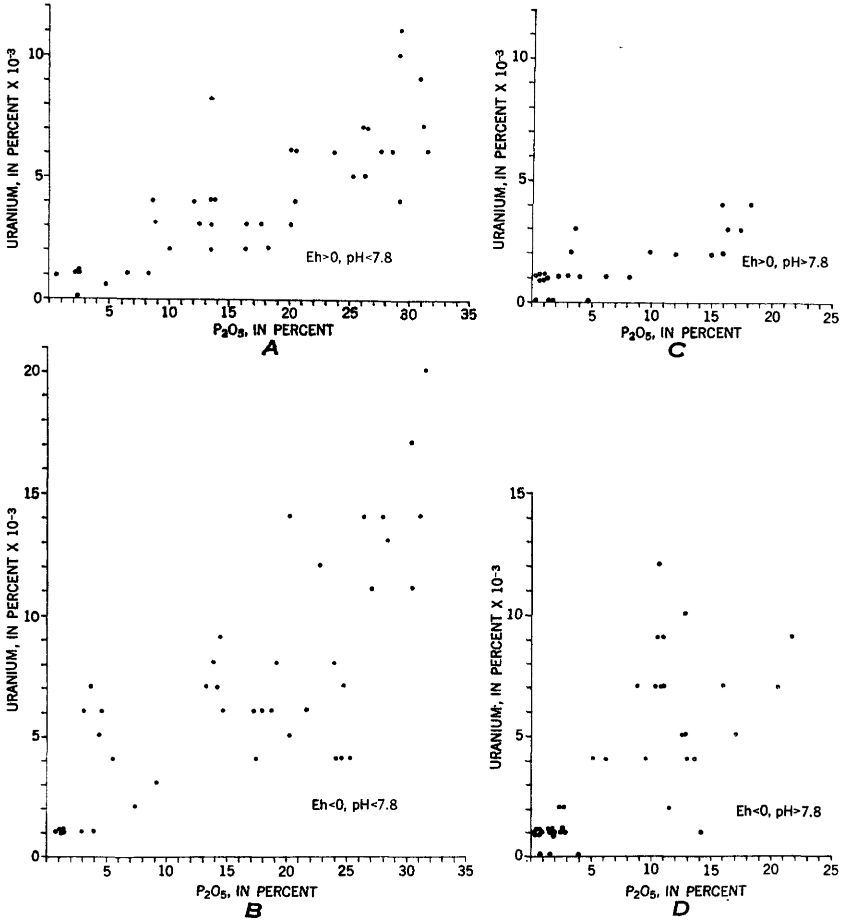


FIGURE 13.—Scatter diagrams showing relation between uranium (U) and P_2O_5 in rocks classified by probable environment of deposition. *A*, Rocks of Eh>0, pH<7.8; *B*, Eh<0, pH<7.8; C, Eh>0, pH>7.8; *D*, Eh<0, pH>7.8.

Figure 15*A* shows how the numbers of "high" and "low" rocks are classified by type (Eh>0 vs. Eh<0, or pH<7.8 vs. pH>7.8).

The actual values for the Eh comparison are displayed in figure 15*B* and for pH comparison in figure 15*C*. In each analysis the quantity

$$\frac{\left(|ad-bc|-\frac{N}{2}\right)^2 N}{(a+c)(b+d)(a+b)(c+d)} \qquad (1)$$

has a chi-squared distribution with one degree of freedom.

The value of (1) for the Eh comparison is 30.312. This is highly significant (far beyond 0.001 level of significance) and leaves little

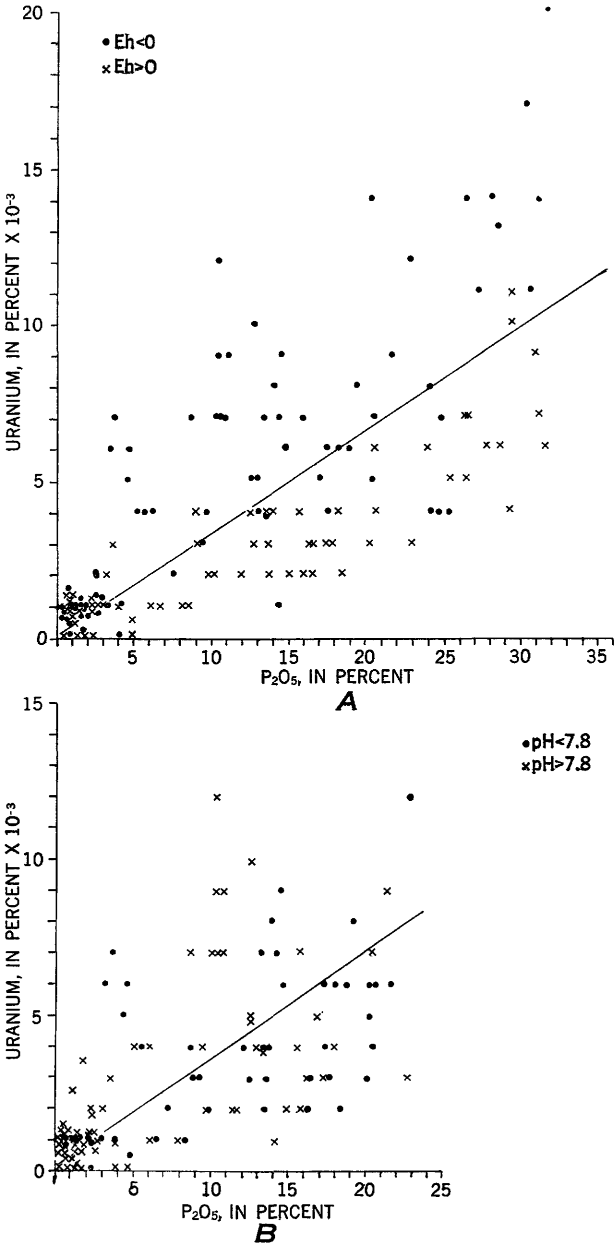
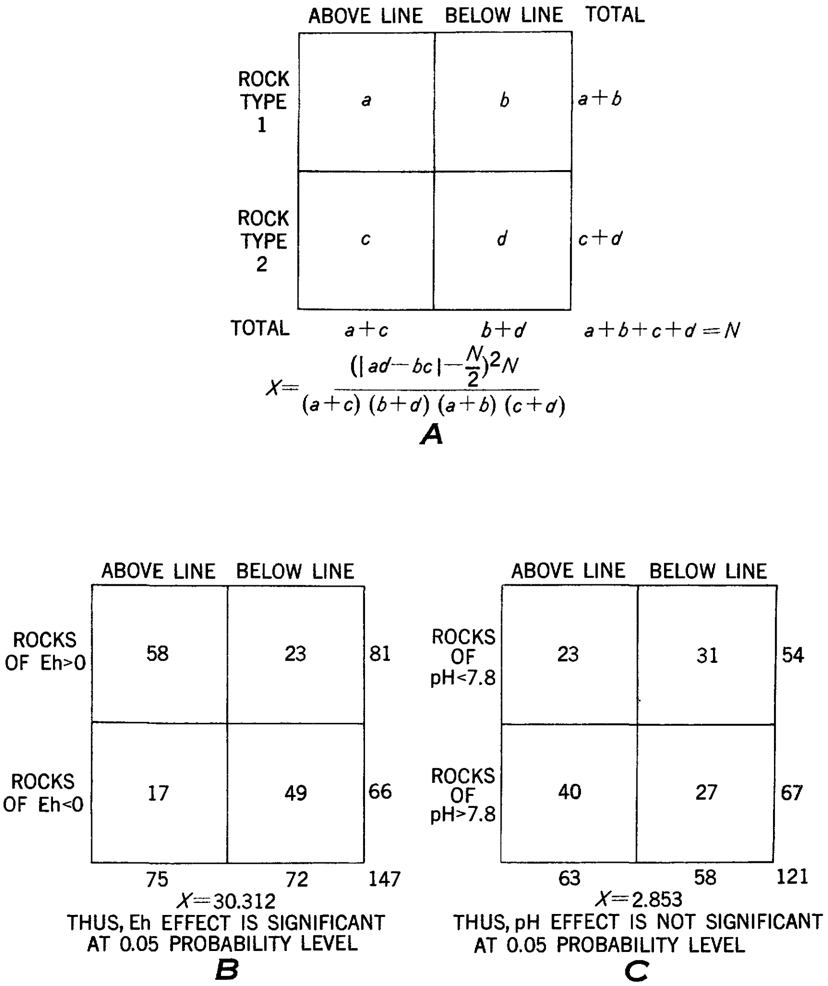


FIGURE 14.—Scatter diagrams showing relation between uranium (U) and P_2O_5. *A*, Rocks classified by probable Eh of environment of deposition. *B*, Rocks classified by probable pH of environment of deposition.



	ABOVE LINE	BELOW LINE	TOTAL
ROCK TYPE 1	a	b	$a+b$
ROCK TYPE 2	c	d	$c+d$
TOTAL	$a+c$	$b+d$	$a+b+c+d=N$

$$X=\frac{(|ad-bc|-\frac{N}{2})^2N}{(a+c)\ (b+d)\ (a+b)\ (c+d)}$$

A

	ABOVE LINE	BELOW LINE	
ROCKS OF Eh>0	58	23	81
ROCKS OF Eh<0	17	49	66
	75	72	147

$X=30.312$

THUS, Eh EFFECT IS SIGNIFICANT AT 0.05 PROBABILITY LEVEL

B

	ABOVE LINE	BELOW LINE	
ROCKS OF pH<7.8	23	31	54
ROCKS OF pH>7.8	40	27	67
	63	58	121

$X=2.853$

THUS, pH EFFECT IS NOT SIGNIFICANT AT 0.05 PROBABILITY LEVEL

C

FIGURE 15.—Distribution-free analysis of relation between uranium (U) and P_2O_5. *A*, Key to diagrams, *B* and *C*. *B*, Analysis of rocks classified by probable Eh of environment of deposition. *C*, Analysis of rocks classified by probable pH of environment of deposition. See text for explanation of method and figure 14 for scatter diagrams.

doubt that the 2 types of rock are not drawn from a common population, and that higher values of U (for given P_2O_5) occur in the reducing environment. The validity of this conclusion rests partly on the fact that the distribution of P_2O_5 values is much the same in both the Eh$>$0 and Eh$<$0 rock classes.

The same kind of test was carried out for the pH comparison. In this analysis only rocks with $P_2O_5<23$ percent were counted in order to make the P_2O_5 ranges of the classes virtually equal (fig. 14*B*). The value of (1) was 2.853; thus, the hypothesis that the 2 classes are from the same population cannot be rejected at the 0.05 level of significance.

HYPOTHESES OF OCCURRENCE OF URANIUM IN APATITE

To explain the dependence of uranium concentration on the Eh of the environment of deposition of the phosphatic rocks, it is of paramount importance to know how the uranium is tied up in the apatite. Two mechanisms have been advanced to explain the occurrence of uranium in apatite. Altschuler and his coworkers (1958, p. 69) have put forward the first conclusive evidence that U(IV) does occur in apatite and probably substitutes for calcium in the apatite lattice. Neuman and his coworkers (1949a, b) have shown that the uranyl ion can be adsorbed on surfaces of apatite crystals in bone. Both of these mechanisms are reviewed below.

SUBSTITUTION OF U(IV) FOR CALCIUM IN THE APATITE LATTICE

Altschuler and his coworkers (1958, p. 69) have shown by chemical analysis that some of the uranium in apatite, of both marine and igneous origin, is tetravalent and present several lines of evidence to show that it probably substitutes for calcium in the apatite lattice. In many of the samples of marine apatite analyzed, over half of the uranium is tetravalent and in some as much as 90 percent is tetravalent. Particularly significant is the fact that tetravalent uranium in apatite nodules dredged from the sea floor off California makes up 55 to 74 percent of the total uranium. Two Phosphoria samples were analyzed, and 18 and 24 percent of the uranium is tetravalent.

ADSORPTION OF THE URANYL ION ON CRYSTAL SURFACES

There is no doubt that apatite can take up appreciable amounts of the uranyl ion. Moore (1954, p. 654) found that phosphate rock from Cokeville, Wyo., extracted 63 percent of the uranium from a solution of uranyl sulfate containing 200 ppm (parts per million) uranium. The phosphate rock contained 0.028 percent U before and 0.11 percent U after the experiment. Moore does not discuss the valency of the uranium after it had been removed from solution by apatite, but there is no reason to suspect it to be other than U(VI). Neuman (1949a, b), using uranyl acetate solutions, found that ashed bone could remove up to 4.8 percent of the uranium in solution. Igelsrud and others (1948, p. 29) placed synthetic apatite in a 0.05 percent uranyl acetate solution; after adsorption, the solution contained only 0.0004 percent uranium. Leaching experiments on this apatite with nitric acid indicated that the adsorption was not physical because only about 1 percent of the uranium in the apatite was dissolved for 50 percent dissolution of the apatite. This result differs from natural rock, however, in that uranium dissolves proportionately with the natural apatite.

The way in which the uranyl ion is adsorbed on the apatite has been investigated by Neuman and others (1949a, b). They found that the most likely mechanism of adsorption is the chemisorption of the uranyl ion by 2 surface PO_4^{-3} groups to form a structure analogous to uranyl pyrophosphate. To do this, the uranyl ion must replace 2 calcium ions as shown by the fact that the adsorption of 1 mole of uranium reduced the amount of exchangeable phosphate and the exchangeable calcium each by 2 moles.

The amount of uranium chemisorbed is reduced both by higher bicarbonate concentration in the solution and by higher hydroxyl concentration, a fact attributed by Neuman and his coworkers to uranyl complex ion formation. That is, the complexing of the uranyl ion by carbonate and the hydroxyl ion reduced the concentration and thereby the chemisorption of the uranyl ion. The amount of uranium chemisorbed on a given amount of apatite, being a surface phenomenon, is dependent on the crystal size of the apatite.

Hendricks and Hill (1950, 1951) [2] have postulated that the chemical composition of apatite is influenced by crystal size and suggest that in marine phosphorites the fluorine present in excess of the lattice requirements of fluorapatite is due to the small crystal size of the apatite. It is true that marine apatite is formed of very small crystals, as shown by the fact that the material for the most part appears isotropic under crossed nicols; igneous fluorapatite, on the other hand, is more coarsely crystalline and anisotropic, and contains no excess fluorine. It should be expected, then, that a correlation should exist between excess fluorine and uranium in apatite if the uranium is adsorbed on crystal surfaces. This is found to be true.

To test the relation between fluorine and uranium, a group of 86 samples that had been analyzed for F, P_2O_5, eU, and U, was selected from the literature on the Phosphoria formation (F. W. O'Malley and others, written communication, 1953; V. E. McKelvey and others, written communications, 1952, 1953; R. W. Swanson and others, written communication, 1953). These samples were collected from scattered localities in the phosphate field and were selected for this analysis simply because they are available. Only those samples whose eU and U values differed by 0.002 percent or less were selected in order to minimize the chance of including secondarily leached or enriched rocks in the group. A few rocks that contain fluorite or have excessively high F/P_2O_5 ratios were excluded from the group, and a few rocks that contain so little fluorine that the calculated excess fluorine is a negative quantity were excluded.

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[2] The facts uncovered in this study fit well with the Hendricks and Hill hypothesis, yet are unexplained or fit with difficulty into alternate hypotheses. Although several objections on the basis of structural considerations can be raised to the hypothesis (Altschuler, oral communication, 1957), no definitive work has been published to discount it entirely. Until such work is done, the Hendricks and Hill hypothesis remains as a real possibility, and is so treated in this paper.

The excess fluorine was calculated by the formula

$$F_x = F - 0.089P_2O_5$$

where F_x is excess fluorine, F is the total fluorine, and P_2O_5 the total phosphorus pentoxide in the rock with all quantities stated in percent. The coefficient 0.089 was obtained by assuming that there are 6 PO_4^{-3} groups in the unit cell, whose formula is $Ca_{10}F_2(PO_4)_6$. Altschuler and his coworkers have used a coefficient of 0.1 calculated from the assumption that the CO_3^{-2} in apatite substitutes for PO_4^{-3} in the unit cell. In the analyses that follow, this difference should have slight effect. A multiple regression (Hald, 1955, p. 624–667) was carried out with F_x and P_2O_5 the independent variables and eU the dependent variable; this gave the regression equation (table 4)

$$e\hat{U}' = 0.443 + 2.215P_2O_5' + 0.7098F_x'$$

where P_2O_5 equals 0.1 P_2O_5 and F_x' equals 10 F_x, a transformation used to simplify the arithmetic in the regression analysis, and $e\hat{U}'$ is the value of uranium (×1,000) predicted by the independent variables. Both regression coefficients are significantly different from zero. The multiple correlation coefficient is 0.634, whereas the partial correlation coefficient of eU' to P_2O_5' with F_x' constant is 0.514, and of eU' to F_x' with P_2O_5' constant is 0.337. The regression computations are shown in table 4. In order that these results may be more easily visualized, eU is plotted against P_2O_5 (fig. 16), F_x (fig. 17), and $e\hat{U}$, the value obtained by substitution of the P_2O_5' and F_x' values of each sample into the regression equation (fig. 18). Notice that the best relation is eU against $e\hat{U}$.

A similar regression analysis was carried out with the data presented by Thompson (1953, 1954). The resulting regression equation is—

$$e\hat{U}' = 1.803 - 0.0004P_2O_5 + 24.013F_x$$

The regression coefficient of P_2O_5 is not significantly different from 0, whereas the regression coefficient of F_x is significantly different from 0. The regression computations are shown in table 5. The fact that Thompson's data show no correlation of eU with P_2O_5 may be due to her methods of sampling. Thompson's samples were close samples, collected from only 5 stratigraphic units of the type sampled during this study. Within each suite of samples, Thompson reports no

TABLE 4.—*Regression analysis. Relation between* $P_2O_5 \times 0.1$, (P_2O_5'), *excess fluorine*$\times 10$, (F_x'), *and equivalent uranium*$\times 10^3$, (eU'), *in samples from the Phosphoria formation in the western phosphate field*

[Symbols used are: *n*, the number of observations; *S*, the sum; *SS*, the sum of squares; *SSD*, the sum of the squares of the deviations from the mean; *SPD*, the sum of the products of the deviations; *f*, the degrees of freedom; s^2, the variance]

	P_2O_5'	F_x'	eU'
n	86		
S	204. 38	244. 2	664
SS	577. 368	1, 014. 54	7, 044
S^2/n	485. 711	693. 41	5, 126. 7
SSD	91. 657	321. 13	1, 917. 3
		P_2O_5' F_x'	P_2O_5' eU'
SP		630. 815	1, 816. 85
$S_{x1}S_{x2}/n$		580. 344	1, 578. 00
SPD		50. 47	238. 85
			F_x' eU'
SP			2, 225. 10
$S_{x1}S_{x2}/n$			1, 885. 45
SPD			339. 65
S/n	2. 376	2. 839	7. 721

$$91.657b_1+50.47b_2=238.85$$

$$50.47b_1+321.13b_2=339.65$$

$$D_{P_2O_5',\ F_x'}=26{,}886.8$$

$$b_1=2.215 \qquad b_2=0.7098$$

$$SSD_{eU'|P_2O_5',\ F_x'}=1{,}147.164,\ f=83$$

$$e\hat{U}'=7.721+2.215(P_2O_5'-2.376)+0.7098(F_x'-7.721)$$

$$=0.443+2.215P_2O_5'+0.7098F_x'$$

$$s^2=13.821 \qquad s=3.718$$

$$s^2_a=0.1607 \qquad s_a=0.4009$$

$$s^2_{b_1}=0.1651 \qquad s_{b_1}=0.4063$$

$$s^2_{b_2}=0.0471 \qquad s_{b_2}=0.271$$

$$s^2_{b_1b_2}=-0.0259$$

Tests (*t*):

$b_1=0$

$$t=\frac{2.215}{0.4063}=5.452,\ f=83$$

TABLE 4.—*Regression analysis. Relation between* $P_2O_5 \times 0.1$, (P_2O_5'), *excess fluorine*$\times 10$, (F_x'), *and equivalent uranium*$\times 10^3$, (eU'), *in samples from the Phosphoria formation in the western phosphate field*—Continued

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Thus, b_1 is significantly different from 0 at 0.05 probability level.

$b^2=0$

$$t=\frac{0.7098}{0.271}=2.619$$

Thus, b_2 is significantly different from 0 at 0.05 probability level.

Correlation coefficients (r):

$r_{eU', P_2O_5'}=0.570$

$r_{eU', F_x'}=0.433$

$r_{P_2O_5', F_x'}=0.294$

$r_{P_2O_5', eU'|F_x'}=0.5137$

$r_{F_x', eU'|P_2O_5'}=0.3372$

$r_{P_2O_5', F_x'|eU'}=0.0637$

$r_{eU', P_2O_5', F_x'}=0.634$

---

correlation to good correlation of eU to P_2O_5, a fact that seems to depend in part on the range of P_2O_5 content (Thompson, 1953, p. 62). The 5 suites of samples were obviously collected with the aim of obtaining as large a range in uranium content as possible between the 5 beds of high-grade phosphate rock. If this is true, there would be no reason to expect a correlation of eU with P_2O_5 for the combined data. Regardless of the explanation of the lack of correlation between eU and P_2O_5 in this group of samples, it is significant that the uranium is directly correlated with F_x with a correlation coefficient of 0.48.

King (1947) has described and sampled the Phosphoria formation in the southern part of the Wind River Mountains in Wyoming. His analyses indicate that the apatite has a high amount of excess fluorine, yet the uranium content of these rocks is low. Therefore, these samples do not fit with the regression analyses presented. The reason for this is not clear; either fluorite is present in the rocks, the fluorine analyses are too high, or a factor that has not been taken into account in this study is operative.

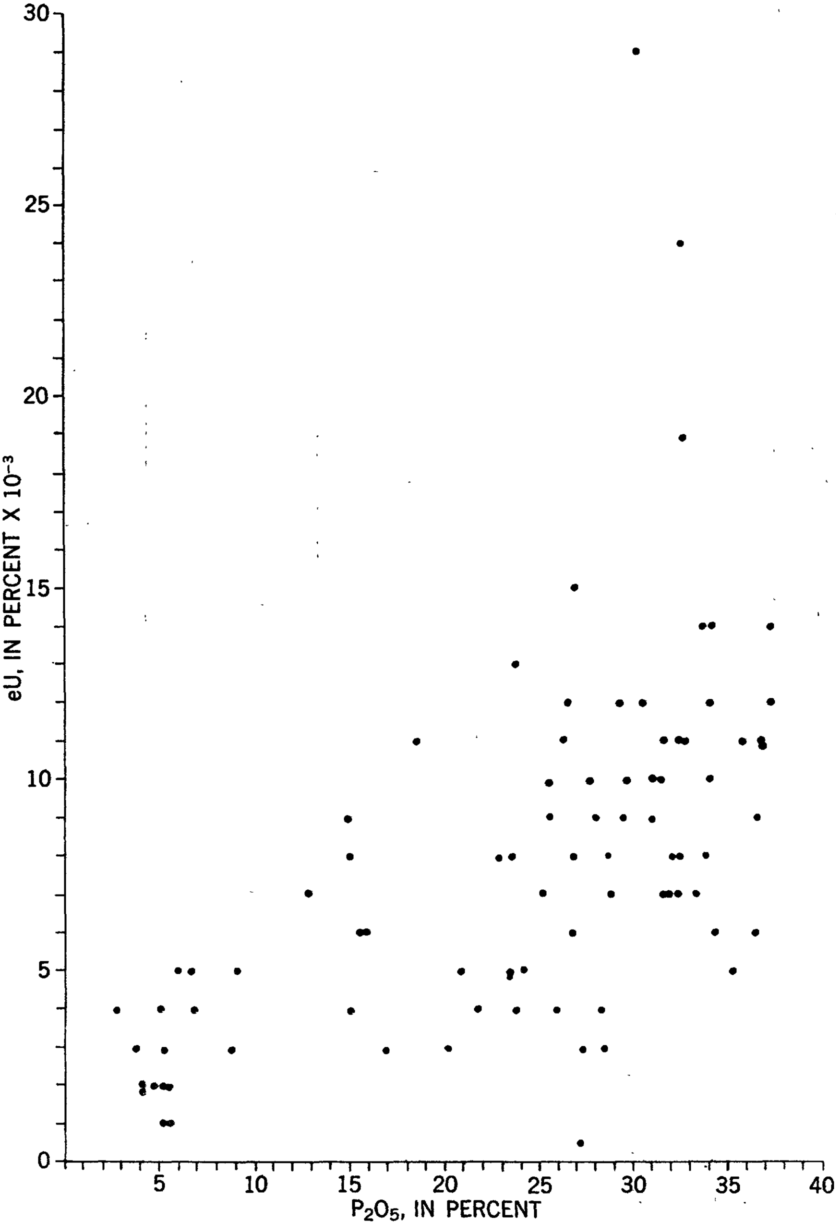

FIGURE 16.—Scatter diagram showing relation between P_2O_5 and eU.

TABLE 5.—*Regression analysis. Relation between* P_2O_5, *excess fluorine* (F_x), *and equivalent uranium* (eU)×10³. *Data from Thompson (1953, 1954)*

[Symbols used are: *n*, the number of observations; *S*, the sum; *SS*, the sum of squares; *SSD*, the sum of the squares of the deviations from the mean; *SPD*, the sum of the products of the deviations; *f*, the degrees of freedom; s^2, the variance]

	F_x	P_2O_5	eU′
n	120		
S	72.45	3,467.78	1,943
SS	48.680	106,248.501	43,607
S^2 *n*	43.742	100,212.484	31,460.4
SSD	4.938	6,036.017	12,146.6
		$F_xP_2O_5$	F_xeU′
SP		2,163.198	1,291.65
$S_{x_1}S_{x_2}/n$		2,093.672	1,173.09
SPD		69.526	118.56
			P_2O_5eU′
SP			57,816.29
$S_{x_1}S_{x_2}/n$			56,149.14
SPD			1,677.15
S/*n*	.6037	28.898	16.19

$$4.938b_1+69.526b_2=118.56$$

$$69.526b_1+6{,}036.017b_2=1{,}667.15$$

$$D_{F_x,\ P_2O_5}=24{,}975.692$$

$$b_1=24.013 \qquad b_2=-0.0004$$

$$SSD_{eU'|F_x,\ P_2O_5}=9{,}300,\ f=117$$

$$e\hat{U}'=16.19+24.013(F_x-0.6037)-0.0004(P_2O_5-28.898)$$

$$=1.803+24.013F_x-0.004P_2O_5$$

$$s^2=79.49 \qquad s=8.915$$

$$s^2{}_a=0.662 \qquad s_a=0.814$$

$$s^2{}_{b_1}=19.211 \qquad s_{b_1}=4.383$$

$$s^2{}_{b_2}=0.0157 \qquad s_{b_2}=0.1254$$

$$s^2{}_{b_1b_2}=-0.2213$$

Tests (*t*):

$b_1=0$

$$t=\frac{24.013-0}{4.383}=5.479,\ f=117$$

TABLE 5.—*Regression analysis. Relation between* P_2O_5, *excess fluorine* (F_x), *and equivalent uranium* (eU)$\times 10^3$. *Data from Thompson (1953, 1954)*—Continued

Thus, b_1 is significantly different from 0 at 0.05 probability level.

$b_2=0$

$$t=\frac{0.0004-0}{0.1254}=3\times 10^{-5}$$

Thus, b_2 is not significantly different from 0 at 0.05 probability level.

Correlation coefficients (r):

$r_{F_x,\ eU'}=0.484$

$r_{P_2O_5,\ eU'}=0.195$

$r_{F_x,\ P_2O_5}=0.403$

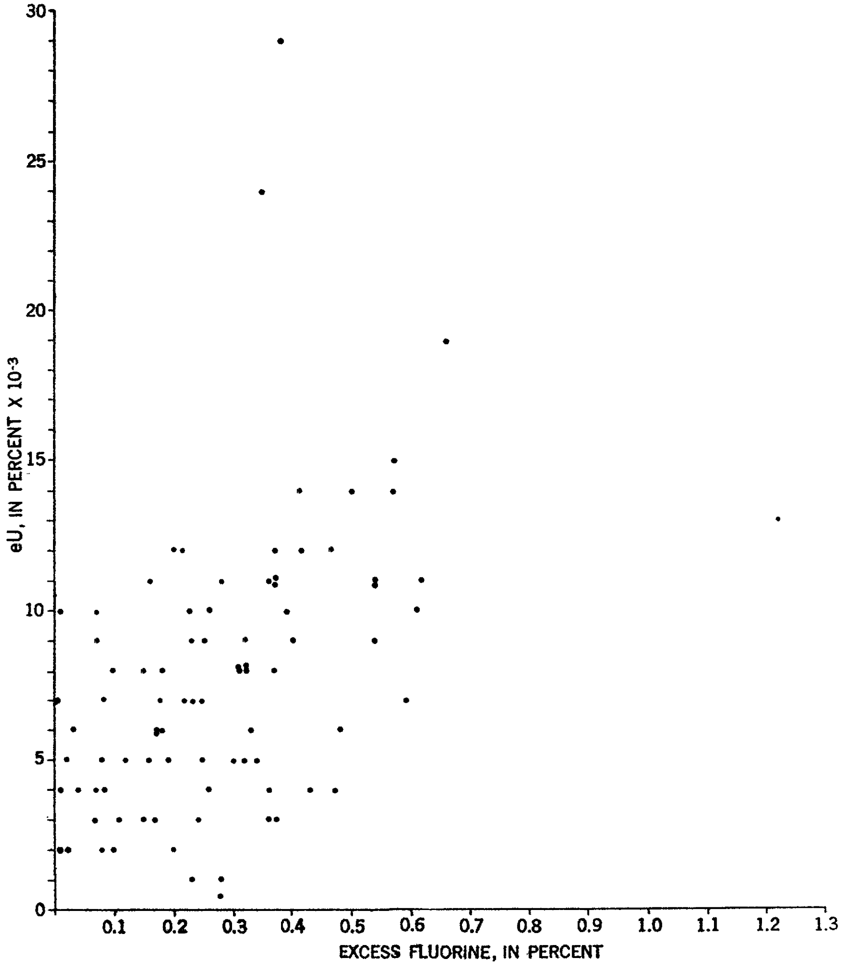

FIGURE 17.—Scatter diagram showing relation between excess fluorine and eU.

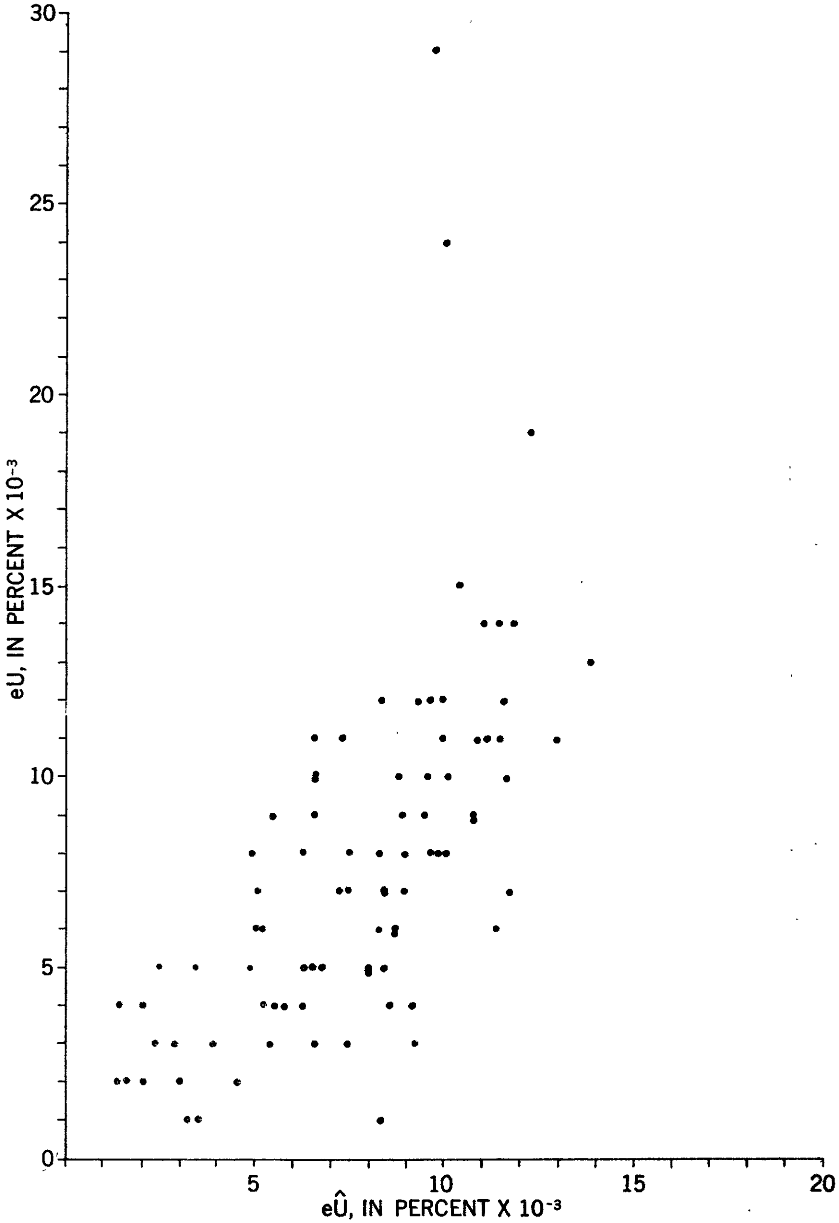

FIGURE 18.—Scatter diagram showing relation between eU and eÛ predicted from both P_2O_5 and excess fluorine.

HYPOTHESES OF CONCENTRATION OF URANIUM BY APATITE

The analysis of the relations between uranium and the environment of deposition of the host rocks shows that apatite deposited under reducing conditions generally contains more uranium than apatite deposited in an oxidizing environment. Furthermore, the pH of the environment plays little part in governing the amount of uranium in apatite. These observations could be explained in two ways, depending on the valence of the uranium.

A lower Eh of the sedimentary environment would result in a greater portion of the dissolved uranium being the U^{+4} ion. Thus, more U(IV) could be incorporated into the apatite structure. The effect of pH on the concentration of U^{+4} would be marked. Increasing pH increases the ratio of U(VI) to U(IV) and would further decrease the effective concentration of U^{+4} by the formation of U(IV) carbonate complex ions. One might expect, then, a smaller concentration of uranium in apatite in dark phosphatic limestones than in dark noncarbonatic phosphorites; however, this is probably not the case. A correlation of U(IV) with excess fluorine would be difficult to explain. Altschuler and his coworkers (1958, p. 48, 75) consider that the excess fluorine is present in the apatite structure, and they examine but reject the possibility that it combines with U(IV) to form a complex similar to the compound UF_4 as an integral part of the apatite structure. Such a complex could explain the correlation between excess fluorine and uranium, though there is more excess fluorine than would be required for the formation of UF_4, especially if only U(IV) rather than total U is considered. On the other hand, it is possible that excess fluorine and U(IV) are indirectly related by a third factor.

Concentration of U(VI) in apatite probably results from its chemisorption on apatite crystal surfaces. The amount would increase with decreasing crystal size. The darker phosphorites are finer grained, probably because the organic matter in the rocks tends to prevent diagenetic recrystallization of apatite to larger crystals (Sheldon, 1957, p. 123–124). Furthermore, it seems possible that original crystal growth was inhibited by films of organic matter. The effect of Eh on the concentration of uranyl ions in sea water is slight because, over the pH range of stability of apatite, dissolved U(VI) in one of its complexes would always be at least 1,000 times as abundant as U(IV). Variations in pH would have a direct effect on the uranyl-ion concentration because of the formation of uranyl phosphate and carbonate complexes at higher pH values, with a resulting decrease in uranyl-ion concentration. As in the case of U(IV), one would expect carbonatic rocks to contain less uranium in apatite than noncarbonatic rocks, but this was found to be unlikely. A correlation between U(IV) and excess fluorine could be explained by the suggestion of Hendricks and Hill (1950,

1951) that excess fluorine increases as the crystal size decreases; thus, a correlation between U(VI) and excess fluorine would not be a direct one but one due to the third factor—crystal size.

A possible direct measure of relative crystallite size of apatite can be obtained by measurement of the broadening of apatite X-ray diffraction lines (Klug and Alexander, 1954, p. 491–538). Four samples from the Meade Peak phosphatic shale member of the Phosphoria formation that had approximately the same P_2O_5 content and exhibited a sizable range in content of eU and excess fluorine were selected. The apatite line at 2θ of 33.15° was chosen for measurement because it was free from interference of lines of other minerals in the rock. The study was made using an X-ray diffraction unit, and the line was step scanned at ⅛° per minute. The results are shown in table 6. These data show enough scatter that the number of samples is inadequate to state confidently that a relation exists between line broadening and the chemical properties of apatite. These preliminary results do suggest, however, that the apatite with greater excess fluorine has the broader X-ray lines. The broadening of the line may be interpreted in two ways. First, the smaller the apatite crystals, the greater the broadening of the peak; and, second, the greater the distortion of the apatite lattice due to ionic substitutions, the greater the broadening. It is impossible to differentiate between the two interpretations with the present data, but it is theoretically possible to distinguish between them by varying the wavelength of the X-rays and observing the effect on the line broadening (Klug and Alexander, 1954, p. 491–538). Thus, further investigation using X-ray techniques would probably help to solve this problem.

TABLE 6.—*Relation between broadening of X-ray diffraction line of apatite, uranium, and excess fluorine contents of apatite*

P_2O_5 (percent)	Excess F (percent)	eU (percent)	Breadth of line $2\theta=33.15°$ at ½ maximum intensity (degree 2θ)	Lot	Sample
31. 8	0. 00	0. 007	0. 2104	1206	178–VEM–47
31. 6	. 22	. 007	. 2000	1206	264–VEM–47
32. 4	. 32	. 008	. 2400	1210	36–RAW–47
32. 6	. 66	. 019	. 2400	1236	1104–RAG

The relative importance of the two processes of uranium concentration in the Phosphoria apatites, the adsorption of U(VI) and the substitution of U(IV) for calcium, is difficult to assess, though it appears likely that both are operative. The two analyses of uranium in the

Phosphoria show that only about one-quarter is U(IV) and thus probably substituting for calcium. It is possible that the remainder is the adsorbed uranyl ion. Available analyses show that modern marine phosphatic nodules contain more U(IV) than the Phosphoria rocks; perhaps, therefore, the Phosphoria sediments originally contained more U(IV).

URANIUM IN BLACK SHALE

Some of the uranium in the Phosphoria formation is not associated with apatite. Two zones of black shale a few feet thick, and containing up to 0.012 percent uranium, have been found in western Wyoming. These are beds of the Meade Peak phosphatic shale member of the Phosphoria formation which lie just below a widespread phosphatic zone that occurs near the top of the Meade Peak over most of the Wyoming Range. Although little analytical work has been done on these beds, it can be said that they are virtually nonphosphatic and noncarbonatic. They are made up almost wholly of quartz silt, clay, and carbonaceous material. Thus, it would seem that these rocks are similar lithologically to the uraniferous rocks in the Chattanooga shale of Devonian and Mississippian age of the Southeastern United States.

The position of these beds within the Meade Peak phosphatic shale member is interesting. They are among the most transgressive beds deposited during the first transgression of the Phosphoria sea across Wyoming (Sheldon, 1957, p. 152). As such, they are a deep-water facies of the Permian rocks of the area. The black shale facies of the Meade Peak grades eastward or shoreward into phosphorite, the phosphorite in turn grades into chert, and the chert into carbonate rock and sandstone. This sequence of facies can best be interpreted as a sequence of sediments deposited on an eastward-shoaling sea bottom whose chemical environment changed progressively eastward from low to high pH and low to high Eh (Sheldon, 1957). With this in mind, it is profitable to examine the possible physical chemistry of the deposition of the uranium.

PHYSICAL CHEMISTRY OF THE DEPOSITION OF URANIUM IN BLACK NONPHOSPHATIC SHALE

The uranium in nonphosphatic shale must be in some mineral phase other than apatite. The mineralogy of the black shales rich in carbonaceous matter and also uraniferous, such as the Chattanooga shale, has been investigated by many people. In a summary article, Breger and Deul (1956, p. 507) state:

> Recent studies of the U.S. Geological Survey indicate physical rather than direct chemical association of uranium with the organic components of certain shales * * * it has been proposed that the decomposition of the organic matter

under reducing conditions leads to the formation of hydrogen sulfide, which is known to reduce the uranyl ion to the insoluble uranium dioxide (Gruner, 1954). The carbonaceous material, in this instance, would have only an indirect association with the uranium, but the possibility cannot be overlooked that the organic matter complexed and carried uranium down from the sea, thereby serving as a primary precipitant.[3] If this was the mechanism of fixation, then the chemical bonds between the uranium and the organic compounds have been broken since the time the shale components were deposited.

Gruner's experiments (1954) on the reduction of the uranyl ion to tetravalent uranium by H_2S were performed at a pH of about 3 or less, an acidity never attained in the ocean.

Some deductions about the depositional environment of the uraniferous black shales can be made. First, the abundance of organic matter indicates that the environment was reducing. Second, the absence of apatite and the fact that these black shales in the Meade Peak are interbedded with phosphatic sediments indicate that the pH of the depositional environment was low, and perhaps acid. The nondeposition of apatite is due to one of two things. In an alkaline environment of low pH the concentration of PO_4^{-3} will be less than required for the solubility product of apatite to be exceeded because of reaction of PO_4^{-3} with H^+ to form HPO_4^{-2} and $H_2PO_4^-$. If the pH is low enough for the environment to be acid, apatite cannot precipitate because it is no longer the stable form of calcium phosphate (Kazakov, 1950). Acid reducing environments have been reported from marine environments, and they are perhaps more common than realized because the neutral point falls at higher pH with lower temperature, owing to the decrease of the ion product of water with decreasing temperature.

Garrels (1955) has shown that UO_2 is the stable uranium oxide in both acid and alkaline reducing environments in the range of pH and Eh values found in ocean waters; whereas $UO_2(OH)_2$ is stable in acid and alkaline oxidizing invironments. Actually, the stability boundary between these two compounds falls to lower Eh values for increasing pH. In the pyrite stability field, in terms of pH and Eh, only UO_2 is stable. Furthermore, at the concentrations of the U^{+4} ion in the sea as calculated from Garrels' equations, the product $[U^{+4}][OH^-]^4$ exceeds the solubility product except where $Eh > 0$ and $pH < 6.5$, and the lower the Eh the more the solubility product is exceeded. Thus, the more reducing the environment, the more favorable are the conditions for precipitation of UO_2. In reducing alkaline sea water, however, the concentration U^{+4} would be effectively decreased by the formation of a U(IV) carbonate complex and also by oxidation of U(IV) to U(VI); hence, UO_2 probably could not precipitate. In an oxidizing environment UO_2 is no longer stable whereas $UO_2(OH)_2$ is. But $UO_2(OH)_2$ could not precipitate because of undersaturation of $UO_2(OH)_2$ in an oxidizing acid environment and because of the formation of uranyl carbonate complexes in oxidizing alkaline environments. Thus, the only physical-chemical environment in which a uranium oxide or hydroxide would be stable and in which its solubility product might be exceeded by appropriate ions would be a reducing acid environment where UO_2 could precipitate.

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[3] This mechanism has also been suggested by Koczy and others (1957) in explaining the deposition of uranium in Baltic Sea sediments.

In the calculations above the concentration of uranium ions in sea water has been used, whereas the activities of the ions should have been used. Lack of data on these activities in solutions with the ionic strength of sea water, about 0.7, makes such calculations impossible at present, but certainly the activities will be much smaller than the concentrations. Whether they are sufficiently smaller to negate the arguments presented is unknown and awaits future experimentation. But, if the ocean is undersaturated at all pH and Eh conditions with respect to the various inorganic uranium compounds, then either precipitation of uranium organic complexes as suggested by Breger and Deul (1956, p. 507) and by Koczy and others (1957, p. 98, 99) or adsorption of uranium by organic compounds must cause the concentration of uranium in black nonphosphatic shales. In either of these events the pH and Eh of the depositional environment would still play a large part, because the reactions of uranium ions with organic compounds are dependent on the activities of the uranium ions. It is likely, then, that an acid reducing environment would be the most favorable for these reactions.

An apparent inconsistency in the distribution of uranium in black shales is presented by the many carbonaceous shales of the Phosphoria that are only slightly uraniferous. These present no problem, because most organic matter probably accumulates in only slightly reducing neutral to alkaline environments, all of which would be unfavorable for UO_2 precipitation.

CONCLUSIONS

The distribution of uranium in the Phosphoria formation depends closely upon the depositional environment of the Phosphoria sediments. These environments probably changed progressively, from the deeper basin parts towards the shallow shelf parts of the Phosphoria sea, from acid reducing to alkaline reducing to alkaline oxidizing. In the acid reducing environment uraniferous carbonaceous shale was deposited, and the uranium possibly is present as finely disseminated UO_2. In the alkaline-reducing environment, carbonaceous phosphorite and carbonate rock were deposited, and the uranium is present in apatite, in part as U(IV) substituting for calcium in the apatite lattice and in part as the uranyl ion adsorbed to apatite crystal surfaces. In the alkaline oxidizing environment, noncarbonaceous sediments accumulated, and uranium is sparingly present in apatite, possibly as both U(IV) and U(VI).

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