Geology and Mineralogy

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE GEOCHEMISTRY OF URANIUM IN APATITE AND PHOSPHORITE*

By

Z. S. Altschuler, R. S. Clarke, Jr., and E. J. Young

October 1957

Trace Elements Investigations Report 701

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

---

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

USGS - TEI-701

GEOLOGY AND MINERALOGY

Distribution	No. of copies
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Austin	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Rapid City	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Spokane	1
Division of Raw Materials, Washington	3
Grand Junction Operations Office	1
Production Evaluation Division, GJOO	1
Technical Information Service Extension, Oak Ridge	6
U. S. Geological Survey:	
Foreign Geology Branch, Washington	1
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	20
Geophysics Branch, Washington	1
Mineral Classification Branch, Washington	1
Mineral Deposits Branch, Washington	2
A. L. Brokaw, Grand Junction	1
N. M. Denson, Denver	1
R. L. Griggs, Albuquerque	1
P. E. Hotz, Menlo Park	2
W. R. Keefer, Laramie	1
H. W. Lakin, Denver	1
R. A. Laurence, Knoxville	1
E. M. MacKevett, Menlo Park	1
L. R. Page, Washington	1
P. K. Sims, Denver	2
Q. D. Singewald, Beltsville	1
A. E. Weissenborn, Spokane	2
TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2
	63

CONTENTS

Page

Abstract 10

Introduction 12

Acknowledgments 16

Mineralogy of apatite 17

  Crystal chemistry 17

  Composition of the sedimentary carbonate-apatites 20

Uranium content of apatite 21

  Factors affecting equivalent uranium determinations 21

  Uranium content of representative apatites 25

  Island phosphorites--secondary uptake of uranium and fluorine .. 28

Problems of occurrence of uranium in phosphorite 31

  Possible modes of occurrence 31

  Absence of uranium minerals 32

  Relation of uranium content to composition of phosphorite 32

    Fluorescence and uranium content 33

    Lack of preferential solution of uranium 34

    Relation of uranium to P_2O_5 34

  Marine versus ground-water origin of uranium in phosphorite 40

    General statement and review 40

    Evidence of young phosphorites and submarine nodules 41

    Necessity of geologic interpretation 42

Page

Case histories of geologic principles governing uranium distribution in phosphorites 45

  Uranium in phosphorite during weathering 45

    Florida Land-Pebble phosphates--general geology 45

    Illustration of leaching 48

    Postdepositional enrichment 52

      1. Aluminum phosphate zone: lateritic weathering and supergene enrichment 52

      2. The Cooper marl--residual enrichment 59

      Contrasting modes of enrichment in mild versus intense weathering 66

      Brown-rock phosphates of Tennessee--residual concentration 68

  Secondary emplacement of uranium in bones 72

  Marine enrichment and reworking 75

Crystallo-chemical nature of uranium in apatite 80

  General statement 80

  Substitution of uranium for calcium in apatite 82

    Theoretical considerations 82

      Relation of uranium to phosphorus 83

    Oxidation state of uranium in apatite 84

      Chemical problems 84

      U(IV) content of sedimentary apatites 84

      U(IV)/U percents reflect geologic history 84

      Primary marine uranium in young phosphorites is mainly U(IV) 87

      Subaerial weathering alters U(IV) to U(VI) in marine phosphorite 88

Page

Crystallo-chemical nature of uranium in apatite--Continued

Substitution of uranium for calcium in apatite--Continued

Oxidation state of uranium in apatite--Continued

Possible relation of U(VI) content to radioactivity and age 88

Secondary sources of U(VI) in phosphorite 89

Relative structural favorability of U(IV) and U(VI) in apatite 93

Test of uranium and fluorine interdependence in apatite 94

Effects of reworking on U(IV) content of apatite 100

Summary of evidence bearing on the primary state of uranium in marine phosphorites 102

Uranium in igneous apatite 105

General statement and analyses 105

Variation of uranium in apatite with uranium in host rock . 109

Oxidation state of uranium in igneous apatite 111

U(IV)/U(VI) ratio reflects magmatic equilibria 113

Relation of U(IV)/U(VI) ratio to age 114

Auto-oxidation 114

External weathering controlled by radioactive decay .. 116

Conclusions 117

Summary 117

Nature of uranium fixation in phosphorites 118

Regenerative capture 121

Equilibrium fixation of uranium in igneous apatite 123

Selected bibliography 124

ILLUSTRATIONS

Page

Figure 1. The structure of fluorapatite 18

2. Relation of uranium to P_2O_5 in Mona Island cave phosphorites 30

3. Relation of uranium to fluoridation in Mona Island cave phosphorites 30

4. Relation of uranium to P_2O_5 in phosphates from Oulad-Abdoun Basin, French Morocco 35

5. Stratigraphic relations in the Land-Pebble phosphate field, Florida 47

6. Sample scheme used for study of uranium distribution in pebbles 51

7. Distribution of oxides through aluminum phosphate zone at Homeland, Florida 53

8. Uranium distribution in various textural components at Homeland mine, Florida 54

9. Phosphatic quartz sandstone from the aluminum phosphate zone, Florida 56

10. Details of contact between aluminum phosphate zone (white) and overlying ferruginous sand mantle 58

11. Contrasting modes of weathering alteration and uranium enrichment in phosphorites 67

12. Mined out area of Tennessee brown-rock phosphates 70

13. Sample locations for comparison of Tennessee brown-rock phosphate with parent limestone 71

Page

Figure 14. Autoradiograph of fossil bone 74

15. Autoradiographs of reworked and first cycle pebbles 78

16. Photomicrographs of arkose with apatite cement 81

17. Uranium versus excess fluorine in Phosphoria formation .. 97

18. U(IV) versus excess fluorine in various phosphorites 98

19. Total uranium in rock versus total uranium in apatite for rocks from Boulder Creek batholith 110

TABLES

Table 1. Resources of some well known uraniferous phosphorites 14

2. Chemical analyses of sedimentary apatite pellets from the Bone Valley formation 22

3. Semiquantitative spectrographic analyses of sedimentary apatite pellets 23

4. Thorium content of Florida pebble phosphorite 24

5. Uranium content of representative apatites 26

6. Partial analyses of cave phosphorite from Mona Island, Puerto Rico 29

7. Comparison of fluorescence and uranium content in apatite nodules from the Bone Valley formation, Boyette mine, Florida 33

8. Size distribution and uranium contents of nodular phosphates from Khouribga, French Morocco 38

9. Correlation coefficients among eU, P_2O_5, F, CO_2, and organic matter in samples of the Phosphoria formation 39

Page

Table 10. Phosphate and uranium contents of bottom samples from the Gulf of Mexico 43

11. Relative contents of uranium and P_2O_5 in marine phosphorites 44

12. Chemical analyses showing distribution of uranium within phosphate pebbles 50

13. Examples of phosphate- and uranium-enriched hardpan in Cooper marl near Charleston, South Carolina 61

14. Comparison of phosphatized and primary Cooper marl from Lambs, South Carolina 61

15. Variations of enrichment with weathering in phosphatized Cooper marl, South Carolina 63

16. Semiquantitative spectrographic analyses of phosphatic hardpan from the Cooper marl 64

17. P_2O_5 and uranium content of weathered and fresh Tennessee phosphates, Akin mine, Columbia, Tennessee .. 69

18. Uranium content of representative clastic apatite from the Land-Pebble phosphate field, Florida 76

19. Total and tetravalent uranium content of sedimentary apatites 85

20. Effect of highly oxidized samples in the recovery of U(IV) from 1.5 M phosphoric acid solutions 90

Page

Table 21. Data on excess fluorine and U(IV) in miscellaneous apatite and phosphorite 99

22. Relative contents of U, U(IV), and P_2O_5 in phosphatic terrace gravel in the vicinity of Charleston, South Carolina 101

23. Uranium and U(IV) content of igneous apatites 107

THE GEOCHEMISTRY OF URANIUM IN APATITE AND PHOSPHORITE

By Z. S. Altschuler, R. S. Clarke, Jr., and E. J. Young

ABSTRACT

Apatite contains only traces of uranium; yet, as apatite is a minor constituent in most rocks and the major constituent of a few very large deposits, it accounts, paradoxically, for both dispersal and concentration of uranium in nature.

Uranium is typically between 0.001 and 0.01 percent of primary igneous apatite and between 0.005 and 0.02 percent of sedimentary marine apatite. Marine reworked apatite becomes enriched in uranium to as much as 0.1 percent. This is demonstrated by the greater uranium contents of the texturally more complex phases within a single deposit.

Uranium can be secondarily leached from or introduced into apatite by ground water. These secondary changes are indicated by the existence of pronounced concentration gradients within single pebbles of apatite as well as by the redistribution of uranium among different mineral hosts in leached and altered sections of phosphorite. The postdepositional enrichment of uranium in phosphorite may be entirely residual as in the Tennessee "brown-rock" deposits, or greatly enhanced by ground-water additions as in the South Carolina phosphates. Moreover, the pattern of enrichment reflects the conditions and intensities of weathering. Highly acid lateritic weathering has caused supergene enrichment of uranium in the aluminum phosphate zone of the Bone Valley formation. In contrast, surficial enrichment characterizes the moderately weathered Cooper marl of South Carolina. Isolated fossil bones or phosphate pebbles

may contain almost one percent uranium as a result of ground-water enrichment. Such enrichment is comparable to the postdepositional uptake of fluorine by bone or insular phosphorite, and in some places the processes are synchronous and show good mutual correlation as they are codependent on the same ground-water source.

It is proposed that uranium replaces calcium in the apatite structure. This is indicated by several lines of investigation. Uranium and calcium contents parallel one another in sections of leached and altered phosphorite. Ionic radii of tetravalent uranium (0.97 A) and divalent calcium (0.99 A) are virtually identical, and much of the uranium in igneous, sedimentary, and bone apatite is found to be tetravalent. Petrographic and chemical analyses and nuclear emulsion studies have shown that uranium in apatite is disseminated rather than locally concentrated. In addition, phosphate deposits are essentially devoid of uranium minerals.

Igneous apatites studied have been found to contain from 10 to 66 percent of their uranium as U(IV). In apatite from a suite of related igneous rocks both the total uranium and the U(IV)/U(VI) ratio vary as the total uranium in the rock. Thus the U(IV)/U(VI) ratio in igneous apatite reflects the prevalent equilibrium conditions in the crystallizing magma.

In marine phosphorite thus far investigated the tetravalent uranium ranges from a few percent to over 90 percent of the total uranium. Taken alone such statistics suggest a great variety in the initial U(IV)/U(VI) ratio of uranium emplaced in apatite. Thus experimental evidence that bone and apatite pellets can remove uranyl uranium from solution suggests that much of the U(VI) found in natural apatite may be of primary origin, fixed as chemically adsorbed uranyl anions. It is proposed, however, that uranium in marine apatite is emplaced primarily as U(IV), structurally fixed. This follows from the fact that the higher U(IV)/U(VI) ratios are found in the younger, unweathered, marine apatites, and in apatites recently reworked by marine transgression. U(IV) is readily oxidized to U(VI), and postdepositional weathering, facilitated by radioactive decay, has most probably lowered the initially high U(IV)/U(VI) ratio in many older phosphorites.

Apatite, by effectively removing the small amounts of U(IV) produced in sea water by reduction of $(UO_2)^{+2}$, causes more U(IV) to be produced for its own uptake. As the marine apatite is far from saturated with respect to uranium, it thus interferes with the attainment of equilibrium while fixing an unusual quantity of U(IV). The name, regenerative capture, is proposed for this type of concentration in which the fixation of an insignificant valence species interferes with the equilibrium producing the ion and thus generates a continuing supply for further uptake and results, ultimately, in unexpectedly large buildups of the trace element in the host mineral.

INTRODUCTION

Apatite contains only trace quantities of uranium, typically several thousandths to a few hundredths of one percent. However, as average rock has at most a few parts per million and average ocean water only one or two parts per billion, it is immediately apparent that apatite is an important concentrator of uranium in nature. The ubiquitous occurrence of apatite as an accessory mineral in igneous rocks establishes its role as an important agent, along with a few other minerals, notably zircon, monazite, and sphene, in dispersing uranium in rocks during primary differentiation. This is particularly true because apatite, unlike many other accessory minerals, is prominent in mafic as well as felsic rocks. Thus, whereas the uranium content may be low in the gabbros, the contribution of apatite to the total budget of uranium in the early differentiates may be correspondingly higher. As apatite is also rather common in shales and limestones in the form of phosphatic nodules, concretions, and fossil replacements, it is evident that apatite plays a major role in the geochemical cycle of uranium.

Beside contributing to the dissemination of uranium, apatite paradoxically is also one of very few minerals causing immense localizations of this element. It does so by virtue of its occurrence in vast accumulations of marine sedimentary phosphate composed essentially of the mineral carbonate-fluorapatite (Altschuler and others, 1953). Table 1 illustrates the magnitude and economic potential of these deposits. Thus, as we annually produce more than ten million tons of phosphate fertilizer in the United States and as an appreciable part of this is processed chemically, an opportunity is afforded to mobilize and extract many hundreds of tons of uranium each year. Indeed, uranium as a byproduct of triple super-phosphate production is now recovered in several plants in the United States (Barr, 1955).

The principal aims of this report are threefold: to survey the uranium contents of a variety of apatite materials and deposits; to portray the geologic and chemical controls of uranium distribution in phosphorites of various origins; to attempt an explanation of the occurrence of uranium in apatite.

Table 1.--Resources of some well known uraniferous phosphorites.

	Reserves minable at present			Additional resources minable under changed conditions			Total resources	
	P_2O_5 1/	Apatite 2/	U 3/	P_2O_5 1/	Apatite 2/	U 3/	Apatite 2/	U 3/
	(millions of long tons)		(thousands of long tons)	(millions of long tons)		(thousands of long tons)	(millions of long tons)	(thousands of long tons)
Florida Land-Pebble field, Bone Valley formation, matrix	330	870	87	600	1,600	160	2,500	250
Hawthorn formation				4,000	11,000	1,100	11,000	1,100
Western field Phosphoria formation	870	2,300	230	5,800	15,000	1,500	17,000	1,700
French Morocco	4,800	13,000	1,300	6,420	16,900	1,690	30,000	3,000

1/ Data on P_2O_5 from LeCornec (1951) for Moroccan deposits and McKelvey and others (1953), for domestic deposits.

2/ Apatite data have been computed on the basis of an assumed average P_2O_5 content of 38 percent in the carbonate-fluorapatite comprising these deposits. Generally such compilations show BPL (bone phosphate of lime or tri-calcium phosphate) and as the BPL is in turn based on theoretical fluorapatite of 42 percent P_2O_5, it is both fictitious and misleading. This table gives P_2O_5 and apatite that is minable, rather than tons of minable rock. The latter term does not correctly reflect absolute composition due to its dependence on a complex of external factors such as grade (amount of diluent), thickness, and overburden depth.

3/ Based on the conservative estimate of 0.01 percent U in the pure apatite.

We shall be concerned largely with the migration and fixation of an element that seldom exceeds 0.01 percent in the rocks studied. It is perhaps best to begin therefore with a discussion of some of the restrictions which this fact imposes on the approach taken. Owing to its unique properties of radioactivity and conferred fluorescence, uranium, unlike most trace elements, may often be followed in the field virtually as one follows a visible, major, mineral component. The same properties have allowed the development of analytical methods (Grimaldi and others, 1952) which permit accurate detection of uranium at extremely low concentrations. Unlike an investigation of a major element, however, a study of a trace constituent, in an impure material like phosphorite, is handicapped by lack of information on bulk composition. Whereas it is true that one may obtain the general composition of the mineral host with moderate accuracy--and even here the carbonate-apatite problem is a vexing intrusion--the tiny quantities of uranium dealt with suggest that most of the trace element assemblage be quantitatively determined. Otherwise, the immediate environment of each uranium sample is but poorly known. Obviously, it is impossible to overcome this difficulty in most cases, because of the prohibitive time and money requirements and the fact that adequate analytical methods are not available for many minor and trace elements. Reliance must be placed instead on a reconstruction of conditions from field and petrographic facts and on selection of several elements for specific analysis. Thus, in studying the phosphorites, uranium contents are evaluated mainly in relation to P_2O_5 content. Where important, fluorine, iron, calcium, aluminum, or organic matter may also be studied. However, implicit in some of the work that follows is the assumption that uranium in phosphate nodules is associated mainly with the apatite composing the nodules, and that trace to minor amounts of included carbonates, clays, iron-oxides, quartz, pyrite, and organic matter contain only insignificant amounts of uranium.

Three lines of evidence validate this assumption.

1. Many phosphorite samples have been analyzed by two different methods, one, using weak acids, in which apatite dissolves readily, and clays, pyrite, iron-oxides, or quartz would remain insoluble or dissolve only on prolonged treatment; the other, using a mixture of hydrofluoric and nitric acids in which all of the rock dissolves. In all cases the uranium determined was essentially the same by both methods.

2. Chemical analyses of the minerals associated with apatite in the Florida and Moroccan deposits showed their uranium contents to be insignificant relative to that of apatite.

3. Nuclear emulsion studies reveal that most of the radioactivity in phosphate nodules derives from apatite.

ACKNOWLEDGMENTS

The field and laboratory studies which this paper summarizes have been part of the U. S. Geological Survey's program of investigation of radioactive raw materials for the Division of Raw Materials of the U. S. Atomic Energy Commission. We have benefited greatly from the unpublished studies of many of our colleagues in the Geological Survey engaged in complementary and parallel studies of phosphorite. We are particularly indebted to V. E. McKelvey and J. B. Cathcart, whose regional studies have contributed much important information on the geologic

occurrence of phosphorite and uranium; to W. W. Rubey, whose earlier unpublished investigations and recommendations were largely instrumental in implementing the Survey's program of phosphorite investigations; and to the late John C. Rabbitt, whose reviews and suggestions in the senior author's unpublished studies are reflected in much that follows. We have also benefited greatly from the advice and interest of R. M. Garrels and F. S. Grimaldi in many helpful discussions of the chemical problems, from the stimulating discussions of regional weathering patterns with C. B. Hunt, and from the thoughtful and constructive reviews of E. S. Larsen, 3d, and R. P. Sheldon, all of the U. S. Geological Survey.

We are deeply grateful to the mining and administration staffs of the many companies engaged in phosphate mining in central Florida. Their whole-hearted cooperation in allowing access to operating quarries during field work from 1949 to 1954 is sincerely acknowledged.

MINERALOGY OF APATITE

Crystal chemistry

It is important in considering the nature of uranium occurrence in apatite and phosphorite deposits to understand the possible variations in apatite composition. Basically, apatite is a hexagonal network structure composed of PO_4 tetrahedra, a simple anion--usually fluorine, and a divalent cation, calcium. Beevers and McIntyre (1946) liken the structure to a honeycomb (fig. 1) with the vertices made up of vertical Ca-O columns in which the oxygens are supplied by PO_4 tetrahedra intervening between columns and linking adjoining columns together in a continuous structure. The fluorine or hydroxyl ions occur vertically above each

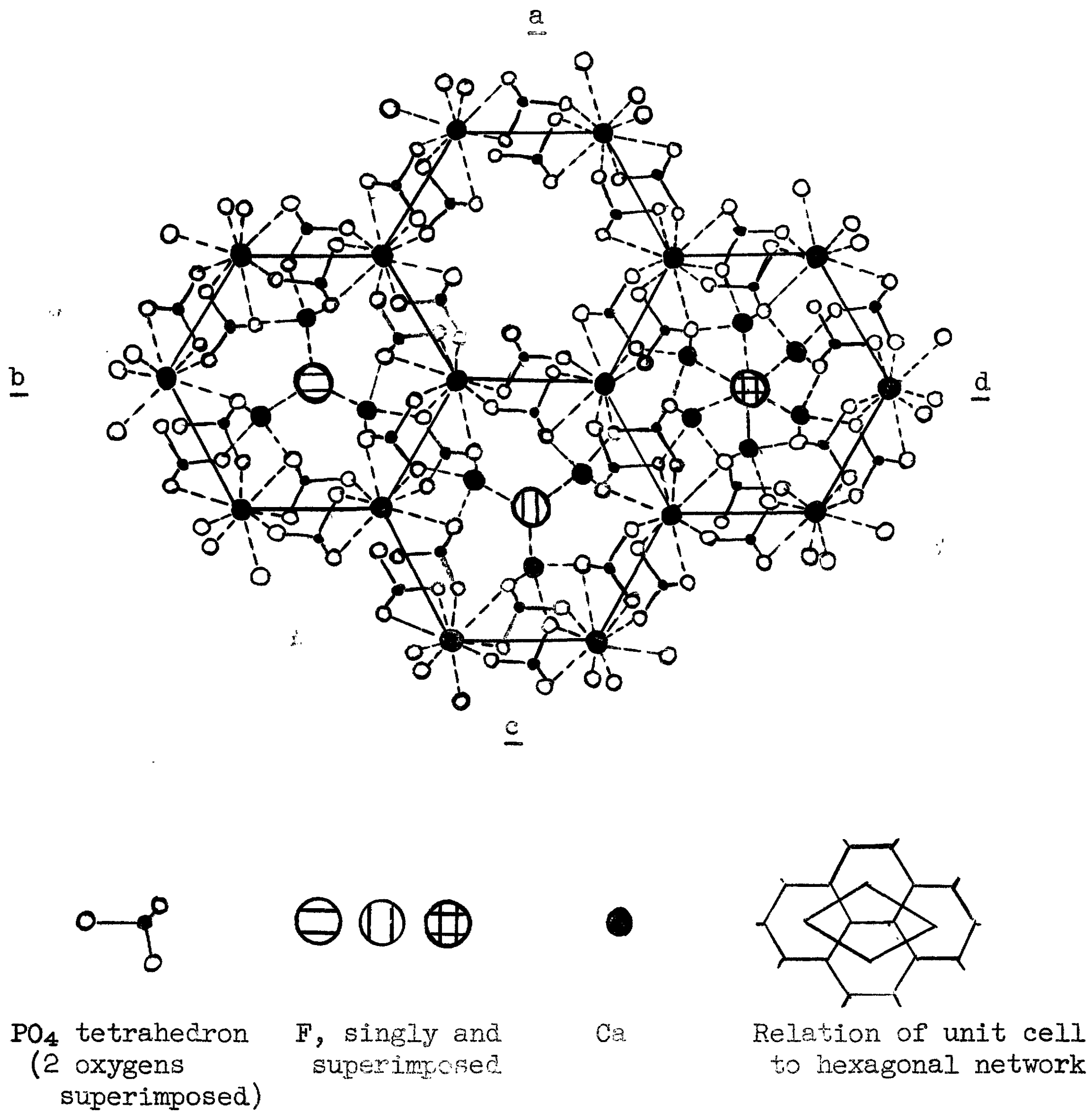


Figure 1.--The structure of fluorapatite showing progressive filling (based on drawings of Beever and MacIntyre, 1946).

a - Incomplete structure showing hexagonal framework and unoccupied channels.
b - Addition of 3 channel calciums and a fluorine occupying same plane.
c - Position of second planar groups of 3 channel calciums and 1 fluorine.
d - Complete structure.

other within the channels of the honeycomb, where they are coordinated to additional calciums (three about each fluorine) that occur in "caves" within the irregular walls of the network (op. cit.).

Apatite is host to many substitutions by cations, anions, and anionic radicals that resemble its normal constituents in size and charge (McConnell, 1938). As a result it may depart significantly from the composition of simple igneous fluorapatite, depending on its environment of genesis. The fluorine position may be occupied wholly or in part by hydroxyl. (Chlorine may also substitute for fluorine; however, as their size difference is appreciable, a structural rearrangement occurs in chlorapatite and it has only limited miscibility with fluorapatite.) In fossil bone, hydroxyl is eventually replaced by fluorine through ion exchange. Minor to major amounts of Sr, Mn, Mg, and Pb are known to replace calcium in apatite, and VO_4 and AsO_4 occur as traces substituting for PO_4 in apatite and form analogues of normal apatite in the pyromorphite series (Palache and others, 1951).

Additional variety is effected by the opportunity for coupled diadochy in which cationic or anionic replacements causing loss or gain in valence are balanced by replacements of opposite kind. Thus, in apatites containing rare earths the imbalance created by the substitution of tervalent cerium for calcium is quantitatively compensated by substitution of tetravalent silicate for phosphate or by the monovalent sodium for calcium (Borneman-Starinkevitch, 1938; Volodchenkova and Melentiev, 1943). An analogous situation exists in many other phosphate mineral groups. For example, monazite, the cerium phosphate, contains thorium and silicate in roughly equivalent amounts.

Composition of the sedimentary carbonate-apatites

The fine-grained microcrystalline carbonate-apatites of the insular and marine phosphorites are best understood in terms of such coupled substitutions. This apatite is generally characterized relative to fluorapatite by a deficit in P_2O_5 content of 3 to 6 percent, an excess of F, OH, or both, of 0.5 to 1.0 percent, and by the presence of 2 to 3 percent of carbonate. The exact mode of occurrence of carbonate in apatite is a controversial question. Hendricks and Hill (1950) have proposed that the carbonate is adsorbed on the surfaces of discontinuities within the apatite crystals. It is significant, however, that carbonate fluorapatite is demonstrably smaller in unit-cell dimensions than fluorapatite (Altschuler and others, 1953). It is felt, therefore, that the structural difference revealed by the characteristically smaller cell must reflect the major and equally characteristic chemical deviations, and that carbonate-fluorapatite is a structurally distinct species as proposed by Gruner and McConnell (1937). Lacking a precise determination of the position of carbonate in the structure we shall adopt provisionally the structural formula which best rationalizes the chemical composition, as follows: $Ca_{10}(PO_4,CO_3)_6F_{2-3}$. Thus excess fluorine (or hydroxyl) serves to balance the charge difference created by the substitution of $(CO_3)^{-2}$ for $(PO_4)^{-3}$.

The chemical and spectrographic analyses in tables 2 and 3 illustrate the chemical nature of the sedimentary carbonate-fluorapatites. Theoretical fluorapatite has the following composition:

$$CaO = 55.5$$

$$P_2O_5 = 42.3$$

$$F = 3.8 \quad (F = O = 1.6)$$

The analyses portray the deficiency of P_2O_5 relative to CaO (augmented by Na, K, Mg, Sr, and other divalent metals shown in table 3), and the excess of F plus (OH). It should be noted in table 2 that the carbonate is substantially all nonleached and therefore assignable to apatite.

Sedimentary carbonate-hydroxylapatite occurs as nodules or massive deposits in caves or islands and is indicative of continental origin. It usually originates as a replacement of limestone by guano solutions. In the presence of fluorine, carbonate-fluorapatite is the stable form and it precipitates as such in marine sediments (Kazakov, 1937). Furthermore, fluorapatites are less soluble than hydroxylapatites, and carbonate-fluorapatite can replace previously formed hydroxyl varieties in bone and island phosphorites.

URANIUM CONTENT OF APATITE

Factors affecting equivalent uranium determinations

The occurrence of uranium in phosphate nodules, bones, and other apatite materials was first demonstrated by Strutt in a remarkable set of analyses based on radioactivity determinations (Strutt, 1906, 1908). Strutt pointed out that the determinations were not affected by thorium which is virtually absent in fossil bone or sedimentary apatite as is born out by the analyses of phosphorite pebbles given in table 4.

Table 2.--Chemical analyses of sedimentary apatite pellets from the Bone Valley formation. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

	B.L.-3, Bonny Lake mine, Ridgewood, Florida			Wa.-10, Watson mine, Fort Meade, Florida		
	1	2	3	1	2	3
Acid insoluble		6.6			2.4	
CaO	49.5		52.9	51.5		52.7
P_2O_5	34.9		37.3	36.6		37.5
CO_2	2.1	2.0	2.2	1.9	1.7	1.9
SiO_2 (total)	6.7			2.9		
SiO_2 (soluble)		0.8	0.9		1.1	1.1
SO_3	0.3		0.3	0.1		0.1
Al_2O_3	1.4		1.5	1.1		1.1
Fe_2O_3	0.4		0.4	0.9		0.9
Na_2O	0.1		0.1	0.2		0.2
K_2O	0.1		0.1	0.2		0.2
H_2O (+)	1.6		1.7	1.8		1.8
H_2O (-)	1.0	0.6	1.1	0.7	0.5	0.7
U	0.016		0.017	0.0075		0.0077
F	3.8		4.1	3.8		3.9
Total	101.9		102.6	101.7		102.1
F = O	1.6		1.7	1.6		1.6
Corrected total	100.3		100.9	100.1		100.5
Nonleachable CO_2		1.8			1.6	

---

1 Analysis by complete decomposition of sample by solution in HNO_3 and fusion of insoluble residue with Na_2CO_3.

2 Partial analyses of same material. Acid insoluble determined after boiling sample for 20 minutes with 1 + 3 HCl. Nonleachable carbonate determined after treatment in 0.5 M tri-ammonium citrate (Silverman, Fuyat, and Weiser, 1952).

3 Corrected analysis, free of insoluble residue. Microscopic examination and the two sets of SiO_2 figures establish that acid insoluble is essentially quartz.

Table 3.--Semiquantitative spectrographic analyses of sedimentary apatite pellets.

Weight percent	B.L.-3 1/	Wa.-10 2/	Va.-7 3/	K.-1 4/	K.-15 4/
Over 10.0	Ca P	Ca P	Ca P	Ca P	Ca P
10.0-5.0	Si				
5.0-1.0	Al		Si		Si
1.0-0.5		Si Al Fe	Al Fe Mg Na	Na Si Al Mg	Na Mg Al
0.5-0.1	Mg Fe Na	Na Mg			
0.1-0.05	Sr Ti	Ti V Sr	Sr Y La Ti Zr B	Cr V Y Fe Sr	Fe Sr Cr V Y Ni
0.05-0.01	Pb Mn Cr	Mn B Y Cr			
0.01-0.005	Ba	Ba La Ni	Mn V Ba Ni Yb	Ni La Ba Ti Zr	Mn Ti Ba La Cu
0.005-0.001	Cu V Y	Zr Yb Cu	Cr Pb Cu Sc	Cu Mn Yb Ag	Zr Mo Yb Ag
0.001-0.0005	Zr		Ag		
0.0005-0.0001	Yb	Ag Be			

1/ Bone Valley formation, Bonny Lake mine, Ridgewood, Florida. Analyst, Katherine V. Hazel, U. S. Geological Survey.

2/ Bone Valley formation, Watson mine, Fort Meade, Florida. Analyst, Katherine V. Hazel, U. S. Geological Survey.

3/ Bone Valley formation, Varn mine, Fort Meade, Florida. Analyst, Katherine V. Hazel, U. S. Geological Survey.

4/ Daily production samples, Khouribga, French Morocco. Analyst, Helen W. Worthing, U. S. Geological Survey.

Table 4.--Thorium content of Florida pebble phosphorite.

(Analyses from U. S. Geological Survey Laboratory)

Locality	Percent Th	Percent U
South Pierce mine, Brewster	< 0.0005	n.d. 1/
Carmichael mine, Plant City	0.001	n.d. 1/
Bonny Lake mine, Mulberry	0.0007	0.017

1/ Although uranium was not determined on these samples, similar materials from the same localities contain between 0.01 and 0.02 percent uranium.

Available analyses of igneous apatite show three or four times more thorium than uranium, and if rich in rare earths, igneous apatite can contain as much as 0.38 percent Th, as reported in apatite from Mineville, New York (McKeown and Klemic, 1956).

Despite the lack of thorium in phosphorite, it is nevertheless preferable to base a discussion of uranium on chemical rather than radiometric determinations. This is particularly true in view of the ease with which apatite can be postdepositionally leached or enriched in uranium and thus be out of radioactive equilibrium regardless of its age. In addition, due to a great variation in the size of the inherent crystallites of the sedimentary apatites (Jacob and Hill, 1953), it is difficult to maintain the standardization necessary to establish comparable equivalent uranium results among a variety of materials, regardless of the fact that they may all be ground to the same apparent size prior to radiometric assay.

Uranium content of representative apatites

Table 5 presents typical and common values obtained in a variety of apatite materials studied by the U. S. Geological Survey. In all cases the analyses are chemical [1] and represent the contents of individual mineral specimens or pure mineral concentrates rather than total rock and hence are of additional value in the geologic literature and do not duplicate the excellent summaries available of uranium in certain phosphorite deposits (Rusakov, 1933; Hébert, 1947; Davidson and Atkin, 1953; McKelvey and Nelson, 1950; McKelvey and others, 1955; Thompson, 1953; Cathcart, 1956).

It is apparent from the above data that uranium content in apatite materials as a group varies from barely detectable traces to the concentration of a minor constituent, approaching 1 percent. Nevertheless, within major occurrences of the same nature, as exemplified by the igneous rocks of the Boulder Creek batholith or all of the immense marine phosphates, the level of concentration is of the same order of magnitude, 0.00X to 0.03 percent. This range in uranium content may be taken to embrace the great bulk of apatite in the lithosphere and departures from it may be safely considered unusual and examples of special history.

---

[1] The uranium analyses reported in this paper that have been performed in the U. S. Geological Survey laboratories have been done by fluorimetric methods. Grimaldi and others (1954) discuss the accuracy of these methods pointing out that they may be as good as ± 4 percent of the uranium content. They state that under routine conditions, "the error generally is greater and may range from ± 8 to 15 percent of the uranium content. When errors occur, the results are generally low." The majority of the analyses in this paper have been done by a fluorimetric-extraction procedure. For this reason, as well as the nonroutine nature of the determinations, it is safe to assume them to be accurate in the range of ± 5 percent of the uranium present.

Table 5.--Uranium content of representative apatites.

(Analyses from U. S. Geological Survey Laboratory)

A. Fluorapatite, $Ca_{10}(PO_4)_6F_2$, from crystalline rocks		Uranium (percent)
1.	Alkali syenite, Renfrew, Ontario, Canada	0.0022
2.	Gabbro, Henderson, North Carolina	0.0006
3.	Shonkinite, Mountain Pass, California	0.0049
4.	Magnetite deposit, Durango, Mexico	0.0009
5.	Magnetite deposit, Mineville, New York	0.0079
6.	Syenite, Kola Peninsula, U.S.S.R.	< 0.001
7.	Tonalite, southern California batholith	0.012
8.	Granodiorite gneiss, Boulder Creek batholith, Colorado	0.0069
9.	Quartz monzonite, Boulder Creek batholith, Colorado	0.0053
10.	Hornblende biotite granite, Boulder Creek batholith, Colorado	0.0078
11.	Mica granite, Boulder Creek batholith, Colorado	0.0047
12.	Quartz diorite gneiss, Boulder Creek batholith, Colorado	0.0049

B. Carbonate-fluorapatite (F = > 1 percent) $Ca_{10}(PO_4,CO_3)_6(F,OH)_{2-3}$ from marine sedimentary phosphorite		
1a.	Pellets, Hawthorn formation, Florida	0.0061*
b.	do.	0.0075
c.	do.	0.0045
2a.	Pellets, Bone Valley formation, Florida	0.009*
b.	do.	0.012
c.	do.	0.019
3a.	Pebbles, Bone Valley formation, Florida	0.011*
b.	do.	0.016
c.	do.	0.024

Table 5.--Uranium content of representative apatites.--Continued.

B. Carbonate-fluorapatite ($F = > 1$ percent) $Ca_{10}(PO_4,CO_3)_6(F,OH)_{2-3}$ from marine sedimentary phosphorite--Continued		Uranium (percent)
4a. Pellets and oolites, Phosphoria formation, Idaho		0.0061*
b. do.		0.016
5a. Pellets and replaced fossils, Khouribga, French Morocco		0.007
b. do.		0.012*
c. do.		0.023
6. Nodules dredged from the sea floor off southern California		
	Sample no. 69	0.0089
	106	0.0068
(Samples, those analyzed for Dietz, Emery, and Shepard, 1942)	121	0.0041
	158	0.0081
	162	0.0125
	183	0.0051
C. Fossil bone, carbonate-fluor-hydroxylapatite ($F = < 1$ percent) $Ca_{10}(PO_4,CO_3)_6(OH,F)_{2-3}$		
1. RW-4468, mammalian (sp. unknown), Mayport, Florida		0.074
2. W-3841, mammalian (sp. unknown), Miles City, Montana		0.83
3. Titanothere bone, Hell Creek formation, Camp Cook, South Dakota		0.015
4. Shark tooth, Bone Valley formation, Florida		0.009
5. Manatee rib, Bone Valley formation, Florida		0.006
6. Conodont fragments, Khouribga, French Morocco		0.079
D. Guano-derived phosphorites, carbonate-hydroxylapatite $Ca_{10}(PO_4,CO_3)_6(OH)_{2-3}$		
1. Angaur Island, Pacific Ocean		0.001
2. Mona Island, Puerto Rico		0.001
3. Cuthbert Lake Rookery, Tampa Bay, Florida		< 0.001

*Denotes author's opinion of typical value for such material.

Island phosphorites--secondary uptake of uranium and fluorine

The unusually low uranium contents of island phosphorite, as illustrated by the Angaur and Mona Island analyses (table 5) are attributable to the lack of uranium in the parent limestones from which they originate by subaerial replacement. Only rarely do island phosphorites contain more than 0.002 percent uranium; and, when they exceed this value, the uranium in all likelihood has been acquired postdepositionally from percolating ground water or from sea water with which such deposits are sprayed or washed by wind and wave. It is interesting in this regard to compare the fluorine and uranium contents of such materials, as fluorine, not being a primary constituent of subaerially formed phosphorites, is a certain indicator of postdepositional replacement.

It can be seen from table 6 and figure 2 that the percent uranium bears least relation to the P_2O_5 content or, inferentially, to the amount of apatite present in the rock. Thus specimens 3, 7a, and 8 are all virtually pure apatite rock yet their uranium contents differ by several hundred percent. On the other hand uranium generally increases as fluorine, or as the ratio of fluorine to phosphorus does. The lack of a constant ratio between the increases is easily explained by the fact that two independent structural emplacements are involved, F for OH, and presumably, U for Ca.

It is unfortunate that so few analyses of the required precision are available for such comparisons, in itself a reflection of the generally recognized lack of uranium in phosphate deposits of continental origin. Nevertheless, the facts that secondary uptake of fluorine and uranium are codependent and related to the same geological process and time of emplacement seem indicated by figure 3, in which the admittedly few points

Table 6.--Partial analyses of cave phosphorite from Mona Island, Puerto Rico.

Sample no.	P_2O_5 1/ (percent)	F 2/ (percent)	U 3/ (percent)	$\frac{F}{P_2O_5} \times 100$	$\frac{U}{P_2O_5} \times 10,000$
Mona 6	26.3	0.07	0.0003	0.27	0.11
Mona 7b	15.8	0.06	0.0003	0.38	0.19
Mona 3	41.4	0.05	0.0005	0.12	0.12
Mona 4	32.4	0.24	0.0011	0.74	0.34
Mona 8	38.6	1.08	0.0028	2.80	0.73
Mona 7a	37.1	0.65	0.0014	1.75	0.38

1/ Analyst, A. B. Caemmerer, U. S. Geological Survey.

2/ Analyst, G. Edgington, U. S. Geological Survey.

3/ Analyst, C. L. Johnson, U. S. Geological Survey.

exhibit a trend that originates at the point of zero content for both percent of fluoridation and uranium content.

Similar accord between uranium content and the percent of fluorine of Cenozoic bones, in which the fluorine is unquestionably of secondary origin, has been noted in the studies of Oakley (1955a,b).

If we note also that marine apatite nodules of recent origin contain appreciable uranium (table 5), it seems evident that the large marine phosphorites derive much, if not all, of their uranium from the ocean water at the time of their formation.

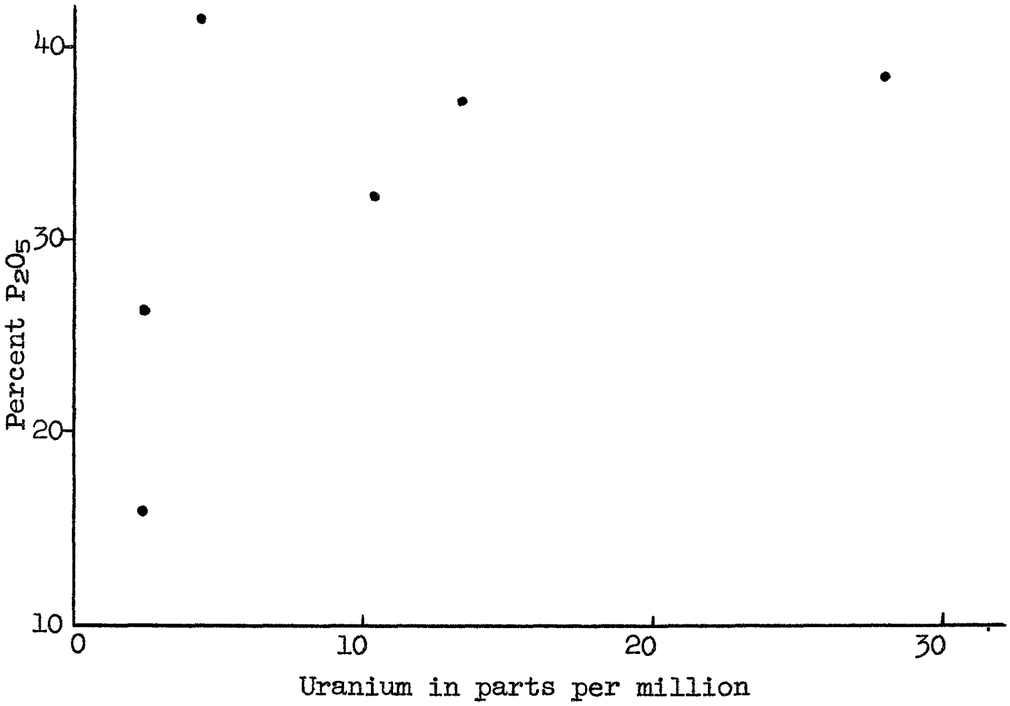


Figure 2.--Relation of uranium to P_2O_5 in Mona Island cave phosphorites.

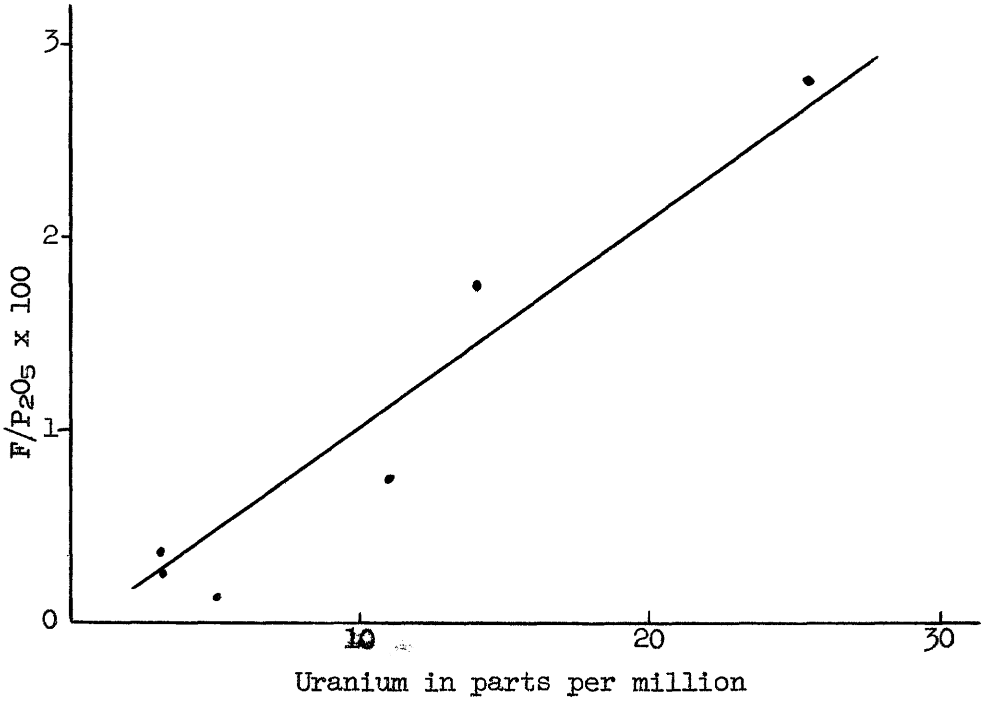


Figure 3.--Relation of uranium to fluoridation in Mona Island cave phosphorites.

PROBLEMS OF OCCURRENCE OF URANIUM IN PHOSPHORITE

Possible modes of occurrence

Two large problems are posed by the analyses given in table 5. In what form and manner does uranium occur in phosphorites? How may its variations within the same deposits or among different deposits of essentially similar material be explained? Thus, the apatite nodules from Florida and Morocco are compositionally and petrographically quite similar, yet those from Morocco contain two or three times as much uranium. Isolated pebbles from the land-pebble field contain as much as 0.2 percent uranium in contrast to the normal concentration.

Regarding the nature of uranium in phosphates several mechanisms may be postulated. The uranium may be present in a separate phase such as UO_2, UF_4, or $Ca(UO_2)_2(PO_4)_2 \cdot 8H_2O$ (autunite). It may be present as isolated U^{+4} ions or $(UO_2)^{+2}$ radicals, chemically adsorbed on surfaces or internal discontinuities (Hendricks and Hill, 1950). It may be present by structural substitution of U^{+4} in apatite as proposed by several investigators (Michael Fleischer, personal communication, 1949; McKelvey and Nelson, 1950; Davidson and Atkin, 1953; Goldschmidt, 1954) on the grounds of theoretical plausibility in view of the fact that the ionic radii of U^{+4} (0.97A) and Ca^{+2} (0.99A) (Green, 1953) are virtually identical. Lastly, it may be substituted structurally in apatite as $(UO_2)^{+2}$ since it has been demonstrated that the uranyl radical will be abstracted from solution by glycol-ashed bone. Such uranium uptake occurs by displacement of two moles of calcium per mole of uranium and also renders surface phosphate "... non-exchangeable to the extent of two moles per mole of uranium." (Neuman and others, 1949a; 1949b). These are puzzling facts for divalent uranyl. Moore (1954) has shown that phosphate can also remove appreciable $(UO_2)^{+2}$ from cold water solution and that the extracted uranium cannot be washed out.

Absence of uranium minerals

It is a fact of signal importance that uranium minerals are virtually unknown in phosphorites. Uranyl phosphates and vanadates are common in other deposits, and they are readily found by virtue of their habit as highly colored "paints" and the fact that many of the species fluoresce brilliantly, thus allowing detection of pinpoint disseminations. Yet these minerals have been noted in only three or four local concentrations in phosphorites (Altschuler and others, 1956; Arambourg and Orcel, 1951; McKelvey and others, 1955).

Relation of uranium content to composition of phosphorite

In efforts to understand the occurrence and variation of uranium in phosphorites, as well as to concentrate it for commercial use, many attempts have been made to correlate it with physical and chemical properties of apatite and phosphorite. Materials from the Bone Valley and Phosphoria formations and from the Moroccan deposits have been fractionated according to their variation in specific gravity, magnetism, color, luster, and particle size. None of these separations led to any positive or consistent correlation with uranium. This is not surprising, however, as it is not to be expected that uranium present in the order of 0.0X or 0.00X percent, or 1 atom per several thousand unit cells of apatite, could sensibly alter the properties of the host rock.

Fluorescence and uranium content

The property of fluorescence is a notable exception, however, and it was found that a consistent relation could be observed between intensity of fluorescence and uranium content within certain samples. In table 7, uranium analyses are given for composite samples of apatite nodules hand-picked on the basis of their fluorescence under ultraviolet light of 3650 A wavelength.

Each of the composite samples in table 7 consisted of many pellets or pebble fragments, and the fluorescence was characteristic of the entire pellet, or pebble, rather than pinpoint or spotty. The correlation of increased uranium content with enhanced fluorescence is, therefore, further indication of the absence of separate uranium phases in phosphorites, even below the limits of microscopic detection, as it illustrates a change in an inherent property of the host mineral, apatite.

Table 7.--Comparison of fluorescence and uranium content in apatite nodules from the Bone Valley formation, Boyette mine, Florida. Analyst, Harry Levine, U. S. Geological Survey.

Fluorescent color	Percent U	Number of composite samples
Yellow	0.017 - 0.021	2
Yellow to brown	0.009	1
Pink or peach	0.006 - 0.010	2
Purple or lavender	0.003 - 0.006	4

Lack of preferential solution of uranium

In solution studies of rock from the Bone Valley and Phosphoria formations with nonoxidizing solvents such as sulfuric, phosphoric, and citric acids, it was found that the percent of uranium extracted was always proportional to the percent of P_2O_5 extracted. This result prevailed regardless of whether the samples were slimes or crushed pebbles, whether calcined or treated raw, and with high acidity or with small volumes of dilute weak acid (Igelsrud and others, 1948, 1949).

It seems evident that uranium in phosphate deposits cannot be accounted for by discrete uranium phases, by absorption, or by loosely adsorbed ions, radicals, or phases. This is indicated by three lines of evidence--the lack of uranium minerals, the fluorescence of uraniferous apatite, and the inability to concentrate or separate uranium by physical or chemical means in the laboratory.

Relation of uranium to P_2O_5

Most investigators have found that uranium varies approximately as P_2O_5 content in phosphate deposits but that a close correlation does not exist between the two. The Moroccan deposits illustrate both the general accord and the lack of detailed agreement. Figure 4 is a scatter diagram in which P_2O_5 is plotted against U for 18 samples representing the average daily production from various beds and locations in the Oulad-Abdoun Basin. They thus represent large tonnages. The tendency for the two factors to be related is apparent from the plot, in which most of the points fall between narrow limits, bounding a region of well-

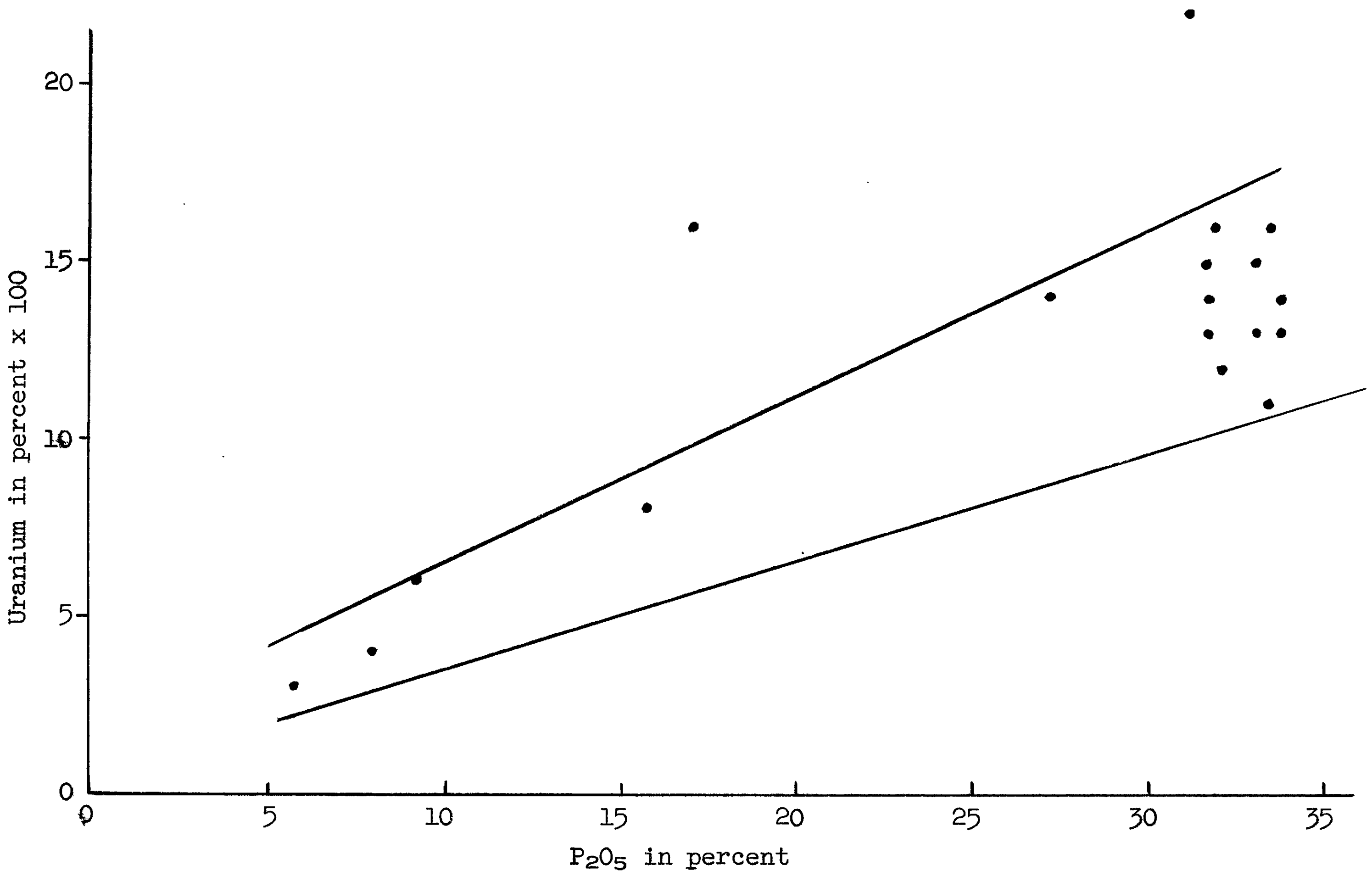


Figure 4.--Relation of uranium to P_2O_5 in phosphates from Oulad-Abdoun Basin, French Morocco.

defined slope. However, when only high-grade samples are studied, that is, those grouping closer together and containing more than 0.011 percent uranium in figure 4, it can be noticed that more scatter prevails.

The approximate dependence of uranium on phosphate content is to be expected on two different grounds previously discussed:

1. Phosphorites are notably devoid of separate uranium mineral phases.
2. Uranium is intimately associated within apatite as revealed by lack of preferential solution and by fluorescence.

Furthermore, the other mineral constituents of the major phosphorites, generally clays, carbonates, and quartz, almost universally contain less than 0.001 percent uranium. Rarely, samples of clay contain more, but in these instances such clays have been phosphatized or contain primary, admixed apatite, and their phosphate can be dissolved with dilute nitric acid leaving a pure clay residue that is relatively uranium free. The ratio of uranium to phosphate dissolved is the same as in the apatite associated with such clays.

In view of the essentially exclusive association of uranium with the apatite within unweathered phosphorites, almost perfect positive correlation between uranium and any parameter of apatite content would be expected within a group of related rocks. However, detailed studies of the relations among uranium and the other chemical constituents of apatite show frequent and striking departures from pronounced positive correlation. The prevailing relation in the Bone Valley formation is for coarse pebble to be richer in uranium and poorer in P_2O_5 content than the finer pebble.

Cathcart (1956) demonstrated this relation and found that a moderate negative correlation (-0.64) exists between P_2O_5 and uranium for samples of +150 mesh pellets and pebbles throughout the land-pebble field. Such negative correlation has not been found elsewhere; and, indeed, deposits even within the land-pebble field, containing 10 percent P_2O_5, will contain less uranium than deposits with 20 percent P_2O_5. In the Moroccan deposits uranium is uniformly distributed through all size grades, as table 8 demonstrates. In the Phosphoria formation McKelvey and Carswell (1956) have demonstrated that maximum uranium content is regionally associated with areas of thickest and highest grade phosphate accumulation.

An equilibrium condition may exist between apatite and uranium in sea water during the precipitation of apatite; however, such equilibrium may vary greatly with time and marine environment. Thus, assemblies of data from different parts of the same formation may represent a variety of different equilibria and an average of such varied groups of data may have the effect of masking, rather than demonstrating, a universal relation. The work of Thompson (1953, 1954), who has explored the relation of uranium to apatite composition in a series of closely spaced, contiguous samples from the Phosphoria formation, was designed to overcome this difficulty. Her results are reproduced in table 9.

The results developed, and noted by Thompson, are that samples with a higher average uranium content show the best positive correlation with P_2O_5 content. The same samples also show the best positive correlation between CO_2 and P_2O_5 and the best negative correlation with organic matter. All samples showed excellent positive correlation between F and P_2O_5. This last is expectable as the phosphate mineral is a carbonate-fluorapatite;

Table 8.--Size distribution and uranium contents of nodular phosphates from Khouribga, French Morocco.

Sieve size (mesh)	Diameter (mm)	Weight percent of fraction	Uranium percent (Analyst, Frank Cuttitta, U. S. Geological Survey)
32	0.630	2.0	0.015
44	0.437	2.3	0.015
84	0.210	35.2	0.016
120	0.149	28.4	0.015
200	0.074	25.9	0.016
325	0.044	2.9	0.015
< 325	< 0.044	3.4	0.012 1/

1/ The finest fraction contains clay diluent. All other fractions are composed entirely of apatite.

and, although free fluorite is common in the Phosphoria, it was not detected in any of these samples (Thompson, 1954). One is struck by the spread in the correlations between eU and P_2O_5 and by the fact that the samples from Reservoir Mountain, which show negative and very poor correlation, do not differ greatly in average eU content from samples WT 603 which show pronounced positive correlation.

Table 9.--Correlation coefficients among eU, P_2O_5, F, CO_2, and organic matter in samples of the Phosphoria formation (Thompson, 1953, 1954).

Locality and sample number	Number of samples	eU x 10^3 percent		P_2O_5 percent		Correlation coefficients			
		Range	Average	Range	Average	eU/P_2O_5	eU/organic	CO_2/P_2O_5	F/P_2O_5
Brazer Canyon WT 605, 604	51	8-29	13	12-34	26	+ 0.2	- 0.2	+ 0.52	+ 0.98
Brazer Canyon WT 603	24	7-36	20	3-34	26	+ 0.8	- 0.6	+ 0.93	+ 0.99
Coal Canyon WT 700	12	6-16	31	1-34	20	+ 0.9	- 0.7	+ 0.98	+ 0.99
Trail Canyon WT 365	26	4-28	8	20-35	30	+ 0.1	+ 0.5	+ 0.29	+ 0.95
Reservoir Mountain WT 910	31	7-30	16	31-36	34	- 0.2	- 0.6	n.d.	n.d.

Equally arresting is the fact that the two groups of samples showing best correlations do so for all of the constituents compared. This suggests that all of the factors are covarying with the same set of environmental conditions and therefore that these 2 sets of samples have sustained the least postdepositional change. This follows from the fact that the rocks are polymineralic, containing organic matter, carbonates, and apatite as separate phases. As the relations among these in primary marine deposition would differ considerably from those that would prevail under subaerial weathering or metamorphism, the CO_2, eU, and P_2O_5 correlations in sets 2 and 3 may all reflect the carbonate-fluorapatite content in relatively unaltered rock. On the other hand, the poor correlation between CO_2 and P_2O_5 in sets 1, 4, and 5 may reflect secondary alteration in terms of the highly mobile calcite; and, as during such alteration uranium may be added or subtracted, and apatite may be affected, eU-P_2O_5 correlations are also notably poorer.

Marine versus ground-water origin of uranium in phosphorite

General statement and review

Evidently, comparisons based on composition alone do not yield consistent explanations of the occurrence of uranium in phosphorites. Davidson and Atkin (1953) after surveying the bewildering variation in the available chemical data, concluded that in most instances the uranium in phosphorites is postdepositionally emplaced from percolating ground water as a proxy for calcium. This explanation adequately accounts for the uranium content of isolated bones and some guano deposits and may account for some part of the uranium of other materials, but it is not tenable when applied to the preponderant occurrences--the marine phosphorites, plus the phosphatic shales and limestones.

Ground-water percolation as the major source and mode of uranium emplacement demands that uranium content would increase significantly with age. Lénoble, Salvan, and Ziegler (1952) observe that radioactivity increases with age in the Moroccan deposits. However, they stress the minute nature of the variation, and Guntz (1952), in discussing the same deposits, emphasizes their regularity of grade, which suggests to him uranium coprecipitated during sedimentation. It is significant also that the Senonian Moroccan apatite contains appreciably more uranium than apatite from the Permian Phosphoria, which is much older, and has had a more varied history.

Evidence of young phosphorites and submarine nodules

Regarding the question of marine versus ground-water origin, it is most noteworthy that apatite nodules dredged from the Gulf of California, (table 5) contain as much uranium as the pellets from the Permian Phosphoria and Miocene Hawthorn formations. Both of the latter have been exposed subaerially, whereas the nodules from southern California waters have remained submerged and, although they may have undergone submarine reworking, most of them are thought to be of Quaternary age (Dietz and others, 1942).

Further information on the magnitude of ocean-derived uranium in recent deposits may be gleaned from the analyses of slightly phosphatic materials dredged from the Gulf of Mexico during recent U. S. Geological

Survey studies (Gould, H. R., written communication). Table 10 presents a few of many hundred similar analyses. The samples represent contemporary accumulations of very slightly phosphatized shell and marl, and it is most significant that the ratio of uranium to phosphate in them far exceeds that of most high-grade marine phosphorites.

Table 11 contains analyses and U/P_2O_5 ratios of representative large deposits and individual samples of apatite, all of materials not demonstrably enriched subaerially.

Although the mechanism causing the high uranium concentration in the phosphatized shells and marls can only be conjectured, the fact remains that enrichment of such magnitude can occur in a purely marine environment. It should also be noted that the nodules dredged from coastal California waters may contain as much uranium relative to phosphate as the relatively rich large deposits in Florida and French Morocco.

Necessity of geologic interpretation

Neglecting the trivial occurrences in guano and bone, spectacular as the actual uranium concentration in the latter may be, it can be stated that most of the uranium in marine sedimentary phosphorite is of marine origin. The neutral to basic nature of apatite makes it susceptible to alteration under the prevailing acidities of most vadose waters. It is thus to be expected that the primary marine uranium may be redistributed by a variety of secondary processes, as indicated by conflicting and varied relations of uranium to composition in the same and among different deposits, and by the evidence of laboratory uptake of uranium by bone and phosphorite. Therefore, it appears that the uranium content of apatite

Table 10.--Phosphate and uranium contents of bottom samples from the Gulf of Mexico.[1]

Laboratory no.	Depth (fathoms)	North latitude	West longitude	Percent U	Percent P_2O_5	Description
105916	24	26°50.1'	83°16.1'	0.0002	0.13	Shell sand
105917	30	26°52.1'	83°33.5'	0.0002	0.11	Shell sand
105918	35	26°50.7'	83°46.1'	0.0002	0.11	Algal sand
105919	45	26°50.1'	83°57.9'	0.0002	0.09	Algal sand
105920	63	26°51.5'	84°08.0'	0.0003	0.28	Shell sand
105921	100	26°52.2'	84°32.7'	0.0002	0.24	Foraminiferal sand and shell
105922	80	26°34.8'	84°15.0'	0.0002	0.20	Foraminiferal sand and shell
105923	62	26°31.3'	83°57.9'	0.0002	0.18	Foraminiferal sand and shell
105924	7	26°18.7'	83°12.5'	0.0001	0.09	Shell sand
105925	8½	26°20.0'	83°22.1'	0.0005	0.08	Quartz sand

---

[1] Analyses from U. S. Geological Survey Laboratory, (Gould, H. R., written communication).

Table 11.--Relative contents of uranium and P_2O_5 in marine phosphorites.

		Percent U	Percent P_2O_5	U/P_2O_5
Gulf of Mexico, 1/ bottom				
samples, range:		0.0001-0.0003	0.08-0.28	
arbitrary mean:		0.0002	0.185	1/925
Pacific Ocean off	Sample no. 162	0.0125	22.43	1/1800
southern California, 2/	do. 69	0.0089	29.56	1/3300
phosphate nodules	do. 158	0.0081	29.09	1/3600
	do. 106	0.0068	21.19	1/4300
	do. 183	0.0051	29.66	1/5800
	do. 121	0.0041	28.96	1/7000
Hawthorn formation, Florida, 3/				
primary apatite pellets		0.0075	37	1/4950
		0.0045	37	1/8200
Khouribga, French Morocco, 4/				
phosphorite		0.015	33.0	1/2200
		0.014	33.6	1/2400
		0.013	33.0	1/2540
		0.013	33.6	1/2580
Land-Pebble field, Florida, 5/		0.018	30.7	1/1760
clastic apatite		0.014	33.4	1/2380
composities		0.010	34.5	1/3450
		0.010	35.2	1/3520
		0.009	33.0	1/3660

1/ Analyses from U. S. Geological Survey Laboratory, (Gould, H. R., written communication).

2/ P_2O_5 and sample numbers from Dietz, Emery, and Shepard (1942); uranium on the same splits by R. S. Clarke, Jr., U. S. Geological Survey.

3/ Uranium by R. S. Clarke, Jr.; P_2O_5, assumed average for such pure apatite nodules, will yield conservative U concentration.

4/ Daily production averages at four stations in Oulad-Abdoun Basin, French Morocco.

5/ Weighted averages of nodules and pebbles from five areas each representing a minimum of 100,000 long tons of phosphorite (data converted from Cathcart, figure 3A, 1956).

can be explained only in terms of the total geologic history of the deposits. The following sections are devoted to an examination of specific deposits and the geologic processes which have governed their uranium content, in hopes of developing a set of principles to explain the range and variation of uranium in most phosphorites.

CASE HISTORIES OF GEOLOGIC PRINCIPLES GOVERNING URANIUM DISTRIBUTION IN PHOSPHORITES

Uranium in phosphorite during weathering

Florida Land-Pebble phosphates--general geology

The Land-Pebble phosphates of Florida present an opportunity to study apatite in a variety of geologic circumstances and thus to evaluate its uranium content in terms of both petrography and petrology. These deposits are mainly in the Bone Valley formation of Pliocene age (Cathcart and others, 1953) and subordinately in the underlying Hawthorn formation of early and middle Miocene age (MacNeil, 1947). The surface of the Hawthorn is irregular, its rock is solution-pitted, and it contains many small slumps and locally large ones within which the overlying Bone Valley thickens (Cathcart, 1950). The Hawthorn was exposed and weathered during late Miocene time, developing an irregular topography and accumulations of phosphatic residue containing primary apatite nodules, inherited as such from the Hawthorn, and secondarily phosphatized limestone pebbles. During a period of Pliocene marine transgression this residuum of the Hawthorn was reworked into the unconformably overlying Bone Valley formation with additions of quartz, clay, and probably phosphate (Altschuler and others, 1956).

The Bone Valley formation is approximately 30 feet thick and consists of two units (fig. 5). A pebbly and clayey sand which is characterized by graded bedding comprises the lower two-thirds and is the unit mined. Grading upward from this is a massive-bedded, less phosphatic quartz sand, which, together with an overlying surface mantle of quartz sands, is discarded as overburden during mining operations.

The upper part of the Bone Valley formation has been leached, altered to aluminum phosphates, and secondarily enriched in uranium in a widespread, transgressive zone which, though discontinuous, underlies several hundred square miles in the Land-Pebble district. This aluminum phosphate zone is the result of lateritic weathering and ground-water alteration, and sections through it exhibit a progressive variation in mineralogy and texture (fig. 5). In typical sections pebbles of carbonate-fluorapatite still prevail at the base, incipiently leached and altered. The calcium-aluminum phosphates, crandallite and millisite, are found in the middle of the zone. At the top, the aluminum phosphate, wavellite, predominates (Altschuler and others, 1956).

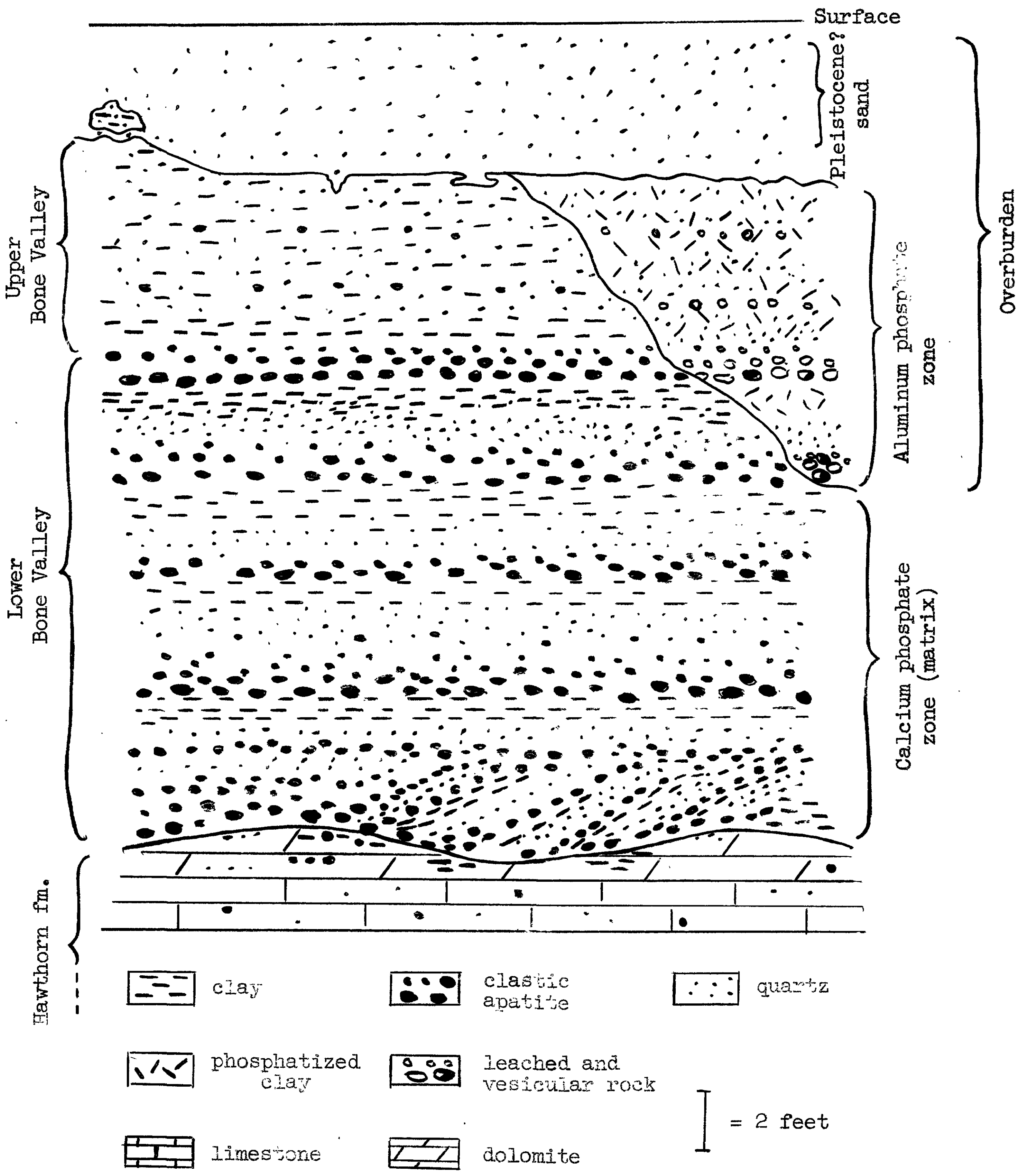


Figure 5.--Stratigraphic relations in the Land-Pebble phosphate field, Florida.

In the Land-Pebble deposits we may thus study and contrast the uranium contents of sedimentary apatite of the following types:

1. Simple structureless nodules from the Hawthorn formation.
2. Nodules from Hawthorn that have been reworked into the Bone Valley and are thus in a second cycle of sedimentation.
3. Simple pebbles of phosphatized limestone from the Bone Valley formation.
4. Complex, reworked pebbles from the Bone Valley formation illustrative of several subcycles of sedimentation.
5. Leached and altered pebbles.
6. Secondarily enriched pebbles.

Illustration of leaching

In a conglomerate rock composed of pebbles resting in a matrix of finer grained material, the pebbles usually cause zones of increased permeability in adjoining matrix by disturbing the packing arrangement of the smaller grains. These areas would be zones of better circulation and as such would be the preferred loci of any leaching or enrichment that occurs within the rock. Thus, the uranium, or the secondary phosphate, might be distributed according to the texture within the phosphate pebblerock. This type of control was pointed out by Graton and Fraser (1935), who noted its influence in gold and copper deposition.

To test the influence of texture on the distribution of uranium, six pebbles were selected and quantitatively analyzed for percent of uranium in zones from the surface to the center. The pebbles were selected from the aluminum phosphate zone of the Bone Valley formation, and the data given in table 12 are described according to the sampling scheme shown in figure 6.

The figures in table 12 reveal a striking increase in uranium content from the surface inward, in all of the pebbles. With the single exception of zone B in pebble 1, this increase is constant and of steep, although nonuniform gradient, and values at the center are easily 100 percent higher than those at the outside.

This graded distribution suggests leaching of the uranium from phosphate pebbles of originally more uniform richness. In this connection it is interesting to note that the sharpest increase in uranium content is, in every case, between zones A and B. Beyond the B zone the increase is of smaller magnitude. This is precisely what would be expected as the surface zones would be more easily attacked.

It is evident that subaerial leaching can effect large changes in the primary uranium contents of marine deposits. The leaching illustrated above occurred postdepositionally in the course of ground-water alteration; leaching can presumably be equally effective during subaerial transport and reworking of similar materials. In this latter case the leaching would not be confined primarily to conglomeratic material and would probably show more pronounced effects in the finer materials of an assemblage, as these have a greater ratio of surface to volume. In any event, the demonstration that leaching did affect the rock's uranium content could probably be accomplished in the same manner or through the use of autoradiography.

Table 12.--Chemical analyses showing distribution of uranium within phosphate pebbles.

Pebble 1 - Selected at random; a small flattened spheroid 2.5 x 2 x 1 cm. The pebble is a micro-conglomerate, made up of precipitated phosphate, phosphate pellets, quartz grains, and still smaller pebbles of similar composition. The other pebbles are similar in character.

Zone	Percent U 1/
A -	0.011
B -	0.023
C -	0.020
D -	0.021

Pebble 2 - Selected at random.

Zone	Percent U 1/
A -	0.007
B -	0.026
C -	0.028
D -	0.033

Pebble 3 - Selected because of high fluorescence, a small fractured pebble of originally high roundness; original central portion is now exposed surface, hence only surface and median zone were sampled.

Zone	Percent U 1/
A -	0.020
C -	0.028

Pebble 4 - Selected because of high fluorescence.

Zone	Percent U 1/
A -	0.011
C -	0.032

Pebble 5 - Selected because of high fluorescence; surface encrustation of brown phosphate which was obviously deposited by circulating solutions since some of it occurs as a circular ridge outlining the area of previous contact with another pebble.

Zone	Percent U 1/
A -	0.012
B -	0.019
D -	0.026

Pebble 6 - Selected because of high fluorescence.

Zone	Percent U 1/
A -	0.007
B -	0.013
C -	0.015

1/ Corrections were made for the percent of quartz in each portion tested. Analyses by staff of U. S. Geological Survey Laboratory.

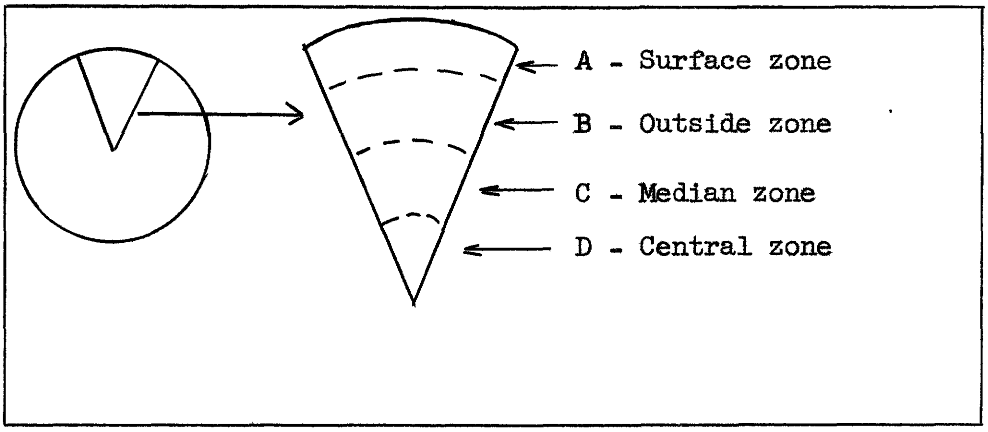


Figure 6.--Sample scheme used for study of uranium distibution in pebbles.

Postdepositional enrichment

1. The aluminum phosphate zone: lateritic weathering and supergene enrichment.--The Bone Valley formation offers instructive examples of enrichment as well as leaching. Unaltered phosphorite in its lower part contains an average of 0.008 percent uranium and 10 to 15 percent of P_2O_5. In contrast, typical rock from the aluminum phosphate zone has 0.012 percent uranium and 8 to 12 percent P_2O_5. In effect it has sustained roughly a two-fold enrichment in the phosphatic fraction.

There is much variation in the composition and uranium content of the aluminum phosphate zone. Nevertheless, the distribution of uranium within it closely follows the distribution of calcium, as shown in figure 7. The uranium content is greatest in the base of the zone, declines gradually toward the middle of the zone, and is relatively low in the upper half. The zone of basal enrichment corresponds to the zone containing apatite pebbles, and analyses for uranium in pebbles, cements, and mineral concentrates within the entire zone show that the apatite pebbles are the richest uranium components of the zone and that the pebbles in the base of the zone are richer than those in the middle. Figure 8 illustrates these relations and shows the contribution of the various textural components to uranium content of the total rock in a section through the aluminum phosphate zone.

Additional evidence of secondary enrichment may be obtained by comparing the uranium contents of composite samples of pebbles from rock of orginally identical petrography above and below the base of the aluminum phosphate zone. Pebbles from within the zone were found to contain 0.056 percent uranium in contrast to their analogues just outside

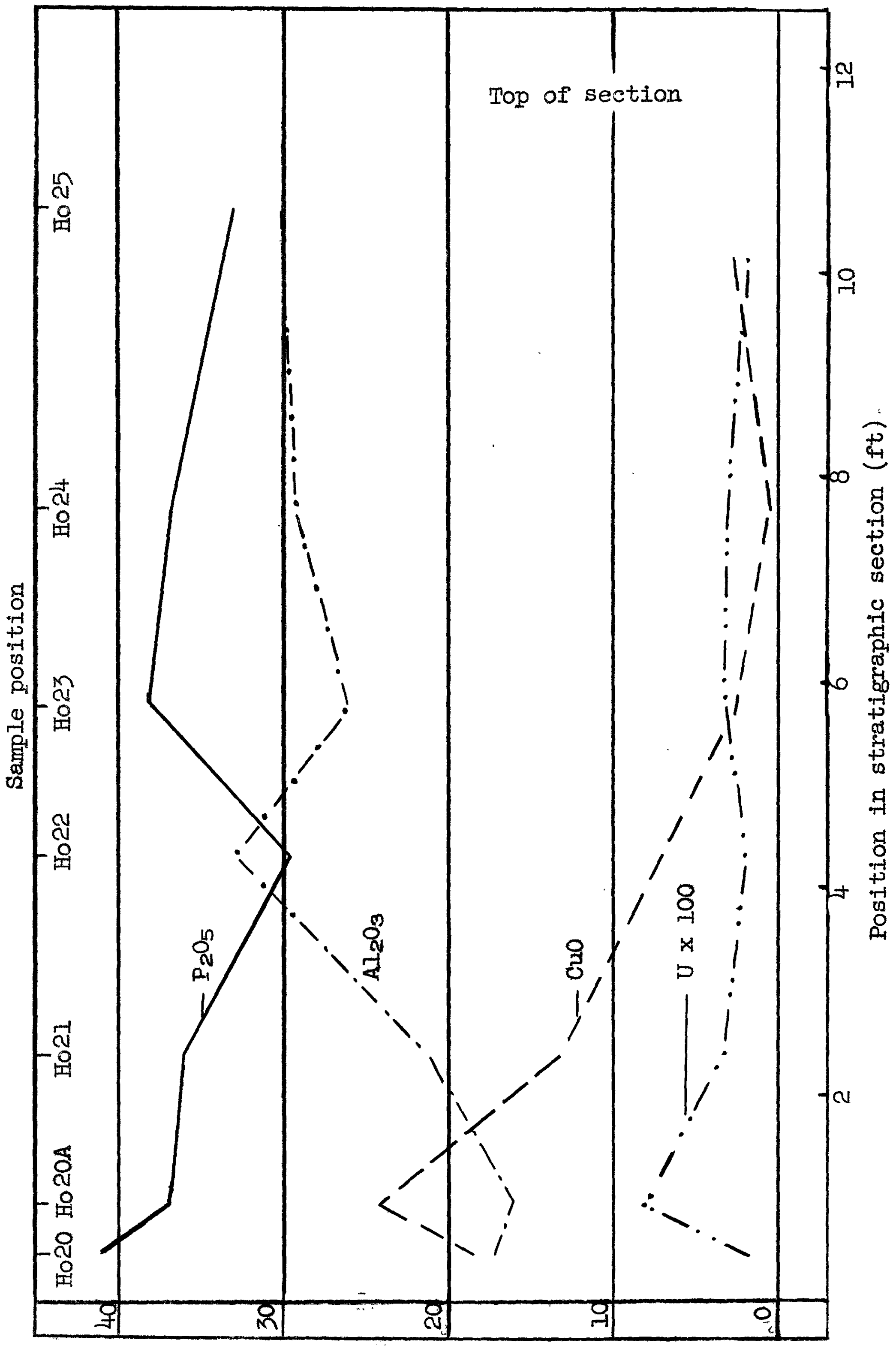


Figure 7.--Distribution of oxides through aluminum phosphate zone at Homeland, Florida, (oxides recalculated on silica-free basis).

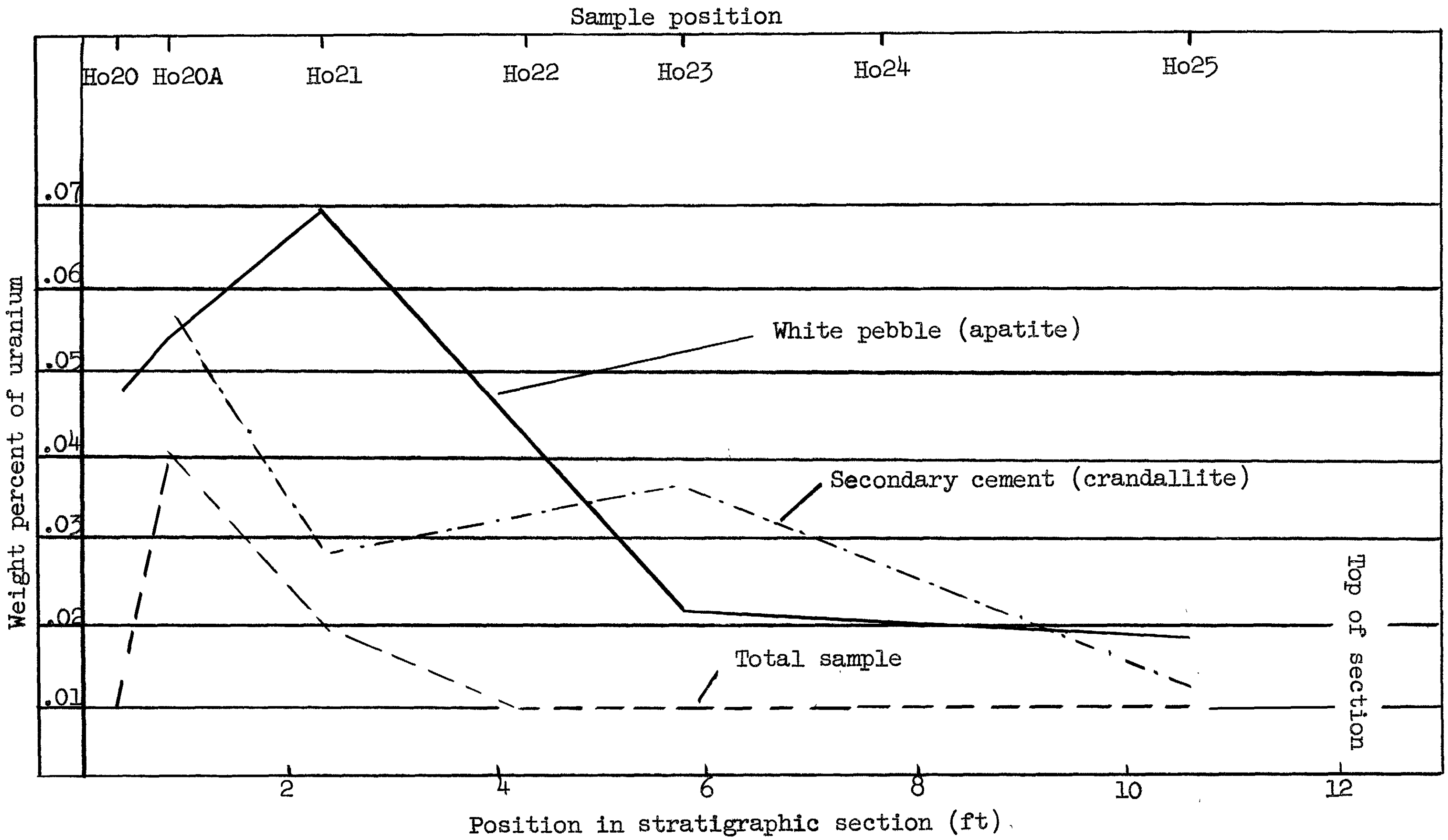


Figure 8.--Uranium distribution in various textural components at Homeland mine, Florida.

the zone which had only 0.023 percent uranium. Furthermore, individual pebbles from the base of the zone contain as much as 0.25 percent uranium. Concentrates of crandallite and millisite from the middle of the aluminum phosphate zone generally contain from 0.03 to 0.05 percent uranium. In contrast, pure wavellite, the dominant mineral in the upper part of the zone, contains only 0.002 to 0.004 percent uranium. Despite the low uranium content in wavellite the upper part of the aluminum phosphate zone generally contains from 0.005 to 0.01 percent of uranium (fig. 7). This fact has led some authors to assume that "...radioactivity is as characteristic of wavellite...as it is of apatite..." (Davidson and Atkin, 1953, p. 13). However, analyses of the wavellitic part of the aluminum phosphate zone usually reveal the presence of trace to minor amounts of calcium (fig. 7) which reflects the presence of small amounts of crandallite which can be seen microscopically and in which much of the uranium resides.

The aluminum phosphate zone is commonly underlain by fossil ferruginous hardpans, relict of old ground-water levels. It is also characterized by secondary leaching and vesicularity and by mineral changes which progress vertically through the section. At the bottom, the zone is characterized by softened and bleached apatite pebbles. In the middle, holes represent former pebbles, and crandallite has replaced clay cement and has been deposited from solution within pebble cavities. Upward, wavellite needles replace the clayey crandallite deposits and the original clay cement (fig. 9). This alteration has caused a depletion of CaO, silicate SiO_2, and some phosphate in the upper part, where there is a complementary increase in Al_2O_3 (fig. 7) combined in acid aluminum phosphate, wavellite, $Al_3(OH)_3(PO_4)_2 \cdot 5H_2O$. The wavellite yields downward to the intermediate

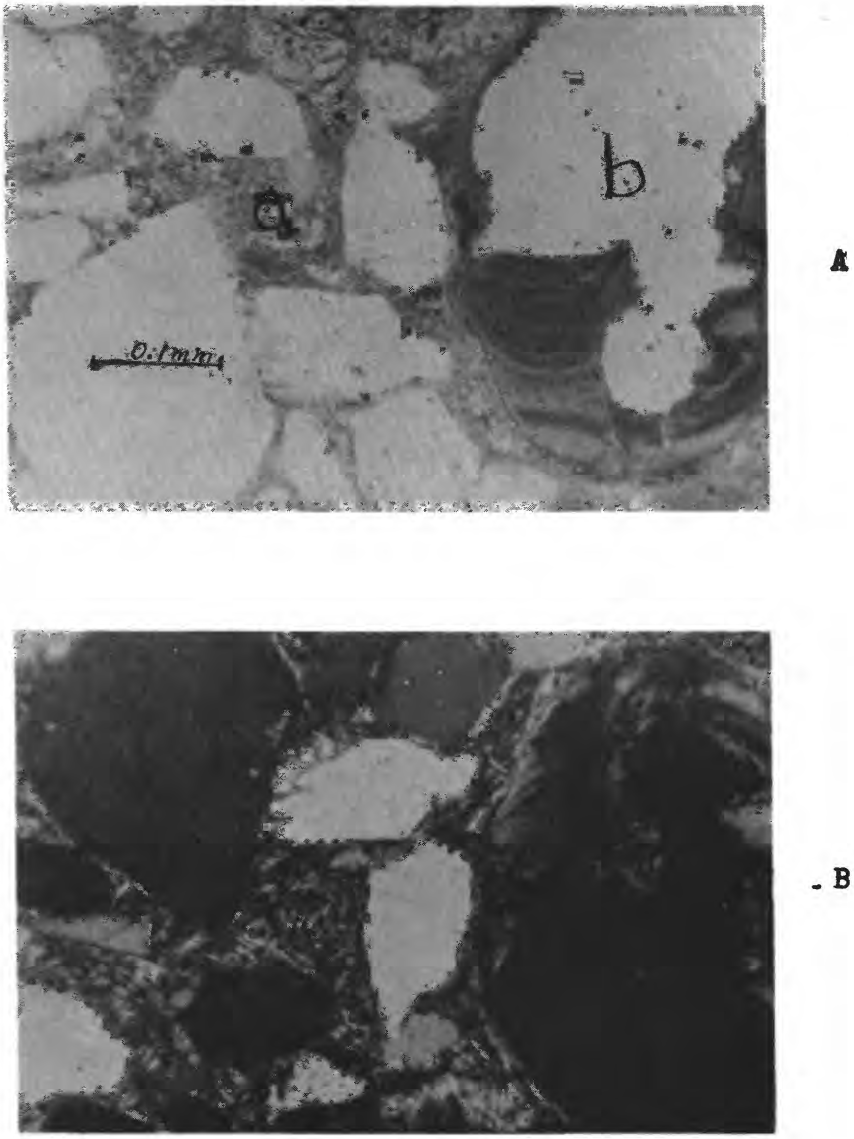


Figure 9.--Phosphatic quartz sandstone from the aluminum phosphate zone, Florida. A--plane polarized light; B--crossed nicols. Original clay cement (a) is now highly porous and almost completely replaced by lathlike wavellite. The large and smoothly bounded cavity (b) is the site of a previous apatite pebble that has been removed by leaching. The cavity is now rimmed and partially filled by layered crandallite, with admixed kaolinite and goethite. The concavely stratified bottom filling of the cavity indicates the downward direction of the original weathering solutions.

Ca-Al phosphates, crandallite and millisite, and finally to the basic apatite at the base of the zone. These features imply a history of postdepositional lateritic alteration by acid ground water. The pattern of uranium distribution parallels that of downward leaching and alteration. Uranium is liberated during the leaching and solution of apatite pebbles in the upper part of the zone. It is kept soluble in the acid ground water and emplaced in the highly porous, partly leached apatite pebbles at the base of the zone where the acids would be neutralized by the yet unaltered calcium phosphate. The correspondence between the curves for CaO and uranium (fig. 7) and the basal enrichment of uranium in apatite (fig. 8) suggest that the uranium substitutes for calcium in the apatite structure. This presupposes that the uranium in apatite is tetravalent, a supposition which will be discussed under oxidation state of uranium.

The theory of supergene enrichment presented above demands the original presence of two or three times more apatite than now occurs in the aluminum phosphate zone. This prerequisite is not supported by the obvious field relations as, in unaltered exposures, it is possible to see a primary stratigraphic change to a less phosphatic clayey sand, from lower to upper Bone Valley (fig. 5). There is evidence, however, that an originally thicker section was available to provide the present enrichment (fig. 10). Briefly, the contact between the upper part of the Bone Valley and the surface mantle of loose quartz sand is irregular in detail and the sands of both zones are virtually identical in size, sorting, and heavy-mineral content. Therefore, a large part of the loose sand mantle is a residue of weathered Bone Valley and the present contact is a lowered one.

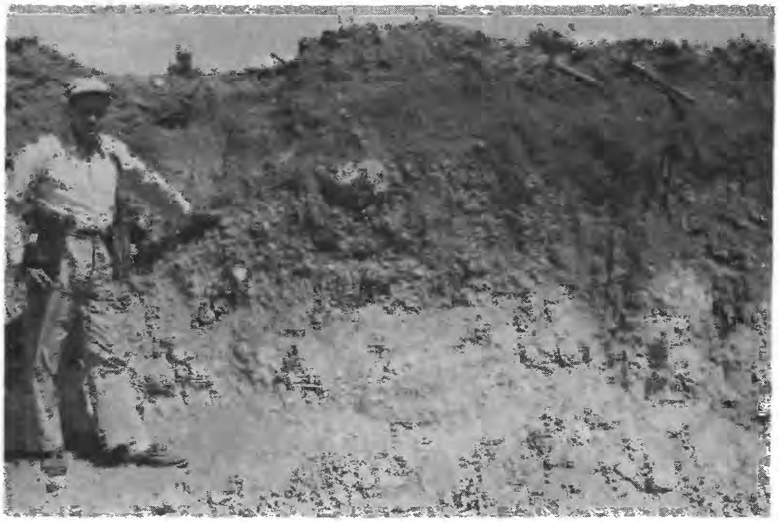


Figure 10.--Details of contact between aluminum phosphate zone (white) and overlying ferruginous sand mantle, Clear Springs mine, Bartow, Fla. Photo illustrates the rubbly and concretionary nature of the weathered zone and the irregular and deeply embayed contact, which, with the residual concretions visible in the overlying sands, reveals the previously higher level of contact.

2. The Cooper marl--residual enrichment.--We have found that unusual and widespread subaerial enrichment of uranium in apatite also occurs in the phosphate deposits of the Cooper marl in the vicinity of Charleston, South Carolina. Being composed principally of limestone, the Cooper marl is only slightly phosphatic. However, it has been postdepositionally weathered and phosphatized; and in the exposures in the vicinity and along the banks of the Ashley River, between Drayton and Middleton Gardens, the deposits are characterized by a thin uppermost zone of nodular induration. The induration takes the form of irregular, discontinuous encrustation and replacement by secondary phosphate. It is obvious that the process was accompanied by moderate leaching, as the indurated fragments that are loose or easily broken out of this zone are marked by cavernous irregularity and prominent pebble and fossil molds, although its fine texture is similar to that of the unweathered underlying rock.

The unaltered Cooper marl "commonly contains about 75 percent lime carbonate and about 2 percent lime phosphate," (Rogers, 1913, p. 187). The Cooper marl was exposed and eroded during Oligocene to Miocene time and later exposed and weathered during Pliocene to Pleistocene time (Rogers, 1913, and Malde, in press). During the last period of weathering the calcite was both leached out of the section and replaced by apatite. The fact that apatite could reprecipitate as a stable phase during weathering suggests that the ground-water alteration was only mildly acid. This is further indicated by the absence of aluminum phosphates or even the intermediate calcium-aluminum phosphates, despite the fact that the region contains appreciable clay.

An immediate consequence of the reforming of apatite at the site of alteration is the refixation of any uranium mobilized by prior solution. This establishes a residual pattern of enrichment. The pattern may be construed as follows:

1. Mildly acid ground water dissolves calcite and apatite.
2. Some, if not much, of the phosphoric acid in solution is immediately neutralized by reaction with the remaining calcite of the marl, producing secondary apatite.
3. Most of the uranium in solution is taken up by the newly formed apatite.

This scheme indicates a disproportionate enrichment of uranium as a result of its preferential uptake in the apatite structure. It has been possible to develop conclusive data in support of this in the phosphates of the Cooper marl. Malde in his study of the Cooper marl noted that "...the uranium content is rather uniform, ranging between 0.001 and 0.005 percent, rarely as much as 0.007 percent and averaging about 0.003."

In contrast to these observations of the prevailing tenor in the unaltered marl, table 13 presents analyses illustrating the overall magnitude of enrichment in the hardpan collected in the area between Rantowles Creek and Ashley River.

The analyses in table 13 demonstrate enrichment of both apatite and uranium, the latter quite pronounced. The selective enrichment of uranium may be shown by comparing analyses of unaltered marl and the overlying fragments of cavernous hardpan from the same exposure (table 14). It should be observed that the enrichment in P_2O_5 is only 6 fold whereas that in uranium is 15 fold.

Table 13.--Examples of phosphate- and uranium-enriched hardpan in Cooper marl near Charleston, South Carolina.

Location	Percent U 1/	Percent P_2O_5 2/
Magnolia Gardens, exposure on west bank of Ashley River	0.048	22.1
Andrews, borrow pit on west side of State Highway 161, half a mile north of Andrews	0.061	28.3
Ashley River banks, west bank at road from Olive Branch Church	0.048	24.8
Ashley River banks, east bank 1.25 miles south of Lambs	0.038	25.8
Bulow Mines, 2 miles southwest of Fort Bull on Fort Bull-Red Top Highway	0.043	27.1
Micah Jenkins Nursery, U. S. Highway 61, half a mile west of St. Peters Church	0.087	24.7

1/ Analyst, G. J. Daniels, U. S. Geological Survey.

2/ Analyst, A. R. Schrenk, U. S. Geological Survey.

Table 14.--Comparison of phosphatized and primary Cooper marl from Lambs, South Carolina (300 yards above old railroad terminus on west bank of Ashley River).

	Percent U 1/	Percent P_2O_5 2/
(a) Unaltered marl	0.005	4.0
(b) Phosphatized hardpan	0.074	25.9
(c) Enrichment factor (b/a)	15	6

1/ Analyst, G. J. Daniels, U. S. Geological Survey.

2/ Analyst, A. R. Schrenk, U. S. Geological Survey.

Another illustration of preferential uptake of uranium during weathering of apatite is obtained by comparing different nodules from the same hardpan samples of phosphatized Cooper marl. At several localities contiguous fragments differed markedly in color, from dark brown to light tan or gray. The lighter color was ascribed to the bleaching effects of oxidative subaerial weathering. On the assumption that the lighter fragments had thus undergone more of such weathering, light and dark fragments were analyzed separately with the thought that differences in uranium content would be shown and that differences in other constituents would reveal the relation of the uranium content to weathering history. The chemical results are given in table 15. Table 16 gives the composition of the same samples by semiquantitative spectrographic analysis.

The two samples are located approximately 4 miles apart and are representative of hardpan and weathering conditions over a wide area; nevertheless, the chemical changes illustrated by the two comparisons are remarkably uniform for secondary subaerial processes. It is apparent from the spectrographic analyses that the differences between the contiguous dark- and light-colored members of each pair are due to weathering. In each pair the relative quantities of Si and Al increase and the iron content drops in the light member. The changes are not large and are of comparable magnitude in each pair. The fact that the carbon content is the same for both members of one pair and is even greater in the light-colored member of the second pair in table 15, proves that the color change was not brought about by oxidation of organic matter as originally supposed. Instead, it is obviously the result of leaching of ferric iron. The persistence of ferrous iron in each case indicates that the leaching was

Table 15.--Variation of enrichment with weathering in phosphatized Cooper marl, South Carolina.

Sample and location	Percent U 1/	Percent P_2O_5 2/	Percent			Percent organic carbon 4/
			total Fe	FeO	Fe_2O_3 3/	
Dark fragment, Ninemile Station, Southern Railroad	0.035	27.0	1.04	0.40	1.04	0.5
Light fragment, half a mile northwest of Goodrich, stream bank, east of railroad trestle	0.11	26.9	0.57	0.38	0.40	0.5
Dark fragment, roadcut, one mile south of Lambs	0.064	27.2	0.73	0.34	0.66	0.6
Light fragment, on Charleston Road	0.12	25.5	0.35	0.38	0.07	1.1

1/ The uranium analyses were made on the filtrate of a nitric acid leach. Additional analyses on the total sample indicate that all the uranium occurs in the soluble, phosphatic fraction of the sample. Analyst, G. J. Daniels, U. S. Geological Survey.

2/ Analyst, A. R. Schrenk, U. S. Geological Survey.

3/ Analyst, A. M. Sherwood, U. S. Geological Survey. (Total iron and FeO determined chemically; Fe_2O_3 computed by difference.)

4/ Analyst, A. B. Caemmerer, U. S. Geological Survey.

Table 16.--Semiquantitative spectrographic analyses of phosphatic hardpan from the Cooper marl.[1] Analyst, Katherine E. Valentine, U. S. Geological Survey.

Sample location:	Ninemile, South Carolina		Lambs, South Carolina	
	dark (less weathered)	light (more weathered)	dark (less weathered)	light (more weathered)
Percent range				
Over 10	Ca P	Ca P	Ca P	Ca P
5-10	--	--	--	Si
1-5	F Si Na	Si F Al Na	Si F Na	Al F Na
0.5-1	Al Fe	--	Al Fe	--
0.1-0.5	Mg Sr K	Fe Mg K Sr U	Mg K Sr	Mg Fe K Sr U
0.05-0.1	Ti	Ti	Ti	Ti
0.01-0.05	B Ba V Y	B Li Ba V Mn Y	Li B Ba V Y	B V Ba Y Li
0.005-0.01	Li Mn Ni	Ni	Ni	--
0.001-0.005	Zr Cr Yb La Sc	Cr La Zr Sc Yb	Zr Cr Mn La Yb Sc	Ni Sc Zr Cr Mn La Yb
0.0005-0.001	--	--	--	--
0.0001-0.0005	--	--	--	--
0.00005-0.0001	Be	Be	Be	Be
0.00001-0.00005	--	--	--	--

---

[1] Order of precedence gives relative percent content; thus in the dark member at Ninemile, F is greater than Si, and Mg is greater than Sr.

accomplished by reducing solutions, a fact further indicated by the persistence or increase in organic carbon.

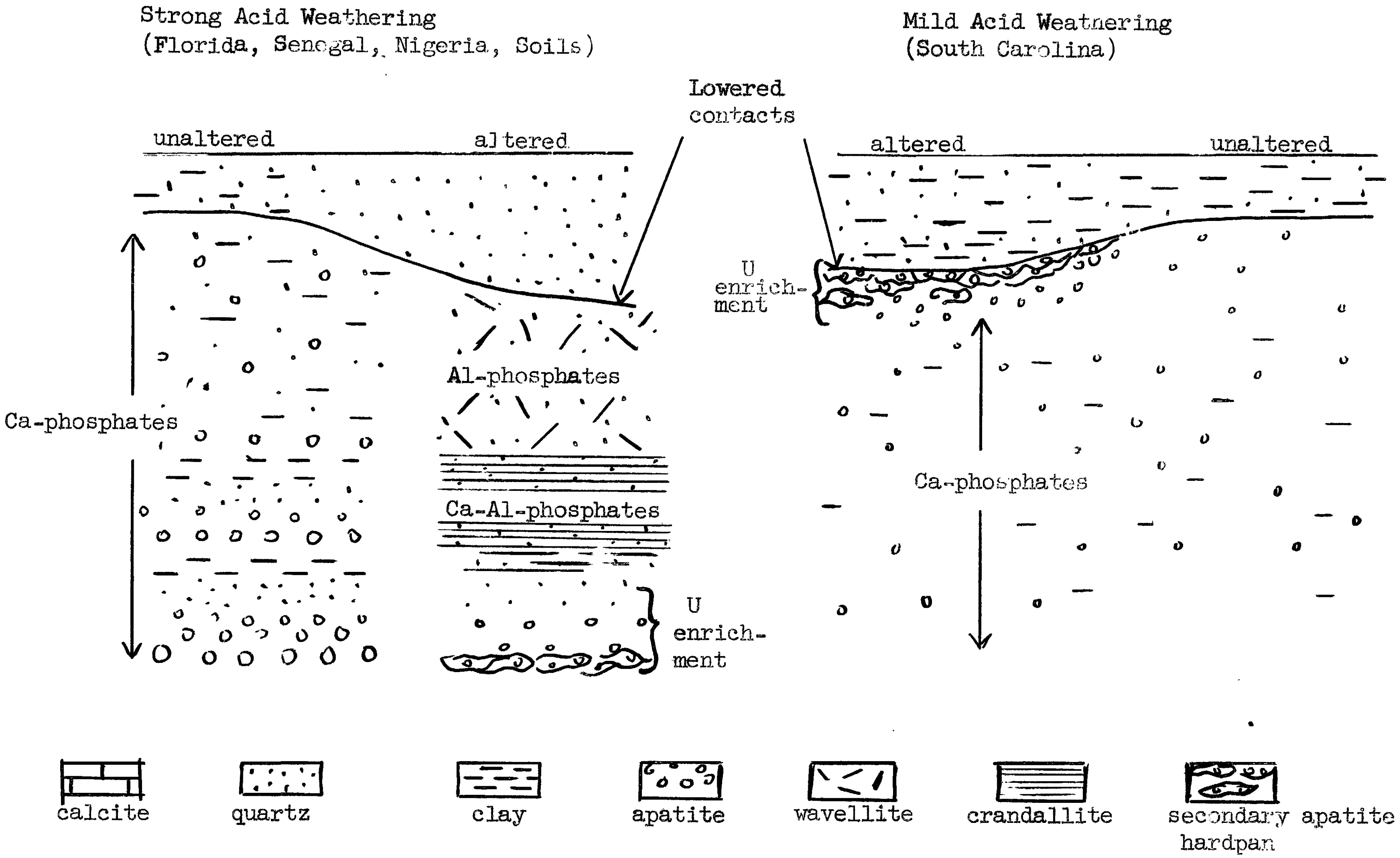
It is suggested that mildly acid humate solutions, derived from the organic-rich soils which are common in the Ashley River flood plain, removed the iron by the formation of organo-ferric complexes and thus effected a partition between ferrous and ferric iron. The solutions dissolved out slight amounts of the other soluble constituents, apatite and undoubtedly calcite. This is demonstrated by the uniform decrease in P_2O_5 content in both pairs. This caused a slight residual enrichment in the relatively insoluble constituents, quartz and clay; hence, Si and Al both increase in the light members (table 16).2/ Thus, the light members of each pair reflect substantially more contact with ground-water solutions, and during such contact, appreciable quantities of uranium were taken out of solution by the apatite. The fact that the bulk chemical changes are small (for example, P_2O_5 and table 16) proves that residual enrichment cannot explain the 2- to 3-fold uranium enhancement of the light over the dark nodules. Patently, the residually enriched uranium of the nodules throughout the region is frequently augmented by significant additions of uranium from ground water.

2/ It is possible that in the Ninemile sample only the relative proportions of Si and F have been reversed. However, in view of the systematic changes in Fe and Al being demonstrated for both samples, it is believed that the Si in the light member of the Ninemile sample actually has increased as in the unambiguous case of Lambs.

Contrasting modes of enrichment in mild versus intense weathering.--In comparing uranium distributions within the Bone Valley formation and the Cooper marl, it becomes evident that two largely different patterns of regional enrichment prevail during weathering, despite the fact that the primary mechanism of enrichment is the same, namely, the takeup of uranium from ground water during weathering. The patterns of enrichment are governed by the mineral assemblages which in turn reflect the diverse conditions and environments of weathering. Figure 11 summarizes and contrasts the results.

In South Carolina the picture is a simple one of uranium enrichment occurring concurrently with the production of apatite at the zone of weathering. The weathering does not appear to have been very intense, as the zone it has affected is quite thin and the mineral transformations are not profound, involving merely the leaching of calcite and apatite and the reprecipitation of apatite. As a result, the zone of enrichment, coinciding with the zone of appreciable weathering is restricted to the uppermost part of the section and migrates only as weathering reduces the section to inert constituents (fig. 11).

In Florida, and in Senegal (Capdecomme, 1953) and Nigeria (Russ, 1924), the prominence of aluminous phases implies a regime of highly acid, lateritic weathering such as would be expected in these tropical areas. The development of purely aluminous phosphate (wavellite) in the upper parts of the weathering zone in turn excludes the concentration of uranium, and the enrichment zone migrates to where calcic phosphates occur (fig. 11), and, accordingly, uranium content increases progressively down section, achieving moderate concentration in the crandallite zone and causing a



nature of new phases:	acid; Al- and Ca-Al-phosphates	basic to neutrals secondary apatite
process :	phosphatization of clay	phosphatization of limestone
type of enrichment :	supergene	residual
hardpans :	at base of weathered section, controlled by ground water	at surface of active weathering

Figure 11.--Contrasting modes of weathering alteration and uranium enrichment in phosphorites.

supergene enrichment in the base of the entire zone where weathering is incipient and apatite still abounds.

The deduction of two different intensities of weathering, strongly and weakly acid, from two different gross petrographies, might be questioned on the grounds that the South Carolina section, containing primary calcite, would have so much greater neutralizing capacity from the Florida section that acid phases could not be generated. In answer to this it can be noted that the Senegalese deposits contained limestone and dolomite but were nevertheless altered to crandallite and other aluminum phosphates. In addition it has been shown that the excessive enrichment of some of the Cooper marl nodules must represent ground-water enhancement beyond the pure residual enrichment of adjoining nodules. This ground-water enhancement implies considerable additional ground-water seepage; yet the apatite, a basic to neutral compound, has remained as a stable phase despite the fact that clays abound in the overlying marls and metasomatic alteration of apatite to aluminum phosphates is rather common under similar conditions in soils. Presumably the acidity was quite low, as even traces of aluminum phosphates or intermediate phases are absent in hardpan of the Cooper marl.

Brown-rock phosphates of Tennessee--residual concentration.--The "brown-rock phosphates" of central Tennessee are a prominent example of residual phosphate accumulation and they were studied for residual concentration of uranium. The brown-rock deposits occur mainly as a residual blanket surmounting the Bigby formation of Middle Ordovician age, (Hayes and Ulrich, 1903) crossbedded formation in which apatite occurs sparsely concentrated within topset and foreset intercalations, and also weakly disseminated throughout the limestone. The deposits "...occur only in areas where limestone of the Bigby formation directly underlies the soil..." (Alexander, 1953) and are absent when mining extends into hillsides where fresh limestone is encountered. It is evident that the deposits were formed during Cenozoic weathering by preferential solution of the limestone (fig. 12). In many areas the residuum occurs as fillings of solution-enlarged joints locally known as cutters. Within such cutters it is possible to sample both the weathering concentrate and the adjoining, closely related parent material.[3] Analyses for one such set of samples from the Akin mine of the Tennessee Valley Authority at Columbia, Tennessee, are presented in table 17. The relation of these samples to the stratigraphy is shown in figure 13.

Table 17.--P_2O_5 and uranium content of weathered and fresh Tennessee phosphates, Akin mine, Columbia, Tennessee. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

	Percent P_2O_5	Percent U
(a) Limestone of the Bigby formation	1.60 1.60	0.00004
(b) Brown-rock phosphate	27.0 27.4	0.00074
(c) Enrichment factor (b/a)	16	18

---

[3] Exact stratigraphic equivalence of these samples cannot be assumed due to draping and compaction within the "cutters."

Figure 12.--Mined out area of Tennessee brown-rock phosphates, Akin mine, Columbia, Tenn., showing control of rectangular joint system in the origin and distribution of the residual phosphates. Pinnacles and blocks of unaltered, crossbedded phosphatic limestone of the Bigby formation occur in rows flanking the valleys created by weathering and mining along the master joints. The subsidiary joint set may be seen dividing and separating individual blocks. Phosphate has been mined from all of the depressions.

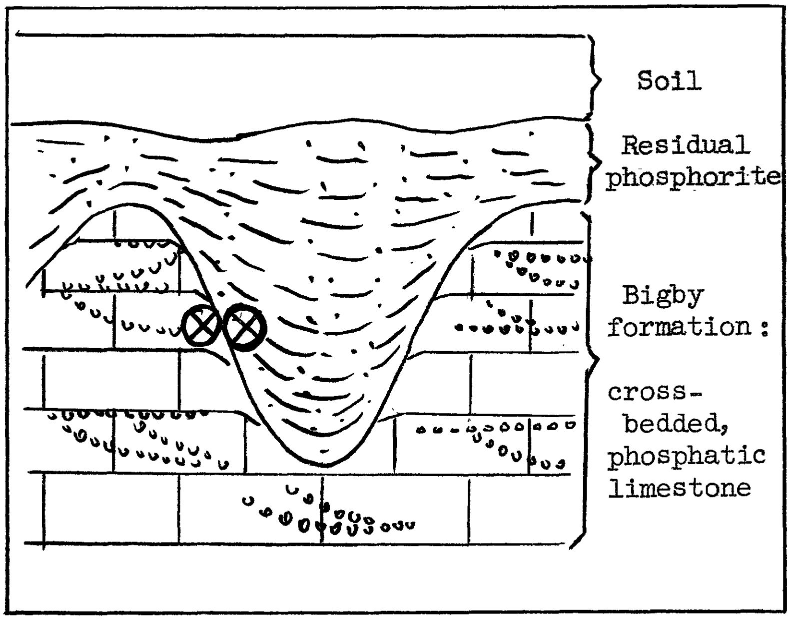


Figure 13.--Sample locations ⊗ for comparison of brown-rock phosphates with parent limestone in Tennessee.

The figures above may be taken as a demonstration of purely residual enrichment. In view of the difficulties in analyses of such small quantities of uranium the differences between the concentration factors of 16 and 18 may be considered negligible. The striking contrast of the above to results in South Carolina (compare table 14) where the enrichment factor for uranium is far greater than for P_2O_5, serves to emphasize the partially external nature of the ground-water enhancement of uranium in the South Carolina deposits.

Secondary emplacement of uranium in bones

Lacking the economic and geologic interest of the phosphorites, bones have not been extensively studied. However, certain well established generalizations may be drawn from available information. Analyses presented by Hébert (1947), Oakley (1955a,b), and Jaffe and Sherwood (1951), all show fresh bone of marine or terrestrial organisms to be essentially nonuraniferous. In addition, comparisons of radioactivity of Cenozoic human and animal bones (Oakley, 1955a,b), reveal that uranium content increases with time, an indication of postburial uptake. As in the guano-derived phosphorites, uranium uptake in bones parallels fluorine uptake; apatite of all types is a favorable receptor for both of these elements.

In view of the above facts and the experimental extraction of uranium from solution by apatite (Moore, 1954) and by glycol-ashed [4] modern bone (Neuman and others, 1949a,b), it seems fairly certain that the uranium of fossil bone is due entirely to secondary enrichment from ground water or marine sources. As Davidson and Atkin (1953) have pointed out, the most

---

[4] A procedure for removing tissue and organic matter.

uraniferous fossil bones come from continental strata of gravelly nature and high permeability. In the highly quartzose and felspathic terrestrial deposits, a fossil bone may be the most, and possibly the only, favorable host for uranium (and fluorine). In such circumstances, ground water charged by regional sources of uranium may effect unusual concentrations of uranium in isolated bones or phosphorite nodules and cause an enrichment far greater than that of the enclosing rocks. Thus, Smith and Bradley (1952) report dinosaur bones from the Cloverly formation which range in uranium content from 0.085 to 0.135 percent, whereas the enclosing rocks contain only 0.001 to 0.005 percent uranium.

Denson and Gill (1956) have shown that the highly uraniferous lignites of the Fort Union and Hell Creek formations in northwestern South Dakota and eastern Montana have derived their uranium from percolating ground waters which were (and still are) enriched by leaching of the overlying tuffs. Undoubtedly, the fossil bones from these formations have become uraniferous through the same agency. The titanothere bone from the Hell Creek formation (table 5) exemplifies this type of enrichment. It is probable that the Miles City fossil (W-3841, table 5) from an unknown surface exposure in the same region derived its unusual uranium content in the same manner.

Petrographic evidence of the mode of such postdepositional enrichment may be seen in figure 14, an autoradiograph of specimen W-3841. It should be noted that the most uraniferous (the lightest) parts of the bone are the peripheral zones and the cavernous and highly permeable internal structures. In contrast to these areas, the intermediate dense areas are relatively low grade. Obviously uranium concentration bears no relation

Figure 14.--Autoradiograph of fossil bone (2x).

to the pronounced difference in apatite concentration. In addition, it was determined by X-ray powder diffraction analysis of different portions of the specimen that the apatite type is the same throughout, and further analyses on separated material showed that the carbon-rich fraction has less uranium than the mineral fraction. Evidently accessibility to solutions was the main control on the localization of the uranium.

Marine enrichment and reworking

It has been shown that postdepositional alteration can cause large variation in the uranium contents of apatite deposits and that many of these variations can be ascribed directly to ground-water leaching or enrichment. This does not, however, explain the nature of the apparently primary variation in unaltered materials. This problem has two aspects, illustrated by tables 11 and 18. Table 11 shows that similar materials from different deposits can differ significantly in uranium content. Thus, the Moroccan deposits, composed of primary apatite nodules of simple texture, have a much higher uranium-to-phosphate ratio than the comparable primary, simple nodules of the Hawthorn formation.

Table 18 demonstrates, in terms of the Bone Valley and Hawthorn formations, the extent to which the components of the same deposits may differ in uranium content.

The following facts are evident from table 18.

1. Pebbles, which are complex in texture, are richer as a class than pellets, which are simple in texture.
2. Pellets from the Bone Valley formation are richer as a class than those from the Hawthorn formation.

Table 18.--Uranium content of representative clastic apatite from the Land-Pebble phosphate field, Florida. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

Locality	Sample no.	Percent uranium
Individual apatite pebbles		
Bone Valley formation, Bonny Lake mine, Ridgewood, Florida	B.L.-1	0.011
Do. do. do.	B.L.-2	0.018
Do. do. do.	B.L.-3	0.016
Do. Homeland mine, Homeland, Florida	Ho-14	0.032
Do. do. do.	Ho-15	0.022
Do. do. do.	Ho-16	0.015
Do. do. do.	Ho-17	0.021
Apatite pellets (composite samples)		
Hawthorn formation, Sarasota, Florida		0.0059
Do. Venice, Florida		0.0067
Do. Land-Pebble field, Florida		0.0045
Do. do.		0.0071
Do. do.		0.0075
Bone Valley formation, Varn mine, Fort Meade, Florida	Va-1	0.008
Do. do. do.	Va-7	0.011
Do. do. do.	Va-10	0.0115
Do. Homeland mine, Homeland, Florida	Ho-12	0.0127
Do. do. do.	Ho-13	0.0123
Do. do. do.	Ho-14	0.0089

It should be noted that the texturally complex pebbles represent materials that have sustained two or more cycles of erosion and deposition. In addition, the nodules of the Bone Valley formation differ from those of the Hawthorn formation only by the fact that the former have been reworked from the latter. The differences in uranium content cannot be explained in terms of relative concentration, as it has been shown (Cathcart, 1956) that the coarse pebbles as a class contain less P_2O_5 than the finer materials. This fact is due to the conglomerate nature of the pebbles which are generally found to contain quartz and carbonate diluent.

All these features coupled with field evidence of stratigraphic unconformity between the Bone Valley formation and the underlying Hawthorn imply a record of marine transgression with many pulses of reworking. It seems reasonable to suppose the re-exposure to sea water sustained by the reworked Bone Valley material allowed additional uptake of uranium. Thus, the uranium content of the complex pebble components in the Bone Valley is enhanced by increments of uranium during successive cycles of reworking. The pellets in the Bone Valley, also reworked from the Hawthorn, are correspondingly higher in uranium than the pellets in the Hawthorn. Within the Bone Valley, however, the pellets are expectably lower than the pebbles as they evidently have not sustained working as frequently, being more prominent above the basal conglomeratic zone, and lacking the textural complexity of the pebbles.

It is possible to test the hypothesis of uranium enrichment during reworking by comparing the autoradiographs of a complex pebble and a pebble of first generation. The results of such a test are shown in figure 15. It should be noted that the complex pebble is not uniformly radioactive, in

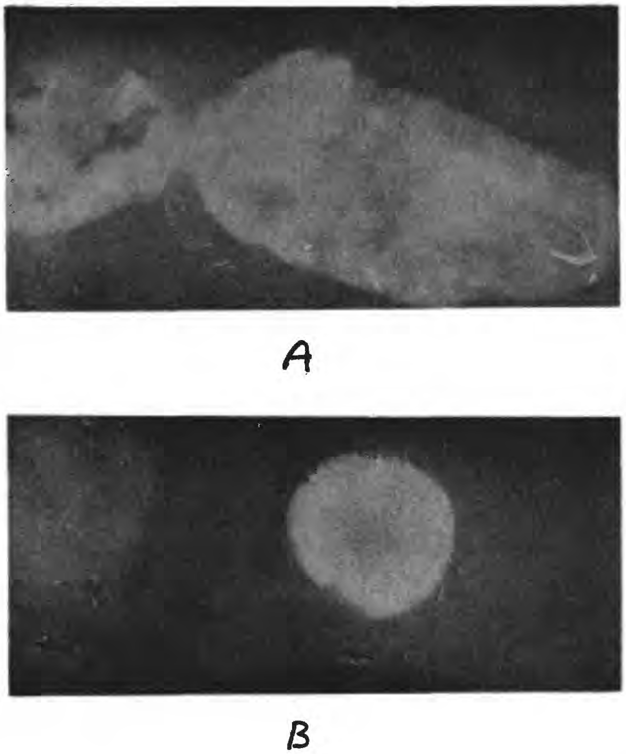


Figure 15.--Autoradiographs of (A) reworked and (B) first cycle pebbles.
(Actual size)

contrast to the prevailing uniformity of the simple pebble. Moreover, within the reworked pebble the most radioactive parts are the oldest or reincorporated materials. The pronounced peripheral enrichment shown by the fossil bone autoradiograph (fig. 14) demonstrates the mode of occurrence that would be expected if the pebbles owed much of their uranium to ground-water enrichment.

The absence of such peripheral enrichment or of any gradational enrichment from the surface inward, regardless of texture, supports the conclusion that ground-water introduction of uranium was not operative. The fact that the intensity of radioactivity varies with the textures created by reworking provides proof of uranium emplacement during the marine reworking. It should be clear that reworking, per se, is merely the mechanism of exposure to the marine source of uranium. Fortunately, however, reworked materials provide a demonstration that increased exposure to source results in increased uranium content.

CRYSTALLO-CHEMICAL NATURE OF URANIUM IN APATITE

General statement

It seems clear that uranium in phosphate deposits cannot be accounted for by discrete uranium phases, by absorption, or by loosely adsorbed ions, radicals, or phases. This follows from several lines of evidence in the preceding sections:

1. The lack of uranium minerals;
2. the fluorescence of uraniferous apatite;
3. the lack of correlation of uranium content with any physical property such as size, magnetism, color; and the inability to concentrate uranium by physical means;
4. the inability to selectively leach uranium;
5. the lack of abnormal concentrations in specific petrographic types of apatite.

Moreover, nuclear-emulsion studies of many phosphorite samples from the Bone Valley and Phosphoria formations have shown that the uranium atoms are intimately dispersed within apatite rather than locally segregated. Figure 16 is a photomicrograph showing the alpha-track distribution obtained from an apatite-cemented arkose from the Gas Hills area of Fremont County, Wyo. Concentrates of cement from this sandstone are found to contain uranium in the tenths of a percent range. The tracks shown in the photomicrograph are the recorded paths of alpha particles emitted during the disintegration of individual radioactive atoms. The intimate and homogeneous distribution of uranium which can be inferred from the lack of clustering or of a preferred pattern in the track

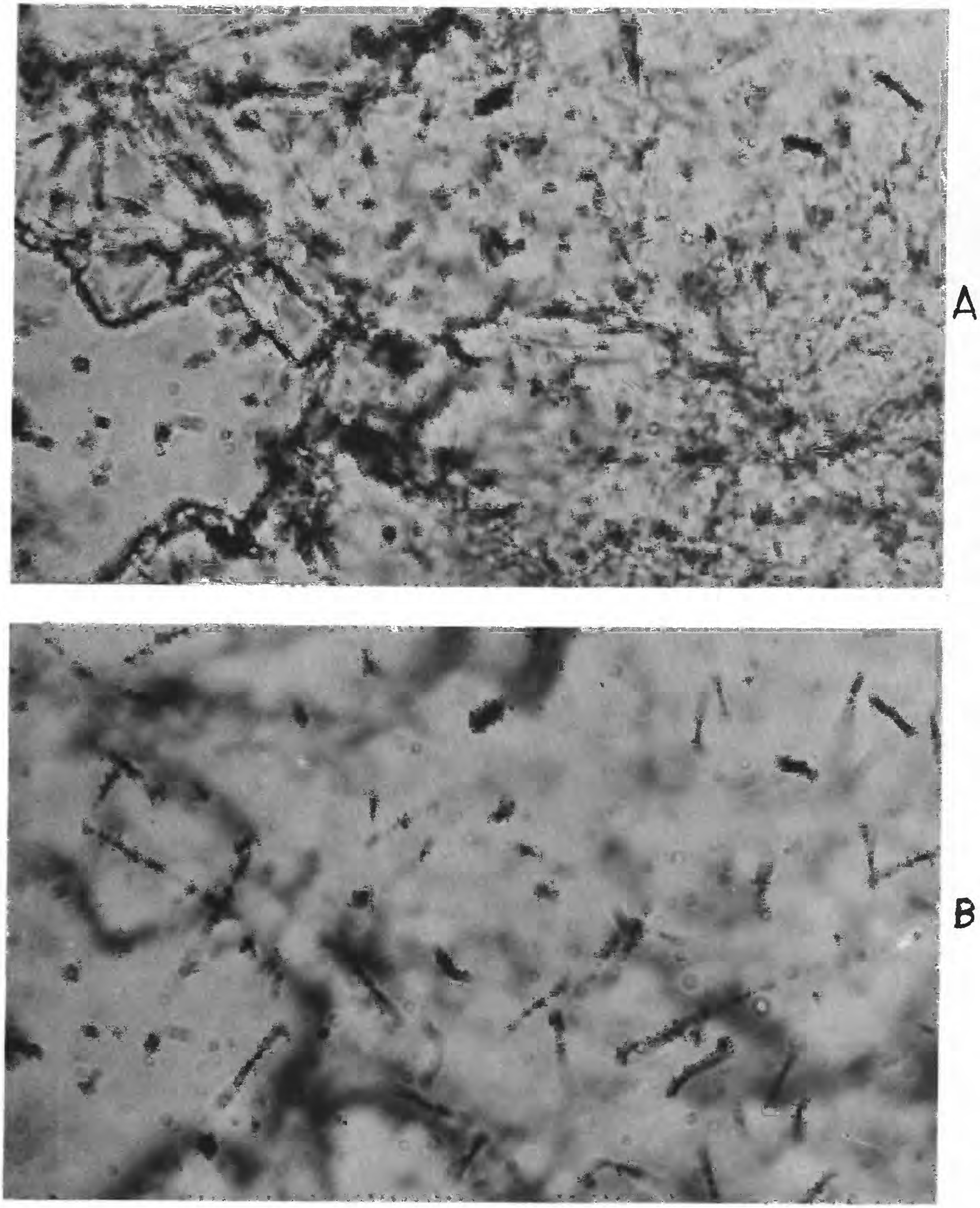


Figure 16.--Photomicrographs of arkose with apatite cement. A. Thin section alone. B. Focused on emulsion, showing alpha tracks from intergranular apatite cement.

31803

distribution is typical of unaltered phosphorite. The uranium distribution has been illustrated with the Fremont County apatite because its high uranium content allows clearer results than are normally obtainable with lower grade materials, which demand exposures of several months and frequently result in fogged emulsions. The Fremont County apatite serves the additional advantage of demonstrating that even in highly uraniferous apatite random dispersion prevails rather than local concentration.

The evidence summarized above and the nuclear-emulsion results indicate that uranium occurs as an integral part of the apatite structure. The evidence from the aluminum phosphate zone of the Bone Valley formation in which uranium and calcium contents parallel one another (fig. 7), despite the fact that one is a mere trace and the other a major constituent, indicates that uranium substitutes for calcium in apatite.

Substitution of uranium for calcium in apatite

Theoretical considerations

The substitution of uranium for calcium is crystallographically plausible in terms of U^{+4} which has an ionic radius (IR = 0.97 A) virtually identical to that of calcium (IR = 0.99 A). The problem of maintaining electrostatic neutrality in substituting a tetravalent for a divalent ion may be reasonably discounted in this case for two reasons. First, the content of uranium in apatite is far too slight to create any appreciable structural dislocation. Thus, a uranium content of 0.01 percent in apatite is equivalent to one atom of uranium for every 2,362 unit cells $[Ca_{10}(PO_4)_6F_2]$ or to one atom of uranium for every 23,620 atoms of calcium!

Second, the deficiency of positive charge created by other replacements common in apatite is orders of magnitude greater than would be required to compensate for the excess of positive charge caused by the replacement of calcium by uranium. For example, from 0.1 to 1.0 percent of sodium is common in apatite as a replacement for calcium, and fluorine plus hydroxyl are in excess in carbonate-fluorapatite to an extent of 0.5 to 1.0 percent.

Relation of uranium to phosphorus.--The suggestion has been made that uranium ions may substitute for phosphate tetrahedra or the phosphorous ion in apatite. Several arguments militate against this hypothesis.

1. The absorption of uranyl by apatite in the laboratory has been found to render phosphate nonexchangeable rather than to proceed by displacement of phosphate as it does of calcium (Neuman and others, 1949a,b).

2. The uranous ion (0.97 A) is too large to substitute for phosphorus (0.35 A) in PO_4 tetrahedra, and it normally requires a much larger coordination with oxygen, as displayed by the eight-fold coordination of U(IV) in UO_2 (Wells, 1950).

3. In the uranium-enriched aluminum phosphate zone of the Bone Valley formation, the uranium concentrates preferentially in the calcium and calcium-aluminum phosphates and is relatively impoverished at the top of the zone (fig. 7) where only wavellite, the pure aluminum phosphate occurs. Despite the fact that the wavellite occurs as an alteration of apatite and crandallite (fig. 9), chemical analyses of pure wavellite reveal that very little uranium is retained by the wavellite in the course of its replacement of the pre-existing uraniferous minerals (Altschuler and others, 1956).

Oxidation state of uranium in apatite

Chemical problems.--Is the uranium in apatite tetravalent? To answer this and questions concerning the industrial recovery of uranium, a method was developed for the analysis of U(IV) in apatite. The details of the method are treated in a companion paper (Clarke and Altschuler, in press).

U(IV) content of sedimentary apatites.--The U(IV) contents obtained on a variety of sedimentary and igneous apatites are given in tables 19 and 23.

The analyses in table 19 reveal a wide spread in the percent of uranium in apatite that is tetravalent. The remainder, in all cases, is safely presumed to be hexavalent in view of the instability, and the absence in natural substances, of tervalent and pentavalent uranium (Garrels, 1955) and of the fact that monovalent and divalent uranium are completely unknown in natural solutions (McKelvey and Carswell, 1956).

Several prevalent notions are open to serious question as a result of these analyses. It was heretofore generally assumed that the traces of uranium are of the same chemical nature in all apatite deposits; that once fixed in apatite, uranium is not changed except insofar as the host mineral is altered; and that the uranium within any single specimen of apatite is entirely hexavalent or tetravalent. These assumptions must all be discarded.

Despite the variety displayed in table 19 the distribution of U(IV) proportions is not haphazard and several important generalizations emerge if the data are regarded in the light of geologic occurrence.

U(IV)/U percents reflect geologic history.--Initially, to establish the validity of subsequent inference, it should be noted that materials with identical histories yield identical results. Thus, samples Ho-14 through Ho-17 in table 19 are composites of the same petrographic fraction

Table 19.--Total and tetravalent uranium content of sedimentary apatites. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

Description	Sample no.	Percent total U	Percent U(IV)	$\frac{\mathrm{U(IV)}}{\mathrm{U}}$ percentage
Bone Valley formation (Pliocene)				
Black pebble	B.L.-1	0.011	0.010	91
Dark pebble	B.L.-2	0.0089	0.0056	63
Fine pebble composite	B.L.-3	0.016	0.013	81
4-8 MM pebble composite	Ho-14	0.032	0.016	50
Do.	Ho-15	0.022	0.011	50
Do.	Ho-16	0.015	0.007	42
Do.	Ho-17	0.021	0.010	48
Apatite pellets	Va-7	0.011	0.005	45
Do.	Va-7a	0.009	0.006	67
Do.	WA-10	0.0075	0.003	40
Do.	PV-5	0.007	0.003	43
Hawthorn formation (Miocene, recently reworked on Gulf Coast beaches)				
Apatite pellets	GP-1	0.0067	0.0039	58
Do.	GP-2	0.0059	0.0037	63
Tennessee phosphates				
Limestone, Bigby formation (Ordovician)	Ak-2	0.00004	0.00001	25
Brown-rock phosphate (Cenozoic weathering)	Ak-1	0.00074	0.00002	3
Moroccan phosphates (Senonian)				
A daily production average	Mor-3	0.012	0.0018	15
Do.	Mor-5	0.012	0.0015	13
Do.	Mor-11	0.008	0.0006	8
Phosphoria formation (Permian)				
Apatite pellets	Conda-300	0.0063	0.0015	24
Do.	RAH-185	0.017	0.003	18

Table 19.--Total and tetravalent uranium content of sedimentary apatites.--Continued.

Description	Sample no.	Percent total U	Percent U(IV)	$\frac{U(IV)}{U}$ percentage
Pacific Ocean, southern California (Miocene)				
Phosphate nodules	69	0.0089	0.0061	69
Do.	106	0.0068	0.0040	59
Do.	127	0.0041	0.0028	68
Do.	158	0.0081	0.0050	62
Do.	162	0.0125	0.0093	74
Do.	183	0.0051	0.0028	55
Fossil bone				
Hell Creek formation	1	0.015	0.0004	3
Taxpayer sample	RW-4468	0.078 0.071	0.054 0.050	70-76
Do.	W-3841	0.85	0.40 1/	--
		0.82	0.50	61
Phosphatic arkose				
Gas Hills, Wyoming		0.74	0.14 1/	--
			0.17	23

1/ Determination from HCl solution; uncorrected for 20 percent deficiency in recovery.

from each of four successive beds in the Bone Valley formation. The particular strata are thin and therefore have the same general relation to the aluminum phosphate alteration higher in the section. Although the total uranium content varies by as much as 100 percent among the samples, the percentage of U(IV) is virtually identical throughout. (It must be recalled that the fluorimetric analyses of uranium are not accurate beyond ± 5 percent.)

The reflection of geologic history in the U(IV)/U percentages is further illustrated by several other groups of samples. The Pacific Ocean nodules, from several localities off the coast of southern California, have sustained different degrees of submarine reworking and are of somewhat composite age, having also sustained accretion to differing extents since Miocene time. They may be described as similar though not identical. In like manner their U(IV)/U percentages are similar but not identical. The apatite pellets from the Hawthorn formation were collected from two beaches along the central west-Florida coast. Both samples represent present-day marine reworking of Miocene apatite. Their U(IV)/U percentages are virtually identical.

Primary marine uranium in young phosphorites is mainly U(IV).--In marine materials which have not been postdepositionally oxidized and which are of relatively young age, more than half of the uranium is tetravalent. Again the nodules from the Pacific serve as an example as they have been interpreted by Dietz, Emery, and Shepard (1942) to have been submerged since their formation during Miocene time. The first three samples in table 19 (B.L.-1, B.L.-2, and B.L.-3), in which 63 to 91 percent of the uranium is tetravalent, were collected from clayey, impermeable strata in the basal conglomerate zone of the Bone Valley formation. Sample B.L.-1 has minute pyrite crystals and petroliferous organic matter dispersed throughout; however, the clay in which it rested was devoid of organic matter and pyrite. The pebble thus reflects the reducing conditions of its time and environment of formation and has not been postdepositionally weathered. Its content of U(IV), 91 percent of the total, is the highest we have found. Samples B.L.-2 and B.L.-3 are from higher strata, contain less organic matter, are lighter colored than B.L.-1, and have no pyrite. Less of their uranium is tetravalent.

Subaerial weathering alters U(IV) to U(VI) in marine phosphorite.--Material that is obviously weathered contains proportionately less U(IV) than comparable or equivalent unweathered material. This may be illustrated by comparing the U(IV)/U percentage obtained from the slightly phosphatic limestone of the Bigby formation with the much lower value obtained from the equivalent "brown-rock" phosphates derived from the Bigby and Cannon by subaerial residual concentration. (See table 19 and fig. 13 for relations of the samples.)

Possible relation of U(VI) content to radioactivity and age.--It may be that the U(IV)/U percentages in marine phosphorites are a function of radioactive disintegration and thus, indirectly, of age. This hypothesis presupposes that all, or most, of their uranium is initially U(IV), a suggestion favored strongly by the analyses of samples from the Bonny Lake mine and the Pacific Ocean nodules. The thesis further demands that the U(VI) present is produced by auto-oxidation, or by some secondary effect whose onset is governed, both as to rate and intensity, by the progress of radioactive decay.

In exploring the possible relations of U(VI) content to age in phosphorites, only three groups of samples may be compared with a modicum of assurance that they have not been weathered. They are (table 19) the Pliocene Bonny Lake pebbles, which contain pyrite and organic matter and were found in green clay beds; the Quaternary Pacific Ocean nodules, which have remained submerged since their formation; and possibly the Permian Phosphoria pellets, which contain minor amounts of organic matter. It may be significant that the two Phosphoria samples show considerably lower U(IV)/U percentages than the other two groups, and that the two latter groups are moderately close in value. However, the extreme view that all of the uranium in apatite is initially U(IV) is not supported by the data. Although, in some cases, (as in the Bonny Lake pebbles) favorable reducing conditions may cause substantially all the uranium in apatite to be taken up as U(IV), the existence of significant amounts of U(VI) in the young and recently dredged Pacific Ocean nodules suggests that the initial U(IV)/U(VI) ratio in apatite is influenced by the oxidation conditions in the marine environment. It is also possible, however, that submarine, postdepositional oxidation can lower the initial U(IV)/U(VI) ratio.

Secondary sources of U(VI) in phosphorite.--Only three analyses for U(IV) have been made on fossil bone; however, the spread in relative proportions of U(IV) and U(VI) (table 19) is indicative of the diversity that might be expected in view of the conceivable variations in the composition of the transporting ground water from which the uranium is emplaced, in the environment of deposition, and in the state of degradation of the organic matter that may be associated with the bones.

Although it is true that apatite readily abstracts U(IV) from solution, in a strongly oxidizing environment the mere presence of apatite is not necessarily effective in producing or even retaining U(IV). To the contrary, it was found that samples of Moroccan apatite pellets and fossil bone which are richly encrusted by hematite have the capacity to oxidize uranous ions in phosphoric acid solutions, as the experiment in table 20 demonstrates.

Table 20.--Effect of highly oxidized samples in the recovery of U(IV) from 1.5 M phosphoric acid solutions. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

Material	Percent 1/ initial uranium		Percent 1/ U(IV) added	Percent 1/ U(IV) determined
	total U	U(IV)		
Synthetic apatite		--	0.050	0.050
Bonny Lake pebbles, B.L.-3	0.016	0.013	0.050	0.061
Moroccan apatite hematite Mor-11	0.008	0.0009?	0.050	0.046
Fossil bone hematite Hell Creek 1	0.015	0.0004?	0.050	0.020

1/ Percents in terms of weight percent of the initial solid sample.

The above data show that the complexing capacities of phosphate and fluoride ions for Fe(III) and U(IV) respectively are not adequate to prevent the oxidation of U(IV) in the presence of excess ferric iron. As this is true in solutions of freely mobile ions, it indicates that slowly dissolving apatite in the environment of such reactions would not prevent the oxidation of U(IV) by excess ferric iron. They also show that the very low values for U(IV) in samples Mor-3, 5, and 11 and Hell Creek 1 in table 19 may be due to oxidation effects during analysis, although it is to be expected that they would be low inherently. In any case the method is not trustworthy for materials with more than trace quantities of oxidizing impurities. It is clear from the above experiment, however, that high U(VI)/U percentages may be anticipated where uranium is emplaced primarily from ground water.

The phosphatic arkose sandstone from the Gas Hills region of Fremont County, Wyo., is a striking illustration of secondary uranium fixation by apatite. X-ray powder-diffraction analyses show the material to be a carbonate-fluorapatite. Deposits of this material occur as cements scattered through the arkosic sandstones and conglomerates of the upper part of the Wind River formation.5/ Associated with them are paints of autunite and other secondary uranyl minerals; however, the sample used was shown by nuclear emulsion study and inspection under ultraviolet light to be free of uranium minerals. The apatite cement is attributed to secondary phosphatization, and the uranium is attributed mainly to secondary

---

5/ All information on occurrence has been obtained from R. G. Coleman, U. S. Geological Survey, who kindly supplied the specimen, the second most uraniferous known to us.

emplacement in the porous cement (R. G. Coleman, oral communication). This interpretation is supported by the occurrence of the uranyl phosphate and vanadate minerals throughout the region.

The alpha-track film of the specimen (fig. 16) reveals intimate and homogeneous dispersion of uranium throughout the cement and a virtual absence of any uranium atom concentrations. It cannot be told whether much or most of the uranium was originally fixed as U(IV) and subsequently oxidized or whether the U(VI) now present was emplaced substantially as uranyl. The local abundance of uranyl minerals and of limonite films in rocks other than phosphorite indicates that oxidizing solutions have permeated the area and have introduced uranium as uranyl.

The material emphasizes that U(VI) like U(IV) can be thoroughly dispersed in apatite and may be emplaced in a manner analogous to that demonstrated by Neuman and his coworkers (1948, 1949a,b). They have shown that glycol-ashed bone will fix appreciable quantities of uranyl ion by exchange with surface calcium. This reaction was found to be surface limited (Neuman and others, 1949b) and involved the displacing of two moles of calcium for every mole of (UO_2) taken from solution and the rendering of two moles of phosphate nonexchangeable. They suggest the formation of a compound analogous to uranyl pyrophosphate to explain these results.

Regarding the form in which uranyl complexes with apatite, several types of compounds should be considered. Uranyl pyrophosphates, or uranyl orthophosphates of the torbernite type could both be stable within the range of conditions presumable (oxidative, weakly alkaline to weakly acid). In addition, complexes of the type UO_2HPO_4 could presumably form by surface reaction with apatite; F. S. Grimaldi (oral communication) verifies that

UO_2HPO_4 could be stable under such conditions. It is believed that uranyl orthophosphate compounds are more probably the form in which primary U(VI) would occur in phosphorites. These would not require the polymerization entailed in pyrophosphate formation and would avoid the anomalous exchange of two divalent calciums for one divalent uranyl group. It is quite possible that an appreciable part of the U(VI) present in unweathered phosphorites is chemisorbed on the surfaces of growing apatite crystallites; and, upon the complete development of the apatite nodules, the U(VI) appears to be intimately and randomly dispersed throughout the apatite. Sheldon (in press) also favors the chemisorption of some hexavalent uranium in the rocks of the Phosphoria formation.

Relative structural favorability of U(IV) and U(VI) in apatite

The above mechanisms share one characteristic in common. Their surface-limited nature is virtually predictable in view of the asymmetry and large size of the uranyl anion (3.4 x 1.4 A, Connick and Hugus, 1952) relative to the calcium ion (IR = 0.99 A). Thus, although the reactions so clearly documented by Neuman and his colleagues involve ion exchange, the results obtained indicate extensive structural rearrangement. It is, therefore, difficult to visualize any intra-crystalline solid solution by such a mechanism, first, because of the structural dislocation involved in formation of pyrophosphate and displacement of two calciums for one uranyl, and second, because the large uranyl anion could not migrate to any extent through the apatite structure. The channels within the hexagonal network of the fluorapatite structure, being barely wide enough to accept the fluoride ion (IR = 1.36 A, Green, 1953), could not accommodate the uranyl anion. Sixty percent of the calcium ions in apatite line the vertical channels and would thus be inaccessible to postdepositional substitution by uranyl. On the other hand, the U(IV) ion could fit easily and migrate to a limited extent within the channels, which are not as fully occupied as the walls and hence offer greater mobility to migrating ions. That such migration occurs is fully substantiated in the replacement of (OH) by F that takes place in fossilization.

Structural considerations thus dictate that much more calcium is accessible for replacement by U(IV) than by U(VI). Furthermore, the U(IV) substitution does not involve any structural dislocation, and the positive charge excess that would result is easily compensated by other known replacements of greater magnitude. It is not surprising, therefore, that samples as uraniferous as RW-4468 and W-3841 (table 19) should have as much as 70 and 61 percent of their uranium in tetravalent form, despite the fact that ground water may be presumed to carry mainly uranyl ions.

Test of uranium and fluorine interdependence in apatite

There are several compelling reasons for detailed examination of the relations between excess fluorine and uranium in marine apatite. These are outlined below:

1. Excess fluorine is characteristic of marine sedimentary apatite, in contrast to normal igneous fluorapatite.
2. Marine apatite is characteristically more uraniferous than igneous apatite.
3. UF_4 could be stable under the pH and Eh conditions of formation, and of subaerial preservation, of marine phosphorite. Although

the formation of independent fluoride minerals is conceivable only under conditions of much greater salinity than those characterizing marine apatite formation (Kazakov, 1937), the possibility of a complex similar to UF_4, as an integral part of apatite, is strongly suggested by the following:

A. The calcium ions lining the channels in the apatite structure are located in the same horizontal plane as the adjacent fluorine ions.

B. These channel calciums are coordinated to fluorine and oxygen (fig. 1), and as the excess fluorine could reasonably replace oxygen, or lodge within the channels in the apatite structure, the existence of UF_4 in apatite may be reasonably postulated, particularly as U^{+4} may be considered to replace calcium.

4. The postdepositional uptake of fluorine and uranium by various forms of sedimentary apatite and bone involve separate replacements; however, their concomitant operation may mask, or be augmented by, their mutual complexing ability.

A general correlation between total fluorine and total uranium was demonstrated in studies of seven Pennsylvanian phosphatic shales of Kansas by Runnels and others (1953). In all likelihood this reflects only the fact that uranium content varies directly as apatite content in unaltered rocks of similar composition in which apatite is the only, or major, uranium host. Similar relationship could be expected in a group of phosphatic limestones and has been demonstrated for Mona Island rocks (fig. 3) and in some suites of rock from the Phosphoria formation (table 9).

The possible genetic relation between excess fluorine and U(IV) in marine apatite should be tested in two ways. On the assumption that all of the uranium was originally fixed as U(IV), excess fluorine should be compared with total uranium. Figure 17 is a scatter diagram on which total uranium is plotted against excess fluorine,[6] as computed from a random selection of 50 of the analyses given by Thompson (1953, 1954) for Phosphoria samples from Trail Canyon, Utah; Coal Canyon, Wyoming; and Reservoir Mountain, Idaho. It can be seen that total uranium is independent of excess fluorine in rocks of the Phosphoria formation.

Assuming that only the U(IV) demonstrably present in apatite was emplaced as such, a comparison was made (fig. 18) of the few data available. The data are compiled in table 21.

The wide scatter of the points in figure 18 indicates that U(IV) and excess fluorine are independent of one another in marine phosphorite. The data are admittedly few; however, the well-defined trends that can be demonstrated to exist among total fluorine, P_2O_5, and uranium, for groups of samples no larger than this (fig. 3, and Runnels and others, 1953), exemplify the extent of mutual dependence that could be expected between F and U(IV) if uranium occurred in apatite as a result of UF_4 formation.

---

[6] Based on 3.8 percent F in pure fluorapatite and 38 percent P_2O_5 in carbonate-fluorapatite. Therefore, excess fluorine is amount in excess of theoretical F/P_2O_5--weight ratio of 1/10.

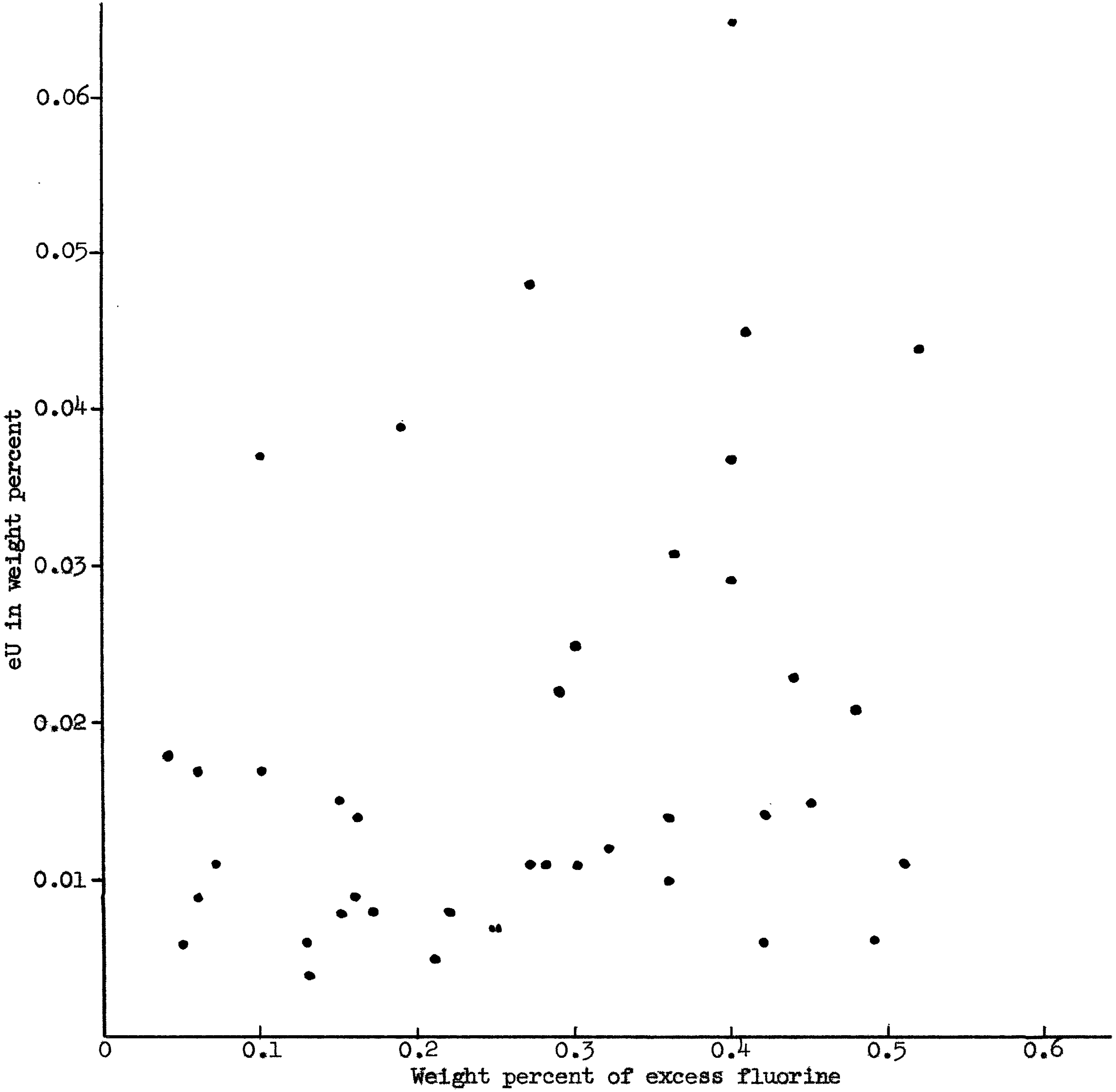


Figure 17.--Uranium versus excess fluorine in Phosphoria formation (data recomputed from Thompson, 1953).

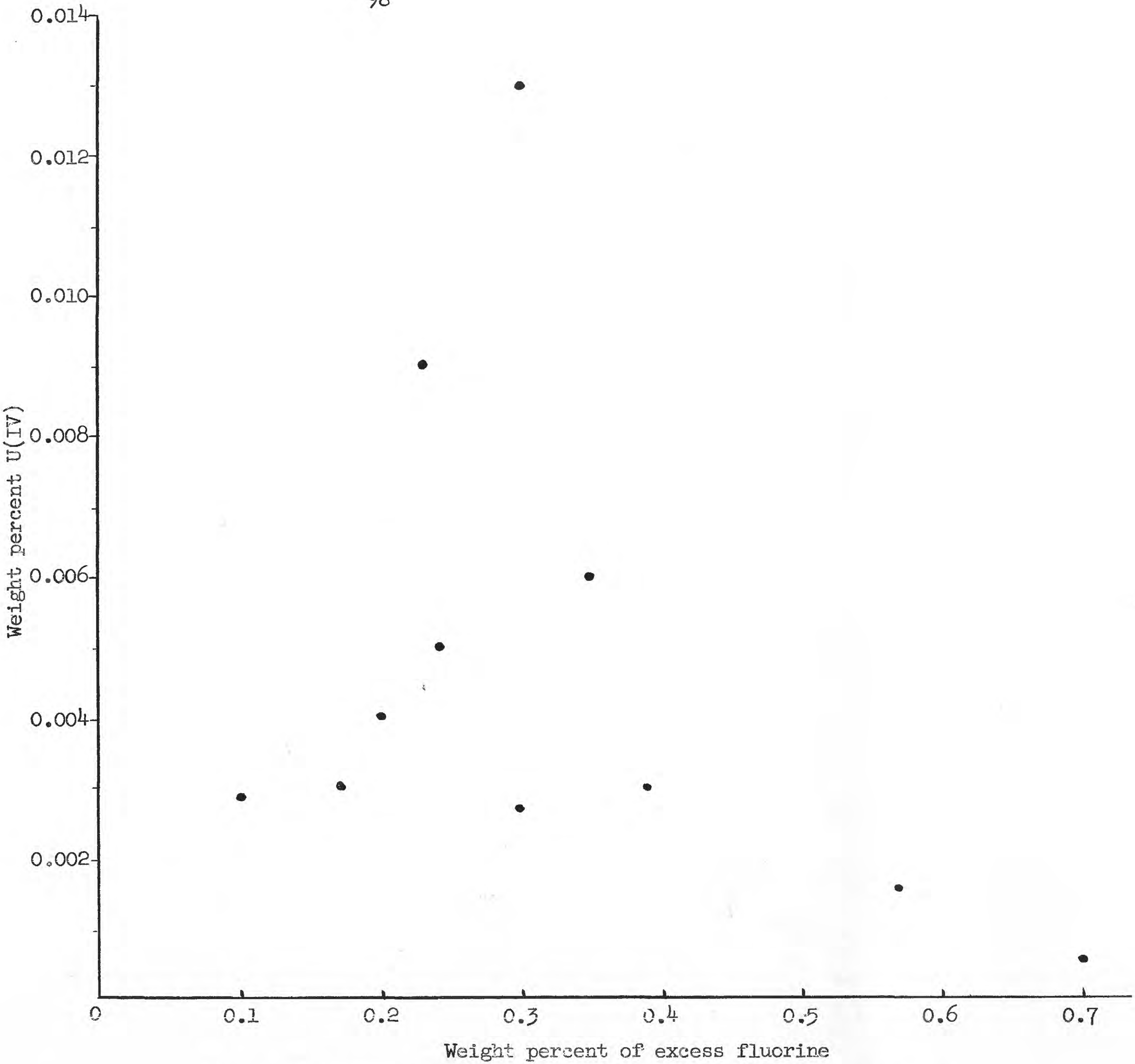


Figure 18.--U(IV) versus excess fluorine in various phosphorites.

Table 21.--Data on excess fluorine and U(IV) in miscellaneous apatite and phosphorite.[1]

Description and location	Sample no.	Percent F	Percent P_2O_5	Percent excess F	Percent U(IV)
Bone Valley formation, Florida, apatite pellets					
Peace Valley mine	PV-5	3.8	34.5	0.3	0.0027
Watson mine	Wa-10	3.8	36.6	0.1	0.0029
Bonny Lake mine	B.L.-3	3.8	34.9	0.3	0.013
Moroccan phosphate, Khouribga, French Morocco (daily production average)	Mor-11	4.05	33.4	0.7	0.0005
Phosphate nodules, Pacific Ocean	69	3.31	29.56	0.35	0.006
Do.	106	3.12	29.19	0.20	0.004
Do.	127	3.07	28.96	0.17	0.003
Do.	158	3.15	29.09	0.24	0.005
Do.	162	2.47	22.43	0.23	0.009
Do.	183	3.36	29.66	0.39	0.003

---

[1] All analyses from U. S. Geological Survey laboratory; F and P_2O_5 on Pacific nodules are given in Dietz, Emery, and Shepard (1942).

Effects of reworking on U(IV) content of apatite

The demonstrated secondary enrichment of uranium in apatite during the course of marine reworking allows the establishment of controls for studying the nature of the uranium extracted from the ocean source. If the uranium additions incident to reworking are mainly U(IV), the U(IV)/U percentages should be higher in the reworked materials of a deposit. Samples were taken in the phosphatic terrace gravels in the vicinity of Charleston, South Carolina, for tests of this thesis. The phosphatic fraction of the samples consisted of sand-size pellets and detrital bone apatite, mainly water-worn shark teeth fragments, plus rounded granules and pebbles of bone and phosphorite. In addition, the samples contained quartz and shell fragments. The coarser material was found to be texturally more complex, indicating more reworking. Accordingly, each sample was split into two fractions on the basis of size and analyzed for P_2O_5, U, and U(IV). The results are given in table 22.

The samples from each locality were fractionated by screening and the obvious shell fragments were handpicked from the coarse fraction in each case. It was not practical to remove shell fragments from the fine fraction. It should be noted in table 22 that the coarse fraction contains less P_2O_5 in all cases, and more uranium in three of the four cases. The lower P_2O_5 reflects the greater textural complexity and greater percent inclusions resulting from reworking. The generally higher uranium content reflects the enhancement of uranium during reworking. The fact that in all cases the U(IV)/U percentages are significantly higher in the reworked materials proves that the additional increments of uranium are largely tetravalent.

Table 22.--Relative contents of U, U(IV), and P_2O_5 in phosphatic terrace gravel in the vicinity of Charleston, South Carolina. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

Location and sample description	Percent uranium	Percent P_2O_5	$\frac{UX1000}{P_2O_5}$	Percent U(IV)	$\frac{U(IV)}{U}$ percentage
Accabee Flats, Ashley River, Charleston, South Carolina					
Acc-1: + 2 mm pebble	0.020	28.4	0.70	0.016	80
Acc-1: medium to fine sand	0.020	31.7	0.63	0.013	65
Acc-2: medium to fine sand	0.018	30.2	0.60	0.013	72
Micah Jenkins Nursery, Johns Island, South Carolina					
Micah-1: + 2 mm pebble	0.027	27.6	0.98	0.021	78
Micah-1: medium to fine sand	0.015	31.2	0.48	0.011	73
Ninemile Station, South Carolina					
Nine-1: + 4 mm pebble	0.037	27.5	1.35	0.025	68
Nine-2: medium to fine sand	0.021	31.4	0.67	0.010	48
Lambs, South Carolina					
Lamb-1: + 2 mm pebble	0.015	28.6	0.52	0.0097	65
Lamb-1: medium to fine sand	0.025	31.5	0.79	0.012	48

Summary of evidence bearing on the primary state of uranium in marine phosphorites

The theoretically plausible occurrence of U(IV) in apatite has been confirmed in these investigations by demonstrating that U(IV) actually does occur and indeed is the predominant ion-species of uranium in some phosphorites. In addition, considerations of the crystal chemistry of apatite lead to the conclusion that structural emplacement of $(UO_2)^{+2}$ is most probably surface-limited and, therefore, not as favorable as structural emplacement of the U^{+4} ion. Nevertheless, the fine-grained nature of most phosphorite results in an exceptionally large inherent surface area (Hendricks and Hill, 1950; Jacob and Hill, 1953) which can accommodate all of the uranium in typical phosphorite as chemically adsorbed uranyl, as has been pointed out by Hendricks and Hill (1950) and Sheldon (in press). It is thus important to examine the significance of the wide range in the U(IV)/U percentages of marine phosphorites (table 19). Do the data accurately represent the primary state of the uranium deposited in apatite?

In answering the above question we must consider laboratory and field evidence bearing on the relative stabilities of U^{+4} and UO_2^{+2} to subaerial exposure. Garrels has shown (oral communcation, and McKelvey and others, 1955) that the reduction of uranyl to uranous uranium can be effective at 25° C, and a pH of 4 or higher, for small amounts of uranyl and a wide range of ferrous iron concentration. The previously cited stabilizing effect of phosphate and fluoride on this reaction can appreciably increase the production of U(IV). It is also probable that U(IV) may be produced from U(VI) by the oxidation of organic matter or H_2S. Both Gruner (1952) and Miller and Kerr (1954) have successfully precipitated UO_2 by such reactions at low temperature and pressure. The presence of apatite in the milieu of such reactions would fix the U(IV) so produced, by ion exchange with calcium. Beyond this, by its extracting action, apatite would actually cause further production of U(IV) for its own fixation as it would disturb the achievement of equilibrium. This action would be even more pronounced than the stabilizing effect of complexing with phosphate or fluoride in solution, as in the latter case, equilibrium may be reached.

All of the above reactions favoring production of U^{+4} presuppose the interaction of uranium with another reducing couple. On the other hand the relative instability of U^{+4}, in the form of UO_2, to air oxidation is revealed by the many secondary minerals associated with vein deposits of uranium and the fact that uraninite or pitchblende is virtually never pure UO_2, but more commonly U_3O_8, or some intermediate value. We have shown experimentally (table 20) that iron-oxide encrusted apatite pellets have the capacity to oxidize U(IV) in solution to uranyl. From the above evidence, as well as the fact that $(UO_2)^{+2}$ is the dominant ion under most natural conditions (Garrels, 1955), it is reasonable to expect that weathering causes a lowering of the initial U(IV)/U(VI) ratio in marine phosphorites. The very features of excessive porosity and surface area which permit contemplation of adsorbed $(UO_2)^{+2}$ in phosphorites also permit thorough permeation by air and oxygen-bearing water. Such extensive contact with oxygen could effect appreciable alteration of U^{+4} to $(UO_2)^{+2}$, despite the fact that other, more obvious weathering changes, might not occur. External oxidation would be augmented by the disruptive effects of radioactive disintegration on the crystal structure and by the liberation of oxygen from water as a result of alpha-particle bombardment (Ellsworth, 1925).

Conclusive evidence that weathering has lowered the initial U(IV)/U(VI) ratio is obtained in the Tennessee phosphorites. There, the residually accumulated "brown-rock" ores maintain essentially the same P_2O_5/U ratio as the underlying parent limestone (table 17), thus proving that uranium has not been added or subtracted. In contrast the U(IV) content has been lowered from 25 to 3 percent of the total uranium (table 19).

The fact that the highest U(IV)/U percentages (and therefore the highest U(IV)/U(VI) ratios) are obtained from youngest and least weathered rocks becomes doubly significant in view of the above evidence. The high U(IV) contents of pebbles from the basal Bone Valley formation of Pliocene age and of nodules dredged off the coast of California (p. 75 and table 19) suggest that the uranium fixed by apatite from marine waters is largely tetravalent and that long exposure has allowed oxidation to lower the U(IV)/U percentages in the Phosphoria and Bigby formations.

Few samples of the Phosphoria and Bigby formations have been studied, and the hypothesis of initially higher U(IV)/U(VI) ratios must be tested with more data and specific comparisons of weathered and apparently unweathered materials. It can be urged in support of the idea, however, that McKelvey and Carswell (1956) infer a history of weathering from changes in P_2O_5 and uranium contents in various exposures of the Phosphoria formation, and they note unquestionable instances of weathering in other exposures. In addition, it is difficult to assume that the U(IV)/U percent of 25, for the Bigby formation, in the Tennessee phosphate field, represents the initial U(IV) content, and not a lowered value, superimposed by oxidative weathering. In view of the striking field evidences of weathering in the origin of the Tennessee "brown-rock" ores (fig. 12) and the substantial decrease of their U(IV)/U percent from 25 to 3, it is highly probable that the immediately underlying parent limestone, the Bigby formation, was also altered and that its primary U(IV)/U percentage was appreciably higher than 25.

It is not possible to suggest how much of the primary uranium taken up by marine apatite was U(IV). It is clear, however, that significant amounts of U(VI) are present initially, even though U(IV) may be the dominant species, and that the primary U(IV)/U(VI) ratio in apatite is undoubtedly influenced by the Eh of the marine waters.

Uranium in igneous apatite

General statement and analyses

In accordance with Goldschmidt's empirical rules, U(IV) should be preferentially emplaced or "captured" in apatite due to its size identity with the Ca^{++} ion and the greater binding capacity of its higher charge. Considering the existence of such preferred emplacement in sedimentary apatite (see postdepositional enrichment, above), and also the progressive increase in uranium content in the younger products of differentiation (Larsen and Phair, 1954; Adams, 1954), apatite might be expected to contain more uranium in the more felsic members of an intrusive series. Unfortunately, too few groups of related intrusives have been investigated extensively enough to test such generalizations. To demonstrate the type of progressive concentration that might be a consequence of capture, it is necessary to compare the uranium contents and the relative amounts of apatite and other uranium-bearing minerals in each rock type, and also the uranium content and the relative volumes of the different rock types. It is, in effect, the problem of illuminating the total budget of uranium before one can understand individual expenditures of it.

The determinations of U and U(IV) in apatite require as much as 100 milligrams of pure mineral. To obtain this quantity of a small accessory mineral large samples of representative rock specimens must be carefully processed through several time-consuming operations. The paucity of uranium analyses for apatite in the literature reflects the prohibitive nature of the task. The analyses 7/ given in table 23 are hardly representative of all igneous apatite. They, nevertheless, give some idea of the range and typical values for uranium content. The apatites, in all cases, were optically clear, subhedral to euhedral, and contained few inclusions. An exception is the apatite from Mineville, New York, which is not properly igneous in origin, is exceedingly high in rare earths, and has many inclusions, (McKeown and Klemic, 1956). Excluding the unusual Mineville material, all the apatites fall within the range of 0.001 to 0.012 percent uranium. Most of them fall within the narrower limits of 0.004 to 0.008 percent uranium.

The rocks samples come mainly from a few batholiths and the selection is heavily weighted in favor of intermediate "acid" igneous types. As exemplified by the Boulder Creek batholith, they reveal the fact that the range in uranium content of apatites from a group of related rocks is not large in contrast to the dispersion that may obtain in sedimentary deposits. Significantly, these analyses also show that the changes are not necessarily progressive, as apatites from the more felsic rocks are not more uraniferous

---

7/ We are greatly indebted to H. W. Jaffe, David Gottfried, E. S. Larsen, Jr., and George Phair, U. S. Geological Survey, for supplying many of the apatite separates.

Table 23.--Uranium and U(IV) content of igneous apatites. Analyst, R. S. Clarke, Jr., U. S. Geological Survey.

Description of parent rock	Sample no.	Percent total U	Percent U(IV) 1/	$\frac{U(IV)}{U}$ percent
Apatite-magnetite deposit, Durango, Mexico	Dur-1	0.0010	0.0006	60
Quartz diorite, southern California batholith, Lakeview Mountain, California	P-4	0.012	0.0057	47
Gabbro, Henderson, North Carolina	P-22	0.00066	0.00036	54
Syenite, Renfrew, Ontario, Canada	P-24	0.0023	0.00052	23
Silver Plume granite, Colorado	GP-28	0.00044	0.00014	32
Silver Plume granite, Colorado	GP-41	0.0022	0.00027	12
Silver Plume granite, Colorado	GP-100	0.0017	0.00039	23
Quartz monzonite, Shelby, North Carolina	53-BE-3a	0.0061	0.0032	52
Quartz monzonite, Shelby, North Carolina	53-BE-3b	0.0065	0.0041	63
Idaho batholith				
Diorite	CPR-117	0.0059	0.0025	42
Diorite	CPR-118	0.0032	0.0017	53
Diorite	CPR-119	0.0015	0.00086	57
Gneissic granite	CPR-122	0.0013	0.00086	66
Boulder Creek batholith, Colorado				
Granodiorite	GP-17	0.0069	0.0019	28
Quartz monzonite	GP-19	0.0053	0.0012	23
Biotite granite	GP-34	0.0078	0.0019	24
Quartz diorite	GP-129	0.0049	0.0012	24

Table 23.--Uranium and U(IV) content of igneous apatites.--Continued.

Description of parent rock	Sample no.	Percent total U	Percent U(IV) 1/	$\frac{U(IV)}{U}$ percent
Boulder Creek batholith, Colorado--Continued				
Granodiorite	GP-49	0.0011	0.00030	27
Quartz monzonite	GP-50	0.0048	0.0011	23
Quartz monzonite	GP-51	0.0044	0.0012	27
Granite	GP-63	0.0023	0.00024	10
Quartz diorite	GP-61	0.0005	n.d.	
Apatite massif, Kola Peninsula, U.S.S.R.		0.001	n.d.	
Apatite-magnetite deposit, Mineville, New York	FK-3	0.079	n.d.	
Shonkinite, Mountain Pass, California	G-25	0.0049	n.d.	

1/ U(IV) was determined after solution of sample in $HCl-NH_2OH \cdot HCl$ solution. Values shown are corrected to compensate for the 80 percent recovery by this method (Clarke and Altschuler, in press).

than those from intermediate rocks. The explanation may lie in the progressive increase in the quantity of the other uraniferous accessory minerals. Studies of E. S. Larsen, Jr., and George Phair and their colleagues confirm this suggestion (oral communication).

Variation of uranium in apatite with uranium in host rock

It is noteworthy that the uranium content of the apatites from the Boulder Creek batholith varies almost directly as the uranium content of the host rocks.8/ This is shown in figure 19. The rocks are slightly to moderately different in composition and are from localities as far apart as several miles. The fact that most of the analyses conform so closely to a uniform trend of concentration of uranium in apatite relative to host rock indicates that the partition of uranium between apatite and the crystallizing magma can maintain a constant ratio over a significant interval of the differentiation span of the magma. That such equilibrium does not necessarily prevail throughout differentiation is indicated by the aberrant point on the plot, GP-63.

8/ We are indebted to George Phair, U. S. Geological Survey, for supplying the uranium contents of total rock for this comparison.

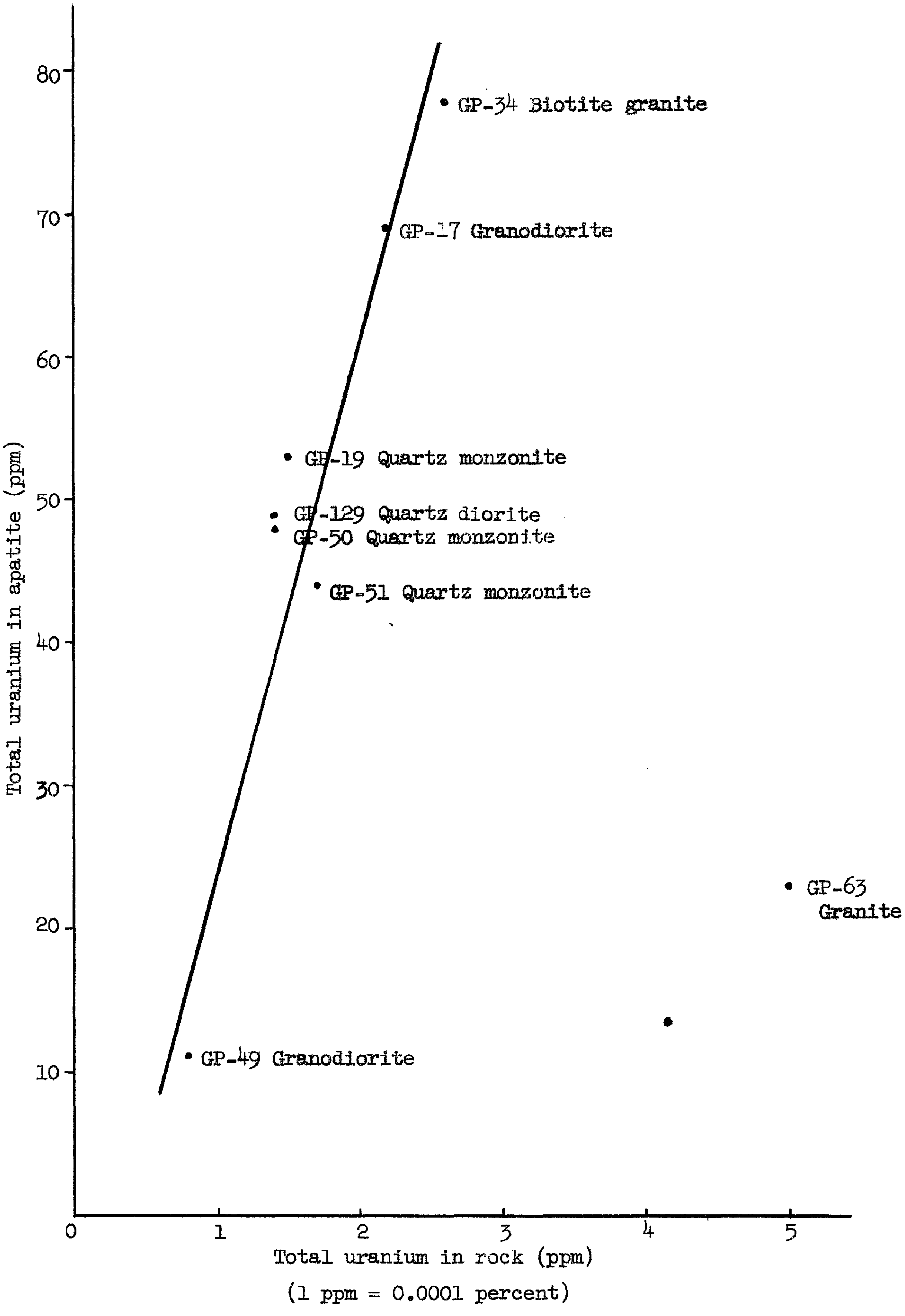


Figure 19.--Total uranium in rock versus total uranium in apatite for rocks from Boulder Creek batholith.

Oxidation state of uranium in igneous apatite

In the absence of analytical data the uranium in igneous apatite has been reasonably presumed to be entirely tetravalent (Tomkeiff,, 1946; Goldschmidt, 1954; Larsen and Phair, 1954; McKelvey and others, 1955). The conclusion is virtually dictated by the following:

1. The common occurrence of uraninite in the same or related rocks;
2. the implications of uranium occurring largely in other calcium and cerium-bearing minerals such as sphene, monazite, xenotime, and allanite, a fact presumably governed by the ability of U^{+4} to substitute for the Ce^{+3} and Ca^{+2} ions;
3. the occurrence of cerium and thorium in igneous apatite;
4. independent evidence of the effectiveness of reducing conditions during the crystallization of the host rocks (Larsen and Phair, 1954; Adams, 1954).

It is reassuring to demonstrate that U(IV) actually occurs in igneous apatite in view of the geologic arguments favoring this occurrence. It is not yet possible to define the controls of the relative U(IV)-U(VI) concentrations in igneous apatite. Many more analyses are required, not only for the valence state of uranium in apatite, but also for other constituents of the parent rock and particularly for isotopes of lead (see discussion, p. 116). It is possible, however, to discuss several alternative hypotheses on the basis of the data presented in table 23.

Of paramount importance is the fact (noted earlier, under sedimentary apatite) that consanguinous rocks yield similar results when their apatites are analyzed for U(IV). The virtual identity in the U(IV)/U percentages of all but one of the Boulder Creek samples could not necessarily be anticipated unless apatites generally showed predominantly one or the other valence state. Rocks from the Idaho batholith show slightly more spread; the lithologies represented also differ more. In attempting to explain the obtained distributions of U(IV) it is important to note that U(IV) percentages have been found to range from 10 to 66, and it is possible that more analyses may substantially widen the range.

It is conceivable that igneous apatite initially fixes more U(IV) during its crystallization than it now contains and that the increase in U(VI) is superimposed by normal oxidative weathering. However, the lack of greater diversity in groups of related specimens argues strongly against so simple a hypothesis. Thus the total uranium content of the Boulder Creek apatites range from 0.0011 to 0.0078 percent. In view of this range and of the demonstrated possible range in U(IV) (10 to 66 percent of the total), the regularity that prevails in the U(IV)/U percentages of the Boulder Creek apatites would be remarkable if it were affected by so variable a process as weathering, in which local, external factors, such as permeability and ground-water composition, play so large a role. It is pertinent to observe that the original rock samples and the apatite separates were carefully screened for evidence of alteration, and only fresh materials were used.

U(IV)/U(VI) ratio reflects magmatic equilibria

Two other hypotheses may be considered to account for the consistent U(IV)/U(VI) ratios [9] in groups of apatites with much more diverse total uranium contents.

1. The U(IV)/U(VI) ratios may be entirely a function of the conditions prevailing during the crystallization of the magma and be inherited unchanged.

2. The U(IV)/U(VI) ratios may be related to radioactivity and to age. This second explanation does not preclude the application of the first, as the percent of U(IV) may have been initially determined by the prevalent equilibria of the magma during crystallization and it may have since been altered regularly by radioactivity.

Much evidence can be marshalled for the first of the above viewpoints. Figure 19 demonstrates that the uranium in the apatite is in equilibrium with the total uranium in the rock and, therefore, assuming the confined crystallization of phanerocrystalline rocks, with the magma from which these rocks crystallized. It follows that the uniform U(IV)/U(VI) ratio in these apatites varies directly with the total uranium in the crystallizing magma. The progressive change in uranium content with differentiation in a series of related igneous rocks has been documented in the radioactivity studies of Billings and Keevil (1946) and the chemical studies of Larsen and

---

[9] Previous sections were concerned with the amounts of the total uranium that is tetravalent; hence the percentage U(IV)/U was used. Here, relative quantities of U(IV) and U(VI) are discussed and their ratio is used. Obviously the ratio and the percentage are based on the same figures and demonstrate the same trends.

colleagues (1956). In addition, Adams has shown that total uranium has a linear relation to total K_2O in the volcanic rocks of the Lassen Peak region. In these rocks "potassium increases systematically during differentiation" (Adams, 1954).

Obviously uranium responds to the major chemical equilibria that control differentiation. The above evidence that trace percentages of U(IV) in apatite are directly related to uranium in the total rock (fig. 19) reveals that the U(IV)/U(VI) ratio in apatite might vary regularly with differentiation. Goldschmidt (1954) points out the progressive development of "magmatic oxidation" displayed by the increasing ratio of ferric to ferrous iron in felsic to mafic rocks, and he also noted that the iron oxide and sulfide mineral assemblages are compatible with the ferric-ferrous ratio. It is reasonable to suppose that uranium in plutonic apatite would similarly reflect the overall oxidation capacity of the magma and that the U(IV)/U(VI) ratio would change accordingly in a large series of related rocks. Precise proof of this, however, must await a much larger assemblage of data.

Relation of U(IV)/U(VI) ratio to age

Auto-oxidation.--The hypothesis that the U(IV)/U(VI) ratio in igneous apatite is a function of radioactivity and varies regularly with age is more difficult to apply. Essentially, it proposes that the U(IV)/U(VI) ratio is governed by auto-oxidation. The concept of auto-oxidation was first proposed by Ellsworth (1924, 1925) who stated that the disintegration of UO_2 or ThO_2 to Pb must automatically oxidize UO_2, or other reduced species present, in the following manner:

$$UO_2 \longrightarrow Pb + 2\ O$$
$$2\ O + UO_2 + Pb \longrightarrow UO_3 + PbO$$

Subsequent decay of the UO_3 thus produced will, in turn, oxidize two more UO_2 (Holmes, 1948) as follows:

$$UO_3 \longrightarrow Pb + 3\,O$$
$$3\,O + 2\,UO_2 + Pb \longrightarrow 2UO_3 + PbO$$

Thus, in net, one mole of UO_3 is produced for each mole of radiogenic lead and, ideally, one might use U(VI)/U ratios to compute the ages of rocks and minerals in substantially the same manner that lead-uranium ratios are now used, as was proposed by Lane (1934).

We can evaluate auto-oxidation in apatite quite simply by premising all initial uranium in apatite as U(IV). On this basis the age of the apatite can be determined by using the charts or the formula published by Wickman (1939). As discussed above, we may substitute the U(VI)/U ratio for the Pb^{206}/U^{238} ratio.

The U(VI)/U ratios of the Boulder Creek apatites (excluding sample GP-63) yield ages between 4.0 and 4.5 billion years. Ages obtained by the ratio of lead to alpha activity (Larsen and others, 1952) in zircon from the same rock are close to 1 billion years (David Gottfried, U. S. Geological Survey, oral communication). This latter age demands a U(VI) content of approximately 15 percent of the total U rather than 75 percent of it.

Ages based on U(VI)/U ratios of the Idaho batholith apatites range from 2.4 to 3.6 billion years. Ages from the lead-alpha activity ratios of zircon from the same rock range from 60 to 110 million years (H. W. Jaffe, U. S. Geological Survey, personal communication). These would demand U(VI) contents of only 0.8 to 1.5 percent of the total U rather than 34 to 58 percent of it.

External weathering controlled by radioactive decay.--Despite the fact that the contribution of thorium has not been taken into account in the above evaluations, the results show so great an excess of UO_3 as to invalidate the hypothesis that auto-oxidation produced the UO_3, or even contributed significantly to it. It is possible, however, that radioactive disintegration can indirectly facilitate and control the ratio of external oxidation by solutions and gases present in the rocks and, hence, produce an effect like auto-oxidation. Such control on crystal permeation by oxidizing agents could be established by progressive increase in crystal damage because of radioactive decay.

In summary it can be stated that the relative U(IV) and U(VI) contents of igneous apatites are most readily attributed to the oxidation conditions that prevailed during the crystallization of the host rocks. In view of the consistency evident among some groups of related rocks, however, it is possible that initial UO_3 contents may be progressively augmented by external oxidation at a systematic rate, and it is of interest to investigate the relations of radioactive decay to such contributions to UO_3 content. To do so requires much more uranium data and a comparison of U(VI)/U ratios with radiogenic lead.

CONCLUSIONS

Summary

Uranium in apatite ranges from a few parts per million (0.000X percent) in the insular phosphorites to almost one percent in subaerially enriched deposits. The most typical deposits, those comprising the greatest concentrations of P_2O_5 in the lithosphere, are far more restricted in range. Primary apatite, both igneous and sedimentary, generally has between 0.005 and 0.015 percent uranium. Thus, igneous apatite seldom exceeds 0.01 percent and primary apatite pellets from the Hawthorn and Phosphoria formations typically contain 0.005-0.008 percent uranium; the rich Moroccan phosphorites contain about 0.012 to 0.014 percent with remarkable consistency.

The uranium in apatite may be leached or postdepositionally enriched, and its enrichment may take place subaerially from ground water or during submarine reworking. Marine enrichment commonly enhances uranium content in apatite to 0.02 or 0.03 percent, as shown in the Bone Valley formation and the South Carolina terrace gravels. The fact that unweathered marine phosphorite seldom exceeds 0.03 percent uranium, however, can be attributed only to the infinitesimal concentrations in the marine source, rather than to any limitations of the apatite structure or to the competition of other ions for replacement sites. This is evident from the much greater content of uranium in subaerially enriched apatite, in which much additional uranium is emplaced long after the normal suite of other trace elements substituting for calcium. Thus pebbles in the Bone Valley formations are supergenely enriched to 0.2 percent U, and fossil bones contain as much as 0.83 percent U. Significantly, the U(IV) content in each of the above is more than half of the total uranium.

The characteristics of geologically young marine phosphorites enlighten us both as to the capacity and the nature of marine sources of uranium. Phosphatic marls from the Gulf of Mexico and phosphorite nodules from the Pacific Ocean have a U/P_2O_5 ratio as high or higher than those of all the world's major phosphate deposits that have been investigated, thus proving that ocean water is an adequate source of uranium in typical marine phosphorite.

Nature of uranium fixation in phosphorites

The suggestion that uranium in phosphorites is dominantly U(VI) fixed as a surface-coordinated uranyl pyrophosphate has been advanced (Bowie and Atkin, 1956) to account for the lack of uranium in calcareous sediments. However, the well-established ability of carbonate to complex uranyl ion and thus increase the solubility of uranium (Bachelet and others, 1952) more probably accounts for the relative lack of uranium in carbonate rocks. Furthermore, the surface-limited reactions of uranyl ion with bone apatite demonstrated by Neuman and others (1949a,b) are structurally much more limited than the isomorphous replacement of Ca^{+2} by U^{+4}, and it is not surprising that an apatite material with as much as 0.83 percent total uranium should contain more than half the uranium as U(IV). Some of the U(VI) present in unweathered phosphorites is probably chemisorbed by surface reaction of uranyl on the growing crystallites of sedimentary apatite. Such reactions are more likely to involve orthophosphate than pyrophosphate formation, in nature. In addition, the high U(IV) content of young phosphorites suggests that postdepositional oxidation has also produced appreciable U(VI) in the older rocks.

Were mere adventitious extraction the sole factor in uranium fixation by precipitating apatite, the ratio of uranium to phosphate in apatite might approximate their relative concentrations in the sea. Uranium in sea water is 1 to 2 parts per billion. P_2O_5 in sea water of the continental shelf is 50 mg/m^3 (Kazakov, 1937). The U/P_2O_5 ratio in sea water is thus 0.02-0.04 and thereby exceeds by far the ratio of U/P_2O_5 found in primary marine phosphorites (table 11). In addition, comparison of U/P_2O_5 ratios both within and among the primary pellets and nodules from the Hawthorn formation, Florida, the Gulf of Mexico, the Pacific Ocean and French Morocco (table 11), reveals considerable variety for comparable materials. Thus, direct and indiscriminate fixation of uranium that is available fails to explain the known uranium contents in apatite. Nor can these known contents be explained merely by citing an "affinity" of uranium for phosphate that is demonstrated by the many uranium phosphate minerals, as these are entirely uranyl minerals, and we have found that in relatively young, primary phosphorite most of the uranium is present in the tetravalent or, uranous, form.

It seems, indicated from the above, that the uranium actually available to apatite must be limited and largely contingent on special circumstances, presumably, the production of U(IV). Garrels (1955) and Sheldon (in press) have shown from thermodynamic considerations of the isolated couple $(UO_2)^{+2}$ and U^{+4} that the uranyl concentration of normal sea water would be many orders of magnitude greater than that of the uranous ion. It is only in an acid reducing environment that the U(IV) concentration becomes significant (Garrels, 1955). Even under these conditions (pH = 6, Eh = -0.3), the $(UO_2)^{+2}/U^{+4}$ ratio is about 100, (Sheldon, in press); however, apatite cannot be considered to form from such relatively high acid water.

It follows from the insolubility of U(IV) in ground water solutions that uranium is delivered to the ocean as $(UO_2)^{+2}$. However, uranyl ion may be readily reduced at low temperature and pressure to U(IV) and as the concentrations of ferrous iron and organic matter in marine phosphorites is generally far greater than the concentration of uranium, the necessary marine reduction of U(VI) prior to apatite fixation may be readily presumed.

The substantial ground-water and marine enhancements of uranium in apatite reveal the potency of apatite to remove uranium selectively from terrestrial or marine solutions. U(IV) produced by reduction reaction between $(UO_2)^{+2}$ and Fe^{+2} or organic matter would be taken up as a proxy for calcium during formation of apatite, or by ion exchange of calcium during marine reworking of previously formed apatite.

Unweathered pebbles from the Bone Valley formation and nodules of Quaternary age from the Pacific Ocean contain dominantly tetravalent uranium, This indicates that the uranium in sea water is, in fact, reduced prior to emplacement in apatite. Further proof of this is obtained from the demonstration that new increments of marine uranium in the transgressively reworked Pleistocene terrace gravels near Charleston, South Carolina are mainly U(IV). In contrast to these findings, the marine phosphorites containing prominent U(VI) have been obviously weathered or are geologically much older (and probably weathered). It is, therefore, believed that the U(VI) present in marine phosphorites derives largely from postdepositional oxidation of U(IV).

Regenerative capture

In contrast to igneous apatite the occurrence of uranium in marine sedimentary apatite is not governed solely by the equilibrium conditions prevailing during the precipitation of the apatite. This follows from the evidence of secondary enrichment during marine reworking; namely, the host mineral acquiring new increments of the trace element by re-exposure to the same or similar solutions. It is also indicated by the wide variation in the U/P_2O_5 ratios in unaltered primary, or first-cycle, phosphorites, a fact which would otherwise demand considerable variation in the uranium content of the marine sources, for which there is no evidence. It is proposed that apatite actively affects the course of the reduction reactions which might normally produce U(IV) in the following manner:

$$(UO_2)^{+2} + \text{Reductant} \rightleftharpoons U^{+4} + \text{Oxidized Reductant}$$

The presence of apatite as a precipitating or solid phase which can sequester the U^{+4} by solid solution or ion exchange for calcium, interferes with the attainment of equilibrium in the above reaction and drives it instead in the direction:

$$(UO_2)^{+2} + \text{Reductant} \longrightarrow \underset{\downarrow}{U^{+4}} + \text{Oxidized Reductant}$$

Thus by removal of U(IV) in an insoluble phase, apatite promotes an additional reduction of uranyl and thereby insures a continuing supply of U(IV) for its own uptake. The removal of U(IV) from sea water is thus not dependent on continuous precipitation of apatite, as uptake may proceed equally by ion-exchange reaction with previously formed apatite. This is indicated by the higher total U and U(IV) contents of reworked phosphate nodules.

The name, regenerative capture, is proposed to describe this type of trace-element concentration in which a stable complex or insoluble phase, by effectively removing an ion species that is normally present in insignificant quantities, prevents the attainment of equilibrium in the oxidation-reduction reaction producing this ion and causes continuous production of the ion. Thus, as long as removal continues, the supply is maintained and a mineral is able to fix unusual concentrations of an ion species which, from mere stability or concentration considerations, would not be expected in large quantities. Regenerative capture can be maintained only as long as the host mineral remains unsaturated with respect to the trace constituent. The fact that apatite can concentrate as much as 0.5 percent U(IV) proves that saturation conditions are seldom realized in typical marine apatite (0.01-0.02 percent U).

The idea of regenerative capture clearly invokes no new chemical principle. Its merit lies in explaining unexpectedly large mineral concentrations of ions present in insignificant concentrations in solution. Regenerative capture applies to uranium in apatite in two important ways. It helps to explain the high U(IV)/U(VI) ratios of some marine phosphorites despite the fact that uranium in the ocean source most probably occurs predominantly as U(VI). It implies that a strongly reducing environment is not a requirement for the fixation of U(IV) by apatite but rather that appreciable U(IV) may be fixed by apatite so long as any reduction of U(VI) is possible.

Equilibrium fixation of uranium in igneous apatite

A completely different situation prevails in igneous apatite. The presence of many other good hosts makes the entire distribution of uranium much more complex and the amount of uranium available to apatite is regulated not only by its inherent capacity but by the capacities of other hosts coextensive with it and thus reflects the total equilibrium in the magma. This is clearly evident from the systematic variation of both the total uranium and U(IV)/U(VI) ratio in apatite with the total uranium in the rock, for suites of related rocks.

SELECTED BIBLIOGRAPHY

Adams, J. A. S., 1954, Uranium and thorium contents of volcanic rocks, *in* Faul, Henry, ed., Nuclear geology: p. 89-98, New York, John Wiley and Sons, Inc.

Alexander, Frank, 1953, Guidebook, field trip to central Tennessee phosphate district--Southeastern Mineral Symposium, Geol. Soc. America: Nashville, Vanderbilt Univ., Tenn. Div. Geology, 8 p.

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

Altschuler, Z. S., Clarke, R. S., and Young, E. J., 1954, Uranium in apatite (abs.): Geol. Soc. America Bull., v. 65, no. 12, pt. 2, p. 1225-1226.

Altschuler, Z. S., Jaffe, Elizabeth B., and Cuttitta, Frank, 1956, The aluminum phosphate zone of the Bone Valley formation, Florida, and its uranium deposits: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 507-513; U. S. Geol. Survey Prof. Paper 300, p. 495-504.

Arambourg, Camille, and Orcel, Jean, 1951, Observations préliminairies sur la présence d'un vanadate d'urane dans les gisements de phosphate du Maroc: Acad. Sci. Paris, Comptes rendus, v. 233, no. 25, p. 1635-1636.

Bachelet, M., Cheylan, E., Douis, M., and Goulette, J. C., 1952, Préparation et propriétés des uranylcarbonates; 2^{e} note: Uranylcarbonates alcino-terreux: Soc. chim. France Bull., p. 565-569.

Baes, C. F., Jr., 1954, The production of U^{4+} by ferrous ion in phosphoric acid solution; the formal electrode potential of the U^{4+}-U^{6+} couple: U. S. Atomic Energy Comm. ORNL-1581 or AECD-3594. (Microcard copy on file in U. S. Atomic Energy Comm. depository libraries.)

Barr, J. A., Jr., 1955, Uranium production from phosphate rock: Remarks at 39th Ann. Mtg. Florida Eng. Soc., Daytona Beach, Florida, U. S. Atomic Energy Comm.

Beevers, C. A., and McIntyre, D. B., 1946, The atomic structure of fluorapatite and its relation to tooth and bone material: Mineralog. Mag., v. 27, no. 194, p. 254-257.

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.

Borneman-Starinkevitch, I. D., 1938, On some isomorphic substitutions in apatite: Acad. Sci. U.R.S.S., Comptes rendus (Doklady), v. 19, no. 4, p. 253-255.

Bowie, S. H. U., and Atkin, D., 1956, An unusually radioactive fossil fish from Thurso, Scotland: Nature, v. 177, no. 4506, p. 487-488.

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

Capdecomme, Laurent, 1953, Etude mineralogique des gites de phosphates alumineux de la region de Thiès (Sénégal): 19th Internat. Geol. Cong., Algiers, Comptes rendus, sec. 11, fasc. 11, p. 103-117.

Capdecomme, Laurent, and Pulou, Rene, 1954, Sur la radioactivité des phosphates de la region de Thiès (Sénégal): Acad. Sci. Paris, Comptes rendus, v. 239, p. 288-290.

Carnot, Adolphe, 1893, Recherches sur la composition générale et la teneur en fluor des os modernes et des os fossiles des différents âges: Annales des mines, ser. 9, tome 3, p. 155-195.

Cathcart, J. B., 1950, Notes on the land-pebble phosphate deposits of Florida, in Snyder, F. G., ed., Symposium on mineral resources of the southeastern United States: Knoxville, Tenn. Univ. Press, p. 131-151.

__________1956, Distribution and occurrence of uranium in the calcium phosphate zone of the land-pebble phosphate district of Florida: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 514-519; U. S. Geol. Survey Prof. Paper 300, p. 489-494.

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

Clarke, R. S., Jr., and Altschuler, Z. S., The determination of U(IV) in apatite: Geochimica et Cosmochimica Acta (in press).

Connick, R. E., and Hugus, Z. Z., 1952, The participation of f orbitals in bonding in uranium and transuranium elements: Am. Chem. Soc. Jour., v. 74, p. 6012-6015.

Davidson, C. F., and Atkin, D., 1953, On the occurrence of uranium in phosphate rock: 19th Internat. Geol. Cong., Algiers, Comptes rendus, sec. 11, fasc. 11, p. 13-31.

Denson, N. M., and Gill, J. R., 1956, Uranium-bearing lignite and its relation to volcanic tuffs in eastern Montana and North and South Dakota: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 464-467; U. S. Geol. Survey Prof. Paper 300, p. 413-418.

Dietz, R. S., Emery, K. O., and Shepard, F. P., 1942, Phosphorite deposits on the sea floor off southern California: Geol. Soc. America Bull., v. 53, p. 815-848.

Du Toit, A. L., 1917, The phosphates of Suldanha Bay: South African Geol. Survey Mem. 10, 34 p.

Ellis, D. A., 1952, The recovery of uranium from industrial phosphoric acids by solvent extraction: U. S. Atomic Energy Comm. DOW-81, 75 p.

Ellsworth, H. V., 1924, Atomic disintegration as a measure of geologic time: Pan.-Am. Geologist, v. 42, p. 273-280.

__________1925, Radioactive minerals as geological age indicators: Am. Jour. Sci., 5th ser., v. 9, p. 127-144.

Fairchild, J. G., 1929, Base exchange in artificial autunites: Am. Mineralogist, v. 14, p. 265-275.

Garrels, R. M., 1955, Some thermodynamic relations among the uranium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: Am. Mineralogist, v. 40, p. 1004-1021.

Goldschmidt, V. M. (edited by Alex Muir), 1954, Geochemistry: Oxford, Clarendon Press, 730 p.

Graton, L. C., and Fraser, H. J., 1935, Systematic packing of spheres with particular relation to porosity and permeability: Am. Assoc. Petroleum Geologists Bull., v. 43, no. 8, p. 785-909.

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

Grimaldi, F. S., May, Irving, and Fletcher, M. H., 1952, U. S. Geological Survey fluorimetric methods of uranium analysis: U. S. Geol. Survey Circ. 199, 20 p.

Grimaldi, F. S., May, Irving, Fletcher, M. H., and Titcomb, Jane, (Compilers), 1954, Collected papers on methods of analysis for uranium and thorium: U. S. Geol. Survey Bull. 1006, 184 p.

Gruner, J. W., 1952, New data on syntheses of uranium minerals. Part I. Annual Report for July 1, 1951 to June 30, 1952: U. S. Atomic Energy Comm. RMO-983, 26 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Gruner, J. W., and McConnell, Duncan, 1937, The problem of the carbonate-apatites. The structure of francòlite: Zeitschr. Kristallographie, v. 97, p. 208-215.

Guntz, A. A., 1952, Sur la presence d'uranium dans les phosphates Nord-Africains: Acad. Sci. Paris, Comptes rendus, v. 234, p. 868-870.

Hayes, C. W., and Ulrich, E. O., 1903, Description of the Columbia quadrangle, Tennessee: U. S. Geol. Survey Atlas, Columbia Folio, 95.

Hébert, Claude, 1947, Contribution à l'étude de la chimie des phosphates de calcium: Annales des mines Mém ., v. 136, no. 4, 93 p.

Hendricks, S. B., and Hill, W. L., 1950, The nature of bone and phosphate rock: Natl. Acad. Sci. Proc., v. 36, p. 731-737.

Holmes, Arthur, 1948, The oldest known minerals and rocks: Edinburgh Geol. Soc. Trans., v. 14, pt. 2, p. 176-194.

Hurley, P. M., and Fairbairn, H. W., 1953, Radiation damage in zircon--a possible age method: Geol. Soc. America Bull., v. 64, p. 659-673.

Igelsrud, Iver, Chocholak, John, Stephan, E. F., and others, 1949, Recovery of uranium from phosphate rock by the Battelle monocalcium phosphate process: U. S. Atomic Energy Comm. BMI-JDS-201, 99 p.

Igelsrud, Iver, Stephan, E. F., Chocholak, John, and others, 1948, Chemical process to recover uranium from phosphate rock: U. S. Atomic Energy Comm. BMI-JDS-126, 29 p.

Jacob, K. D., Hill, W. L., Marshall, H. L., and Reynolds, D. S., 1933, The composition and distribution of phosphate rock with special reference to the United States: U. S. Dept. Agriculture Tech. Bull. 364, 90 p.

Jacob, K. D., and Hill, W. L., 1953, Laboratory evaluation of phosphate fertilizers, in Pierre, W. H., and Norman, A. G., ed., Soil and fertilizer phosphorus in crop nutrition, v. IV, ch. 11, p. 299-345, of Agronomy, a series of monographs, prepared under the auspices of the American Society of Agronomy: New York, Academic Press Inc.

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, 19 p., issued by U. S. Atomic Energy Comm. Tech. Inf. Service Extension, Oak Ridge, Tenn.

Kazakov, A. V., 1937, The phosphorite facies and the genesis of phosphorites, in Geological investigations of agricultural ores USSR: Sci. Inst. Fertilizers and Insectofungicides Trans. (U.S.S.R.), no. 142, p. 95-113. (Special issue in English published for 17th Internat. Geol. Cong.)

Lane, A. C., 1934, Fivefold check of uraninite age?: Am. Mineralogist, v. 19, p. 1-13.

Larsen, E. S., Jr., Keevil, N. B., and Harrison, H. C., 1952, Method for determining the age of igneous rocks using the accessory minerals: Geol. Soc. America Bull., v. 63, p. 1045-1052.

Larsen, E. S., Jr., and Phair, George, 1954, The distribution of uranium and thorium in igneous rocks, in Faul, Henry, ed., Nuclear geology: p. 75-89, New York, John Wiley and Sons, Inc.

Larsen, E. S., Jr., Phair, George, Gottfried, David, and Smith, W. L., 1956, Uranium in magmatic differentiation: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 240-247; U. S. Geol. Survey Prof. Paper 300, p. 65-74.

Le Cornec, J., 1951, Estimate of world supplies of the principal plant nutrients by cost range: U. N. Sci. Conf. Conserv. and Utiliz. Res. Proc., v. 2, Mineral resources, p. 270-274.

Lenoble, Andre, Salvan, Henri, and Ziegler, Valery, 1952, Decouverte de l'uranium dans les niveaux phosphates du Maroc: Acad. Sci. Paris, Comptes rendus, v. 234, no. 9, p. 976-977.

McConnell, Duncan, 1938, A structural investigation of isomorphism of the apatite group: Am. Mineralogist, v. 23, p. 1-19.

McKelvey, V. E., and Carswell, L. D., 1956, Uranium in Phosphoria formation: Proc. Internat. Conf. on the peaceful uses of atomic energy, Geneva, 1955, v. 6, p. 503-506; U. S. Geol. Survey Prof. Paper 300, p. 483-487.

McKelvey, V. E., Cathcart, J. B., Altschuler, Z. S., and others, 1953, Domestic phosphate deposits, in Pierre, W. H., and Norman, A. G., eds., Soil and fertilizer phosphorus in crop nutrition, v. IV, ch. 11, p. 347-376, of Agronomy, a series of monographs, prepared under the auspices American Society of Agronomy: New York, Academic Press Inc.

McKelvey, V. E., Everhart, D. L., and Garrels, R. M., 1955, Origin of uranium deposits: Econ. Geology, Fiftieth Anniversary Volume, 1905-1955, pt. 1, p. 464-533.

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

McKeown, F. A., and Klemic, Harry, 1956, Rare-earth-bearing apatite at Mineville, Essex County, New York: U. S. Geol. Survey Bull. 1046-B, p. 9-23.

MacNeil, F. S., 1947, Correlation chart for the outcropping Tertiary formations of the eastern Gulf region: U. S. Geol. Survey Oil and Gas Inv. Prelim. Chart 29, with text.

Malde, H. E., Geology of the Charleston phosphate area, South Carolina: U. S. Geol. Survey Bull. _____ (in press).

Miller, L. J., and Kerr, P. F., 1954, Progress report on the chemical environment of pitchblende, in Annual Report for June 30, 1953 to April 1, 1954, pt. 2: U. S. Atomic Energy Comm. RME-3096, 98 p.; see p. 72-92.

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

Neuman, M. W., and Neuman, W. F., 1948, The deposition of uranium in bone, II--Radioautograph studies: Jour. Biol. Chemistry, v. 175, no. 2, p. 711-714.

Neuman, W. F., Neuman, M. W., Main, E. R., and Mulryan, B. J., 1949a, The deposition of uranium in bone, V--Ion exchange studies: Jour. Biol. Chemistry, v. 179, p. 335-340.

__________1949b, The deposition of uranium in bone, VI--Ion competition studies: Jour. Biol. Chemistry, v. 179, p. 341-348.

Oakley, K. P., 1955a, Analytical methods of dating bones, in Techniques in Archaeology: Advancement of Science, v. 11, no. 45, p. 3-8.

__________1955b, The composition of the Piltdown hominoid remains: British Mus. Nat. History Bull., Geology, v. 2, no. 6, p. 254-265.

Palache, Charles, Berman, Harry, and Frondel, Clifford, 1951, Dana's system of mineralogy, v. 2, 7th ed.: New York, John Wiley and Sons, Inc. 1224 p.

Pannell, J. H., 1950, Air oxidation of uranous solutions: U. S. Atomic Energy Comm. MITG-261, 18 p.

Pienkowski, S., 1953, Radioactivite d'un groupe de phosphorites polonais: Acad. Polonaise Sci. Bull., Cl. III, v. 1, p. 39-41.

Piggot, C. S., and Urry, W. D., 1941, Radioactive relations in ocean water and bottom sediments: Am. Jour. Sci., v. 239, p. 81-91.

Rogers, G. S., 1913, The phosphate deposits of South Carolina: U. S. Geol. Survey Bull. 580-J, p. 183-220. [1915]

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, pt. 3, p. 93-104.

Rusakov, V. P., 1933, O soderzhanii radiya i toriya v fosforitakh. [The radium and thorium content of phosphorites]: Akad. Nauk, SSSR, Leningrad, Doklady (Comptes Rendu) ser. A, no. 3, p.25-33.

Russ, W., 1924, The phosphate deposits of Abeokuta Province: Nigeria Geol. Survey Bull. 7, p. 9-38.

Schreyer, J. M., 1954, The chemistry of uranium (IV) orthophosphate solutions. Part I. The solubility of uranium (IV) orthophosphates in phosphoric acid solutions: U. S. Atomic Energy Comm. ORNL-1747, 34.p.

Sheldon, R. P., Geochemistry of uranium in the Phosphoria formation: Econ. Geology (in press).

Silverman, S. R., Fuyat, R. K., and Weiser, Jeanne D., 1952, Quantitative determination of calcite associated with carbonate-bearing apatites: Am. Mineralogist, v. 37, p. 211-222.

Smith, K. G., and Bradley, D. A., 1952, Radioactive dinosaur bones from the Camp Davis region, western Wyoming: Mich. Acad. Sci. Papers 1951, v. 37, p. 257-263.

Strutt, R. J., 1906, On the distribution of radium in the earth's crust: Royal Soc. London Proc. ser. A, v. 78, p. 150-153.

__________1908, On the accumulation of helium in geologic time: Royal Soc. London ser. A, v. 81, p. 272-277.

Thompson, M. E., 1953, Distribution of uranium in rich phosphate beds of the Phosphoria formation: U. S. Geol. Survey Bull. 988-D, p. 45-67.

__________1954, Further studies of the distribution of uranium in rich phosphate beds of the Phosphoria formation: U. S. Geol. Survey Bull. 1009-D, p. 107-123.

Tomkeiff, S. I., 1946, The geochemistry of uranium: Sci. Progress, v. 34, no. 136, p. 696-712.

Volodchenkova, A. I., and Melentiev, B. N., 1943, Apatites of two textural types from apatite-nepheline rocks of Chibiny: Acad. Sci. U.R.S.S., Comptes rendus (Doklady) v. 39, no. 1, p. 34-35.

Weiner, J. S., Oakley, K. P., and Le Gros Clark, W. E., 1953, The solution of the Piltdown problem: British Mus. Nat. History Bull., Geology, v. 2, no. 3, p. 141-146.

Wells, A. F., 1950, Structural inorganic chemistry, 2d ed., 727 p.; Oxford, Clarendon Press.

Wickman, Frans E., 1939, Some graphs on the calculation of geological age: Stockholm, Sveriges geol. Undersökning, ser. C, no. 427, Arsbok 33, no. 7, 8 p.