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GEOLOGICAL SURVEY

RELATION OF URANIUM AND PHOSPHATE IN THE PHOSPHORIA FORMATION

by

V. E. McKelvey

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IN THE PHOSPHORIA FORMATION

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CONTENTS

	Page
Abstract	1
Introduction	3
Regional geology of the Western Phosphate Field	4
Geology of the Phosphoria formation	6
General relations	6
Age	9
Lithology	9
Composition and mineralogy	9
Rock types	13
Areal variations in thickness and quality of the phosphate rock	15
Origin	18
Paleogeographic setting	19
Time of deposition of the phosphate and minor elements	20
Source of the Phosphoria sediments	21
Factors leading to the concentration of phosphate and minor elements	23
Occurrence of uranium in the Phosphoria formation	26
Composition and mineralogy of uraniferous rocks	26

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CONTENTS (cont'd)

Page

Areal variations in uranium content........................ 27

Origin.. 29

Methods of prospecting for uranium in the Phosphoria formation... 33

Suggestions for prospecting for uraniferous phosphate in other areas.. 35

Guano deposits.. 35

Guano (phosphatized) limestone.......................... 36

Apatite deposits.. 37

Sedimentary deposits... 38

Nonmarine residual deposits............................... 40

Conclusion... 41

Acknowledgments.. 42

References cited.. 43

LIST OF ILLUSTRATIONS

	Following page
Figure 1. Index map of the Western Phosphate Field, showing limits of the Phosphoria, Park City and Embar formations and their phosphate deposits.	4
Figure 2. Boundary between areas of simple and complex structure in the northern Rocky Mountains.	5
Figure 3. Typical sections of the Phosphoria formation in Wyoming and Idaho.	6
Figure 4. Typical sections of the Park City formation in Utah.	7
Figure 5. Typical sections of the Phosphoria formation in Montana.	8
Figure 6. Generalized section of the phosphatic shale member of the Phosphoria formation in the Slug Creek quadrangle, Idaho.	15
Figure 7. Total phosphate in the phosphatic portion of the Phosphoria formation.	17
Figure 8. Total thickness of rocks in the Phosphoria formation containing more than 31 percent P_2O_5	18
Figure 9. Total thickness of rocks in the Phosphoria formation containing more than 25 percent P_2O_5	19
Figure 10. Total thickness of rocks in Phosphoria and Park City formations containing more than 18 percent P_2O_5.	20
Figure 11. Frequency distribution of phosphate analyses in rocks of the Phosphoria formation containing specified amounts of uranium.	26
Figure 12. Variations in uranium content of rocks of the Phosphoria formation containing specified amounts of phosphate.	26

Figure 13. Variation in phosphate content of rocks of the Phosphoria formation containing specified amounts of uranium. 26

Figure 14. Relation between uranium and CO_2 in rocks of the phosphatic shale member at Coal Canyon, Wyoming and Brazer Canyon, Utah. 26

Figure 15. Relation between uranium and carbonate CO_2 in rocks of the phosphatic shale member at Coal Canyon, Wyoming, and Brazer Canyon, Utah. 26

Figure 16. Relation between uranium and acid insoluble in rocks of the phosphatic shale member at Coal Canyon, Wyoming, and Brazer Canyon, Utah. 27

Figure 17. Relation between uranium and organic matter (judged to be loss on ignition, minus CO_2 and water) in rocks of the phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyoming, and Brazer Canyon, Utah. 27

Figure 18. Maximum uranium content thus far reported from the Phosphoria formation and its close stratigraphic equivalents. 27

Figure 19. Total thickness, U and P_2O_5 content of beds containing 0.01 percent U or more in units of 1 foot or more in the Phosphoria formation and its close stratigraphic equivalents. 27

Figure 20. U and P_2O_5 content of beds of phosphatic shale member of Phosphoria formation, at Conda, Idaho; Coal Canyon, Wyoming; and Brazer Canyon, Utah. 29

Figure 21. Comparison between chemical and radiometric analyses. 34

ABSTRACT

The Phosphoria formation and its close stratigraphic equivalents extend over an area of some 100,000 square miles in Montana, Idaho, Wyoming, Utah, and Nevada. In the eastern part of the field the geologic structure is simple and pre-Cretaceous rocks are thin; but west of a line approximating meridian 111° the structure is complex and the pre-Cretaceous rocks are thick. This boundary, by reason of combined structural, stratigraphic, and petrologic evidence, is taken as essentially that between the Cordilleran miogeosyncline to the west and its platform to the east. The thickest and highest quality phosphate deposits are confined to the area slightly to the west of meridian 111° and are thought to have accumulated near the edge of the shelf, presumably where ascending deep cold waters, rich in CO_2 and phosphate, became more alkaline because of a decrease in partial pressure of CO_2 and an increase in temperature.

Some of the highly phosphatic beds of the Phosphoria formation contain 0.01-0.02 percent uranium. Although many highly phosphatic beds are only weakly uraniferous, the most highly uraniferous beds are all highly phosphatic and it seems certain that the uranium is in or attached to the phosphate mineral. A strongly negative relationship exists between uranium and carbon dioxide, for of the rocks containing 0.01 percent or more uranium, none contain more than about 2 percent carbonate CO_2. It seems probable that some of the same CO_2 relationships that controlled the precipitation of the phosphate also

affected the solubility of uranium in the sea water. Although it seems unlikely that the sea was at any place saturated with uranium as it was with phosphate, uranium may have been selectively removed from the sea water by adsorption on precipitated phosphates.

Little is known about the occurrence of uranium in other types of phosphate deposits, but, in view of the frequent association of uranium with phosphate, not only in the bedded phosphorites, but in many other minerals and compounds, other phosphate deposits should be tested. The guano, guano (leached) limestone, and the nonmarine residual deposits appear less promising as sources of uranium than do the marine sedimentary deposits and the "vein" apatite deposits.

INTRODUCTION

Some of the highly phosphatic beds of the Permian Phosphoria formation of the Northwestern States contain 0.01-0.02 percent uranium. They are similar in this respect to some of those in other important phosphate-bearing formations, such as the Pliocene Bone Valley formation of Florida; the Cretaceous and Eocene phosphorites of Algeria, Tunisia, Morocco, and Egypt (Hébert); the Cretaceous phosphorites of the Ivota River region, and the Tertiary phosphorites of the Volsk region of Russia (Rusakov).

Of the many other phosphorite deposits, few if any in this country, and probably elsewhere as well, have been tested adequately for uranium.

Although detailed studies of the uranium in the Phosphoria formation are under way, they have not yet progressed far enough to reveal the origin, and mineralogy of the uranium, or even the nature of its habits and variations. Nevertheless, the information at hand may help guide the search for uranium in other types of deposits. It is the purpose of this paper, therefore, to summarize the data on the geology of the Phosphoria formation and its uranium deposits, as well as methods currently used in prospecting the formation for uranium; and to make some suggestions for prospecting other types of deposits for uranium.

REGIONAL GEOLOGY
OF THE WESTERN PHOSPHATE FIELD

The Phosphoria formation, and its partial stratigraphic equivalent, the Park City formation, extends over an area of some 100,000 square miles in Montana, Idaho, Utah, and Nevada (fig. 1; McKelvey). That part of this area lying west of approximately meridian 111° is the eastern part of the Cordilleran miogeosyncline (Kay; Eardley); and the area to the east is the bordering shelf or platform area. The stratigraphy and structure of these areas are markedly different (fig. 2).

The geosynclinal portion of the field is characterized by several tens of thousands of feet of marine sediments, including rocks of every period from Cambrian to Jurassic. These rocks consist mainly of limestone, dolomite, and clean quartz sandstone, but minor amounts of other chemical precipitates, such as phosphate, are present also. Sediments of post-Jurassic age are dominantly continental clastics, largely restricted to intermontane basins.

The structure of the geosynclinal area is complex. It is characterized by steep dips and tight, closely spaced folds, many of which are overturned to the east, and most of which have a parallel strike and and are continuous for miles. Overthrust, reverse, and transverse faults of both large and small displacement are abundant--in fact many segments of the Phosphoria are so crushed and broken by faults as to be unsuitable for mining. Normal or valley faults of large displacement and relatively recent origin are abundant also. Worthy of note too are large granitic intrusives of Cretaceous and Eocene age (e.g. the Idaho and Boulder batholiths) and widespread lava flows of Miocene and Pliocene age.

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Figure 1

Index map of the western phosphate field, showing limits of the Phosphoria, Park City, and other formations (solid line) and their phosphate deposits (dashed line). The eastern and southeastern boundaries shown on the map represent fairly accurately the true limits at the time of deposition. The western limits at the time of deposition cannot now be accurately reconstructed because the Permian rocks there either have been eroded away or are concealed beneath thrust plates of older rocks. The southern and southwestern limits are now poorly defined because not enough stratigraphic work has been done to differentiate the facies of the Permian Phosphoria formation from those of the Kaibab limestone, Gerster formation, and Arcturus formation and other western facies which may be at least partial age equivalents. Numbers show the location of measured sections on figures 3, 4, and 5.

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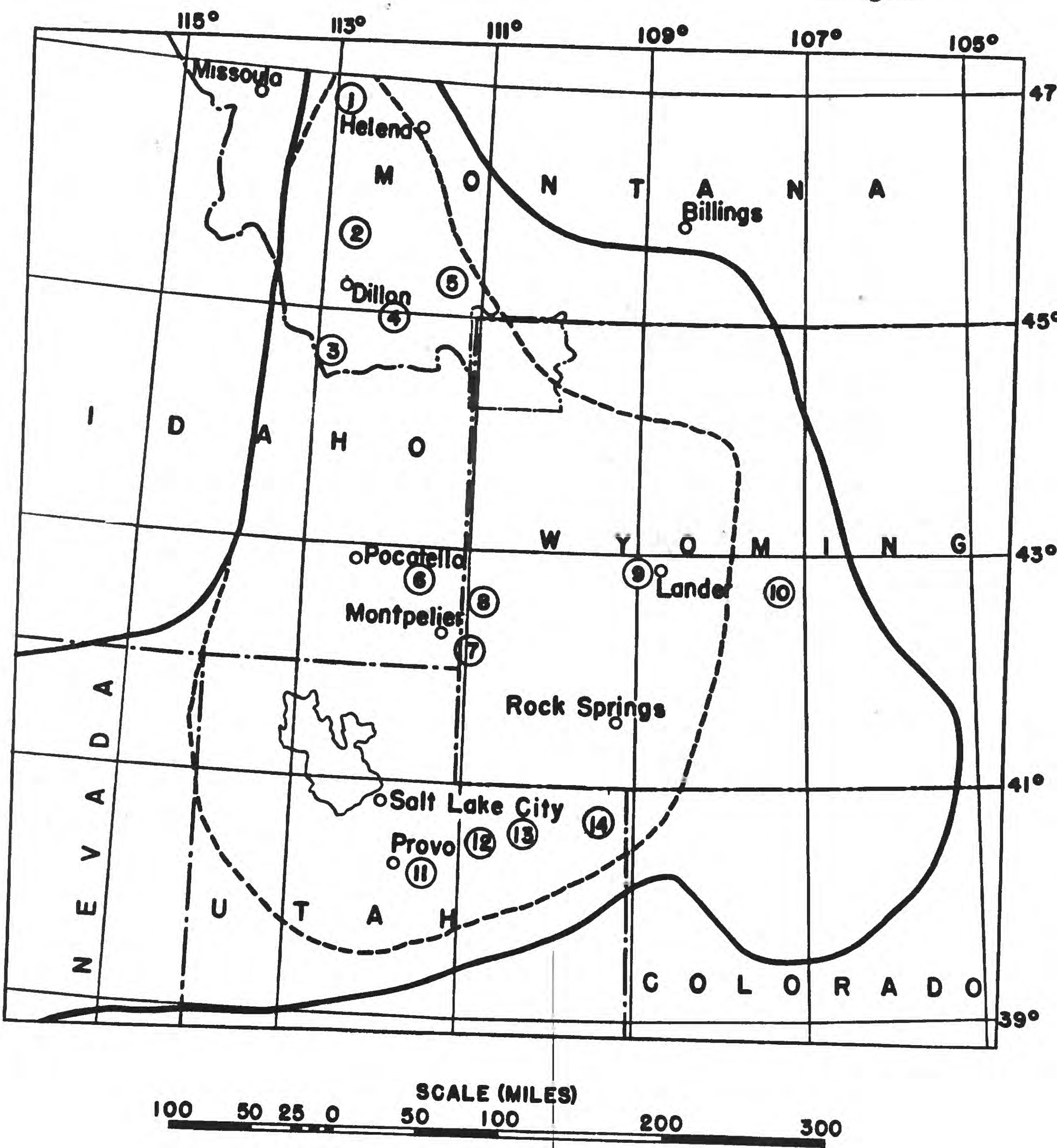
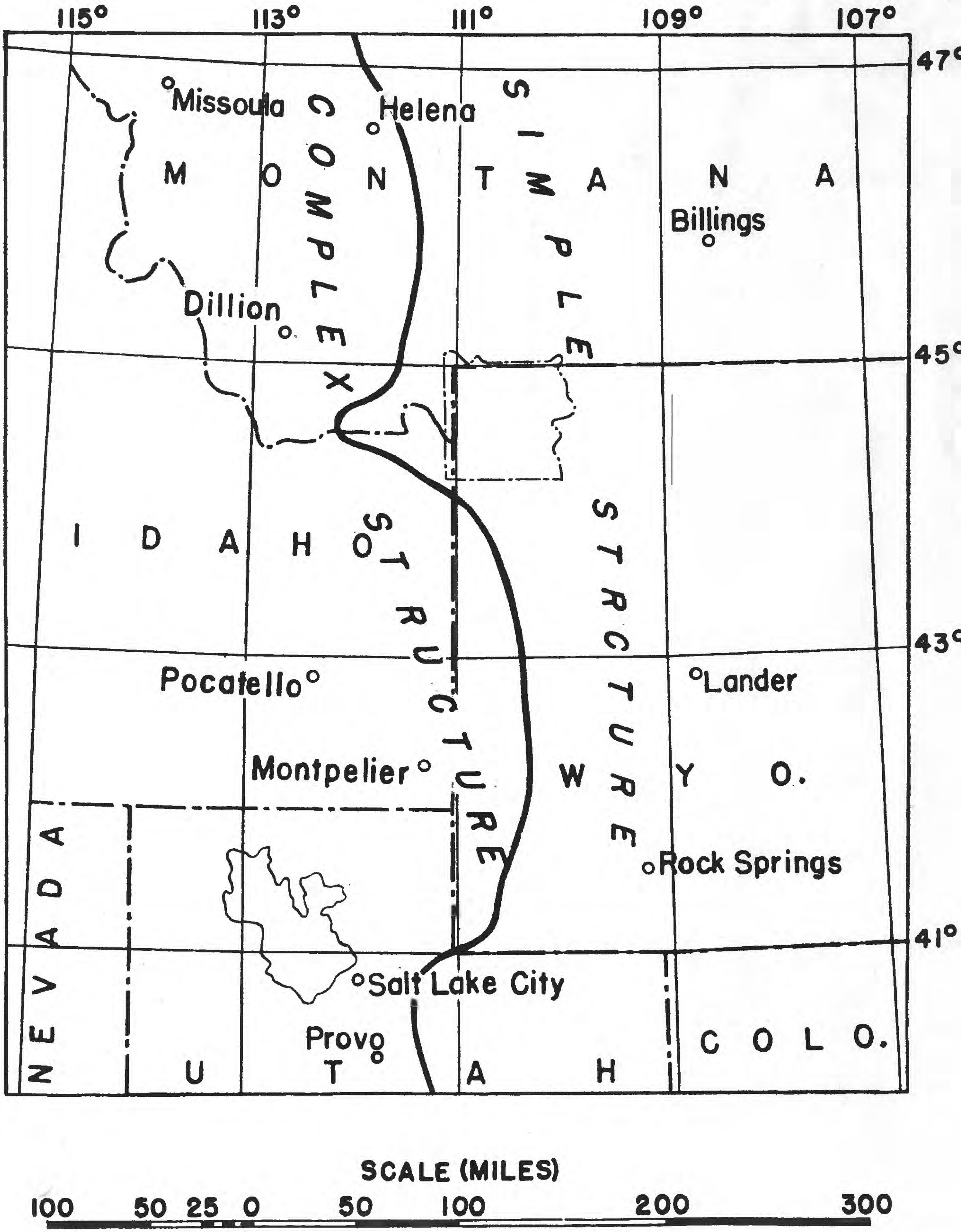
Fig. 1


115°
113°
111°
109°
107°
105°
47°
45°
43°
41°
39°
Missoula
Helena
M O N T A N A
Billings
Dillon
I D A H O
W Y O M I N G
Pocatello
Lander
Montpelier
Rock Springs
N E V A D A
Salt Lake City
Provo
U T A H
C O L O R A D O
1
2
3
4
5
6
7
8
9
10
11
12
13
14
SCALE (MILES)
100
50
25
0
50
100
200
300

The pre-Cretaceous rocks of the shelf area resemble those of the geosyncline in general lithology. Detritus, especially quartz sandstone, forms a greater part of the section, however, and non-marine clastics and evaporites are interbedded with the marine sediments. The shelf rocks are much thinner than those of the geosyncline and are measured in thousands rather than tens of thousands of feet. Gaps in the stratigraphic record, some representing the duration of a full geologic period, are present in parts of the area. The post-Jurassic sedimentary rocks of the shelf are widespread in distribution and consist of tens of thousands of feet of mostly non-marine detritus (including much conglomerate and dirty sandstone), coal, evaporites, and minor amounts of carbonate rocks.

The structure of the shelf area is simple. Dips are gentle and most of the folds are broad, open, and without dominant orientation. Although some faults, including thrusts, occur, large areas are unfaulted. Most of the intermontane basins are synclinal, and block-fault basins are rare or absent. A few granitic intrusions are present, but most of the exposures of granite in the shelf area are a part of the pre-Cambrian basement. Tertiary volcanic rocks are found in many places near the geosynclinal border of the area, but are sparsely distributed elsewhere.

Fig. 2



Boundary between areas of simple and complex structure in the northern Rocky Mountains.

GEOLOGY OF THE PHOSPHORIA FORMATION

General relations

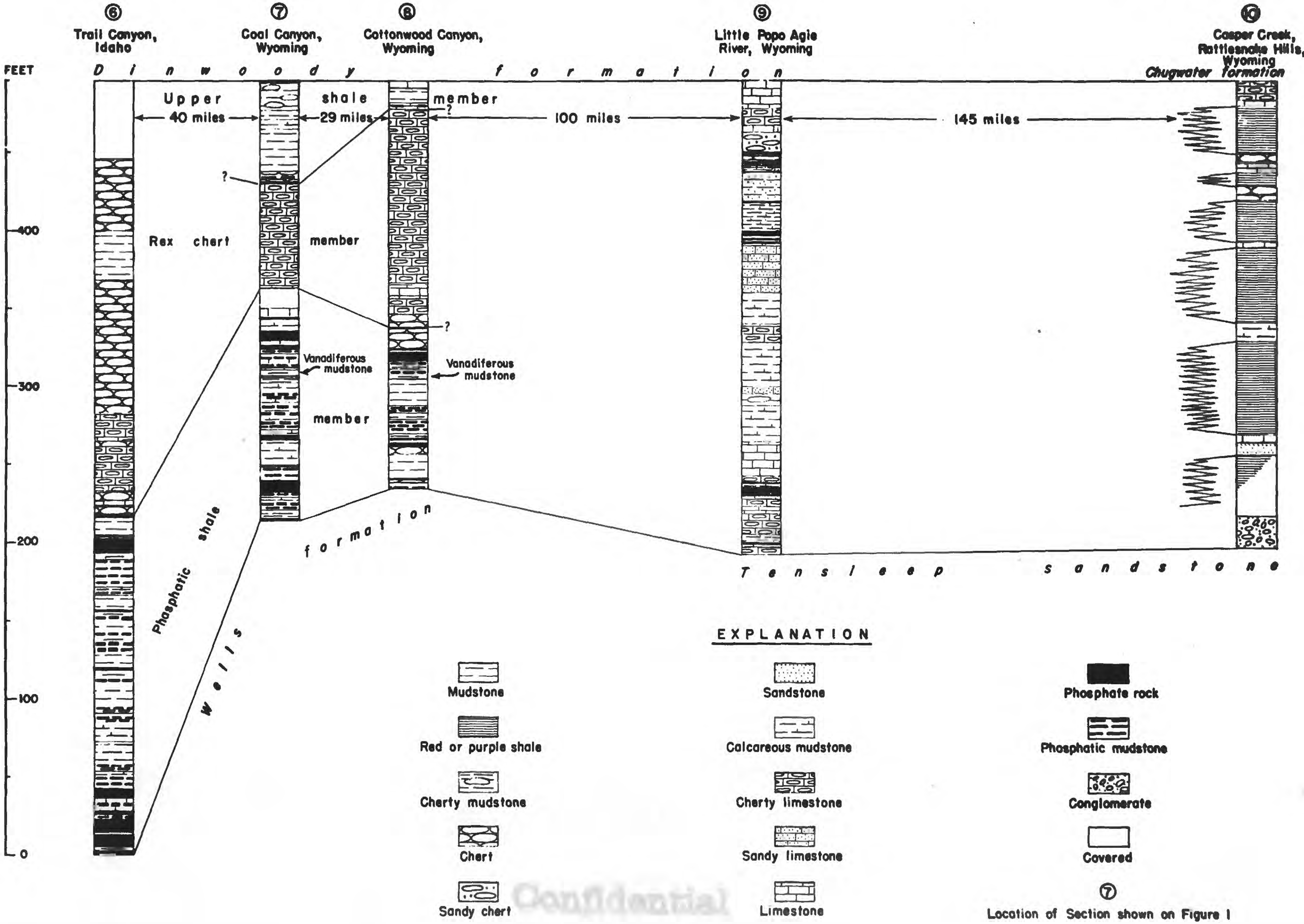
At its type locality in southeastern Idaho (Richards and Mansfield), the Phosphoria formation consists of a lower, phosphatic shale member, about 180 feet thick, and an upper member, the Rex Chert, 240 feet thick; a third member, a cherty mudstone or shale 15 to 75 feet thick, overlies the Rex in most of southeastern Idaho and western Wyoming, though it is not well defined at the type locality of the Rex member in the Crawford Mountains of Utah (Gale and Richards). The Phosphoria is underlain by the Wells formation, the uppermost 50-100 feet of which consists of limestone (in part cherty and sandy) and the remainder of which is largely sandstone. The Triassic Dinwoody formation, which consists mainly of calcareous siltstone, overlies the Phosphoria formation in southeastern Idaho, but tongues out into nonmarine red beds of the Woodside formation to the east and south.

These units of the Phosphoria formation are easily recognizable over a wide area in Idaho and adjacent areas, but in central Wyoming the whole aspect of the formation is different, for it is thinner and contains a greater proportion of sand and carbonate and much less phosphate and shale (fig. 3). Farther east, in southeastern Wyoming, the phosphate is entirely absent, and the formation tongues out into nonmarine red beds of the lower Chugwater formation (Thomas). Although the better known phosphate deposits lie east of Fort Hall in Idaho, the Phosphoria formation has been identified further west near Malta, Idaho (Anderson, pp. 35-37). Both the lower phosphatic shale and the Rex chert

Figure 3

Typical sections of the Phosphoria formation in Wyoming and Idaho. The Rattlesnake Hills section was measured by H. D. Thomas (1934); the Lander section by Ralph H. King (1947); the Salt River Range section by J. D. Love and L. E. Smith; the Coal Canyon section by V. E. McKelvey, and the Trail Canyon section by L. E. Smith, R. A. Hoppin, and V. E. McKelvey, all of the U. S. Geological Survey.

Fig. 3



⑥ Trail Canyon, Idaho
⑦ Coal Canyon, Wyoming
⑧ Cottonwood Canyon, Wyoming
⑨ Little Popo Agie River, Wyoming
⑩ Casper Creek, Rattlesnake Hills, Wyoming
FEET
400
300
200
100
0
D i n w o o d y f o r m a t i o n
Chugwater formation
Upper shale member
40 miles
29 miles
100 miles
145 miles
Rex chert member
Vanadiferous mudstone
Vanadiferous mudstone
Phosphatic shale member
formation
Wells
Tensleep sandstone
?
EXPLANATION
Mudstone
Red or purple shale
Cherty mudstone
Chert
Sandy chert
Sandstone
Calcareous mudstone
Cherty limestone
Sandy limestone
Limestone
Phosphate rock
Phosphatic mudstone
Conglomerate
Covered
⑦ Location of Section shown on Figure 1

are reported to be present there and to total about 900 feet in thickness (Baker and Williams). The quality and thickness of the phosphatic beds, however, are unknown.

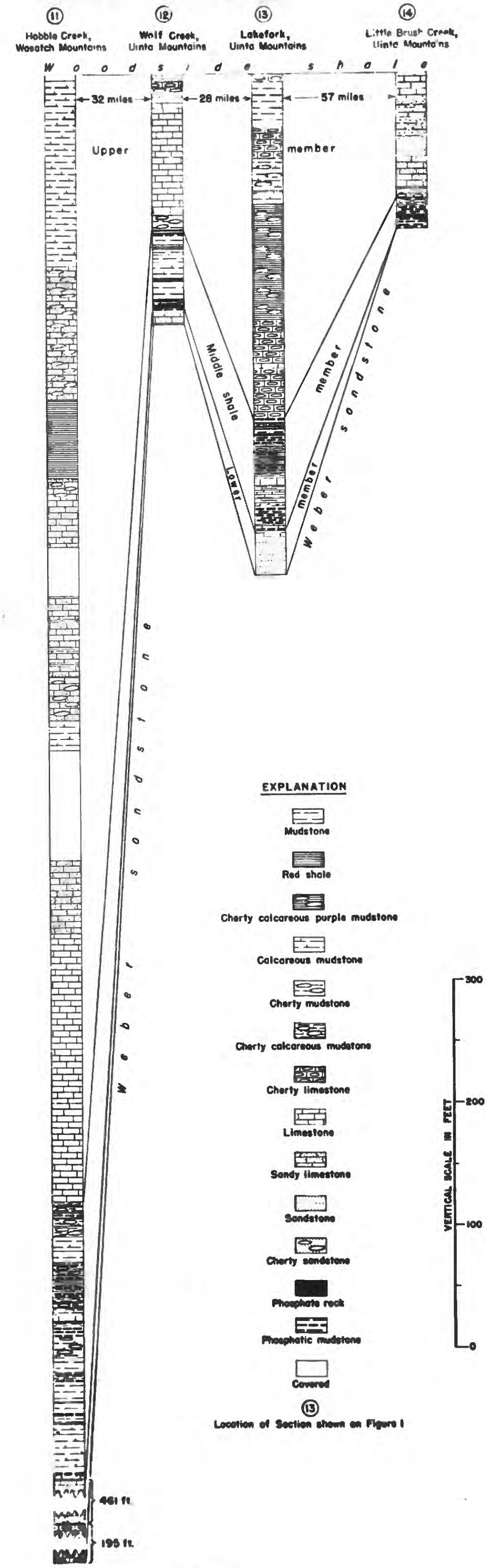
The westward thickening of the Phosphoria formation is displayed in other states and so, to some extent, are the other lithologic variations. In Utah, the stratigraphic unit known as the Park City formation is the partial equivalent of the Phospheria, and at Park City, its type locality (Boutwell), it lies between the Carboniferous (Pennsylvanian) Weber quartzite and red beds of the Triassic Woodside formation (fig. 4). It consists of a lower, cherty limestone member, which may be the stratigraphic equivalent of the Wells formation in southeastern Idaho; a middle shale member, which is somewhat phosphatic, but contains no high-grade phosphate beds, equivalent to the phosphatic shale in southeastern Idaho; and an "upper Productus limestone", equivalent to the Rex chert of southeastern Idaho. Eastward, the lower member thins out, the phosphate deposits disappear, and the shale and upper limestone members are more clastic and finally tongue out into nonmarine red beds in eastern Utah and Western Colorado (Thomas and Krueger). As in Idaho, the Park City thickens greatly to the west. In the Confusion Range, near the western border of Utah, the formation is 4,500 feet thick, but its phosphate content is unknown (Newell, 1948).

In southwestern Montana, the Phosphoria formation consists of two to five lithologic units, provisionally termed units A, B, C, D, and E (fig. 5). Unit A, at the base, consists of a sequence of cherty carbonate and clastic rocks; unit B, of phosphate rock and phosphatic mudstone; unit C, mainly of carbonate rock; unit D, of phosphatic mudstone;

Figure 4

Typical sections of the Park City formation in Utah. The Little Brush Creek section was measured by D. M. Kinney; the Lake Fork and Wolf Creek sections by J. W. Huddle; and the Hobble Creek section by A. A. Baker, R. S. Sears, M. D. Stewart, G. F. Hosford, and D. F. Sprouse, all of the U. S. Geological Survey. Note: the line at the top of the Park City formation may not be the same time-line at every locality, for the upper part of the Park City formation tongues out into red beds similar to the Woodside shales in the eastern part of the area; see Thomas, H. D. and Krueger, M. L.

Fig. 4



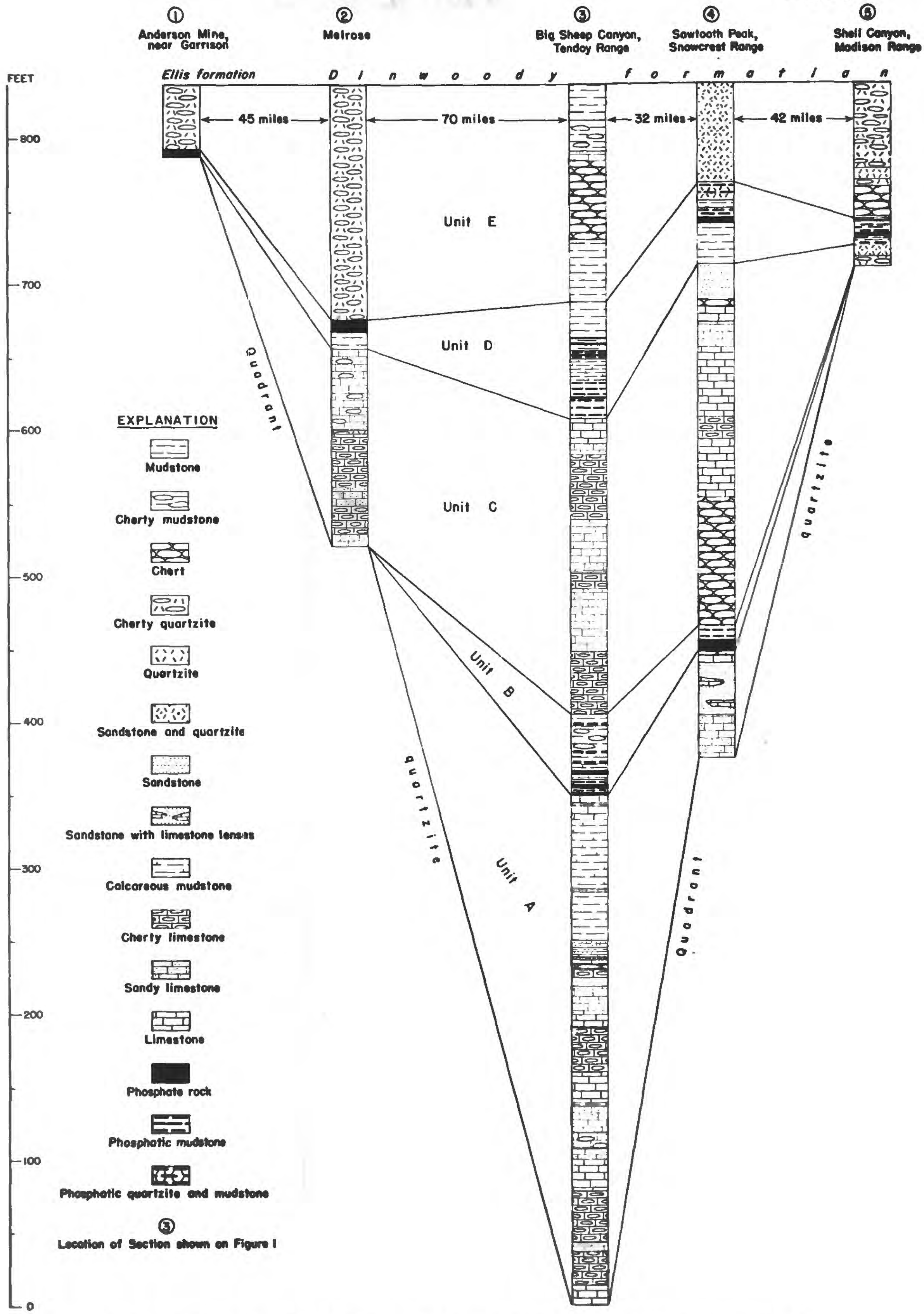
⑪ Hobble Creek, Wasatch Mountains
⑫ Wolf Creek, Uinta Mountains
⑬ Lakefork, Uinta Mountains
⑭ Little Brush Creek, Uinta Mountains
Woodside shale
32 miles
28 miles
57 miles
Upper member
Middle shale member
Lower member
Weber sandstone
Weber sandstone
461 ft.
195 ft.
EXPLANATION
Mudstone
Red shale
Cherty calcareous purple mudstone
Calcareous mudstone
Cherty mudstone
Cherty calcareous mudstone
Cherty limestone
Limestone
Sandy limestone
Sandstone
Cherty sandstone
Phosphate rock
Phosphatic mudstone
Covered
⑬ Location of Section shown on Figure 1
VERTICAL SCALE IN FEET
300
200
100
0

and Unit E, of chert. In the Centennial Range unit E is overlain by a thin section of dark mudstone, which has not been recognized elsewhere in Montana. Unit A may prove to be the stratigraphic equivalent of the upper part of the Wells formation in southeastern Idaho and the lower limestone member of the Park City formation of Utah; units B, C, and D may be equivalent to the phosphatic shale member; and unit E to the Rex member. In the vicinity of Dell and Lima the total thickness of the Phosphoria is 485 feet. The clastic-carbonate sequence (unit A), the lower phosphate (unit B), and the lower carbonate (unit C) disappear eastward in the Madison Range and northward in the Garrison-Drummond area.

In summary, the Phosphoria formation along the eastern margin of the marine basin in which it was deposited contains no phosphatic rocks, and consists of marine layers, principally carbonate and sandstone, interbedded with nonmarine red beds. Westward, as in central Wyoming and eastern Utah, thin phosphatic rocks are interbedded with limestone, mudstone, and sandstone; still farther west, as in western Utah and southeastern Idaho, the formation thickens, and the bulk of it is composed of chemical precipitates (limestone and phosphate rock), very fine detritus (clay and silt), and organic matter.

These westward changes in facies and thickness of the formation are similar to those of many other of the Paleozoic and early Mesozoic formations. It is noteworthy that throughout much of the area the most pronounced changes in the Phosphoria as well as many of the other formations take place in the vicinity of meridian 111°, the approximate boundary between the platform or shelf and the geosyncline.

Fig. 5



TYPICAL SECTIONS OF THE PHOSPHORIA FORMATION IN MONTANA

The Madison Range section measured by R. A. Swanson; Sawtooth Peak section by F. S. Honkla and O. A. Payne; Dell section by W. R. Lowell; and the Melrose and Garrison sections by M. R. Klepper; (all of the U. S. Geological Survey). Stratigraphic correlation by M. R. Klepper

Age

Most Permian specialists now agree that the phosphatic shale member of the Phosphoria formation is equivalent to part of the Guadalupe series (Kazanian) and possibly part of the Leonard series (Artinskian and Kungurian) as well (Miller and Cline; Miller and Furnish; Newell; Thompson, et. al.; Licharew, in Williams, 1938). The age limits of the Phosphoria have not been established but Baker and Williams (1940) class the lower member of the Park City formation in the area near Provo, Utah, as Kaibab (Leonard); Frenzel and Mundorff (1942) define beds at the base of the Phosphoria or top of the underlying Quadrant in the Three Forks, Montana, area as Wolfcamp; and Newell and Kummel (1942) have shown that the overlying Dinwoody formation in southeastern Idaho is probably upper Otoceratan--i.e. early, but not earliest, Triassic. Baker and Williams and later Frenzel and Mundorff recognized the possibility that the base of the rocks of Phosphoria lithology may not be the same age everywhere.

Even though the upper and lower age limits of the Phosphoria formation are uncertain, without question it represents a major portion of Permian time.

Lithology

Composition and mineralogy

Lime, phosphate, silica, carbon dioxide, organic matter, magnesia, alumina, iron oxide, and fluorine, listed in approximate order of abundance, are the principal constituents of the phosphatic shale member in southeastern Idaho and adjacent areas, but in addition more than 25 other elements have been reported (Table 1). The Rex member is composed

largely of silica and calcium carbonate. Elsewhere the principal constituents of the formation as a whole are probably silica and calcium and magnesium carbonate, and the other constituents are present in only minor quantities.

The principal minerals of the Phosphoria formation are quartz, minerals of the fluorapatite group, calcite, dolomite, and clay minerals. Two fluorapatite minerals, both having the same X-ray structure and chemical composition, have been identified. One is an isotropic-appearing mineral described as collophane; the other is a birefringent mineral whose optical properties are those of francolite (approximately $10CaO.3P_2O_5.CaF_2.CO_2$). Other minerals, present in most places in minor amounts, are mica, feldspar, purple fluorite, pyrite or marcasite, glauconite, which is present in the platform facies only and not yet recognized in the geosynclinal area, and a number of secondary vanadium minerals, such as hewettite ($CaO.3V_2O_5.9H_2O$), pascoite ($2CaO.3V_2O_5.11H_2O$) and sincosite ($CaO.V_2O_4.P_2O_5.5H_2O$).

Efforts to identify the mineral that carries the vanadium and other minor metals in unaltered rocks have been unsuccessful, principally because these minerals are so exceedingly fine-grained and so obscured by organic matter that they cannot be studied microscopically. Chemical analyses, interpreted by W. W. Rubey, indicate that the vanadium is probably in a clay mineral (hydromica), and the occurrence in the clayey rocks of the formation of some of the other minor metals, such as nickel, zinc, and chrome, makes it seem probable that some of the other metals occur in clay minerals too. Although minor amounts of these metals are found in some of the phosphate rocks, it is certain that they are not

Table 1

Elements reported from the Phosphoria formation

(listed in order of maximum amount reported)

	Maximum (percent)	Rock type or bed from which reported	Minimum (percent)	Rock type or bed from which reported
SiO_2	77.02	Chert	none	Phosphate rock
CaO	52.4	Phosphate rock	0.6	Mudstone (vanadiferous zone)
CO_2	43.22	Dolomite	0.04	Mudstone (vanadiferous zone)
P_2O_5	39.6	Phosphate rock	0.05	Mudstone (vanadiferous zone)
Organic matter	25.8	Shale	0.6	Phosphate rock
MgO	20.01	Dolomite	0.03	Cherty phosphate rock
Al_2O_3	14.99	Mudstone	0.08	Chert
Fe_2O_3	10.00	Chert	0.3	Phosphate rock
F	7.0	Phosphate rock (fluoritic)	0.02	Limestone or dolomite
K_2O	5.07	Mudstone	0.06	Phosphate rock
H_2O-	4.47	Mudstone	0.03	Limestone
S	4.1	Mudstone (vanadiferous zone)	none	Dolomite
Sr	1/3.6	Phosphate rock	none	Vanadiferous zone
Na_2O	3.2	Mudstone	0.1	Dolomite
H_2O+	1.4	Phosphate rock	0.6	Phosphate rock
ZnO	1.3	Mudstone (vanadiferous zone)	none	Mudstone

(Table continued on next page)

Table 1 (cont'd)

	Maximum (percent)	Rock type or bed from which reported	Minimum (percent)	Rock type or bed from which reported
TiO_2	1.0	Mudstone (vanadiferous zone)	none	Phosphate rock
Cr_2O_3	0.8	Clay	none	Mudstone
Mn	0.6	Mudstone (vanaderiferous zone)	none	Mudstone
NiO	0.3	Clay (vanadiferous zone)	none	Mudstone
MoO_3	0.1	Mudstone (vanadiferous zone)	none	Phosphate rock
BaO	0.07	Phosphate rock	none	Mudstone
Se	0.068	Mudstone (vanadiferous zone)	0.019	Mudstone
PbO	0.05	Mudstone (vanadiferous zone)	none	Mudstone, limestone, etc.
U	0.034	Phosphate rock	none	Chert, limestone

Smaller quantities of CuO, Cl, SnO, Co_2O_3, As_2O_3, Sb_2O_3, BeO, I, Ag, Cb, B, and rare earths have also been reported. Bi, Cd, Hg, B, Li, W, Ga, Au, and Pt have never been reported, although several hundred samples have been tested spectrographically for them.

1/ Reported to me orally by D. L. King, San Francisco Chemical Company.

present in the phosphate minerals, for, in both size and gravimetric separations of the phosphate rock, the minor metals are concentrated in the opposite fractions from those in which the phosphate minerals are concentrated. Uranium, on the other hand, is apparently in or otherwise tied to the phosphate minerals. This will be discussed more fully later.

Rock types

Rocks of the Phosphoria formation consist of mixtures of three types of materials: chemical sediments (dominantly phosphate, calcite, dolomite, and chert, but locally including minor amounts of pyrite or marcasite, gypsum and glauconite); detritus (chiefly quartz, clay, mica, feldspar); and attritus (i.e. organic matter). These three types of materials might be envisioned as occupying the corners on a ternary diagram, on which points representing the composition of most Phosphoria rocks would be scattered over the interior of the diagram and few, if any, would fall at the corners. In southeastern Idaho and adjacent areas most of these materials are of silt- or clay-size, though elsewhere in the field (platform facies), sand-sized particles are abundant, especially in the non-phosphatic portions of the formation. Some of the chemical particles, especially the phosphates, are structurally aggregated into oolites, pisolite, or nodules which give the rocks a coarse-textured appearance.

For purposes of classification, organic matter, which is difficult to evaluate quantitatively in the laboratory, much less in the field, is

disregarded and the sediments considered to be of two types: chemical and detrital. The rock name of the chemical sediments is derived from the name of the mineral forming more than 50 percent of the rock (or the dominant mineral if no one mineral forms more than 50 percent of the rock) and is modified by adjectives representing minerals which make up more than 20 percent of the rock. The rock name of the detrital sediments is based upon texture and qualified by adjectives in the same way as the chemical rocks. Because the differentiation of the finest-grained detrital rocks is too difficult to attempt in the field, siltstones and claystones are grouped under the general term mudstone.

Classing the rocks in this way, the Phosphoria formation contains six pure rock types: Phosphate rock, limestone, dolomite, chert, mudstone, and sandstone; 36 types composed principally of mixtures of two minerals, as phosphatic limestone, dolomitic mudstone, cherty phosphate rock, argillaceous sandstone, etc.; and 216 rock types in which three minerals each occur in amounts of more than 20 percent of the rock. Generally it is not possible to differentiate the three-mineral rock types in the field, and the breakdown presented here may seem overly theoretical. On the contrary, however, all of these types are present--many at a single locality, and it is one of the notable features of the formation that few of its rocks are composed of one material alone; most of them are mixtures of several very different types of materials.

Most of the phosphatic and argillaceous rocks are dark colored--black where fresh, but various shades of brown or gray where weathered. The carbonate rocks and the cherty rocks are dark too in many areas, especially

in the geosynclinal facies, but elsewhere they are various shades of light gray or light brown. The phosphatic and argillaceous rocks as well as most of the interbedded carbonate rocks are not resistant to weathering. They rarely crop out and are generally concealed by a few to more than 30 feet of soil or talus. Where exposed in trenches most of them are soft or medium hard, jointed and fractured. Most of the cherty rocks and many of the carbonate rocks and sandstones are hard and resistant to weathering and crop out in conspicuous combs or ridges.

Areal variations in thickness
and quality of the phosphate rock

The areal variations in the lithology of the Phosphoria formation are an important clue to its origin; in addition, an understanding of them is valuable in appraising known phosphate deposits and in further prospecting, both in the western field and elsewhere. Description of areal variations will be restricted to some of the variations of the phosphate rocks, not only because they are the uranium-bearing rocks, but because they are the rocks around which must center any exploitation of the minerals of the Phosphoria.

Nearly all the phosphate in the Phosphoria formation of southeastern Idaho and adjoining areas is concentrated in two zones--a lower and an upper zone--of the phosphatic shale member, and the thickest and highest-quality phosphate beds are at the base of the lower zone and the top of the upper zone (fig. 6). The lower phosphate bed is the only one mined throughout most of southeastern Idaho. In Wyoming and Utah, on the other hand, the lower phosphate bed either is not present, or is not as phosphatic as it is in southeastern Idaho, but the upper phosphate bed is

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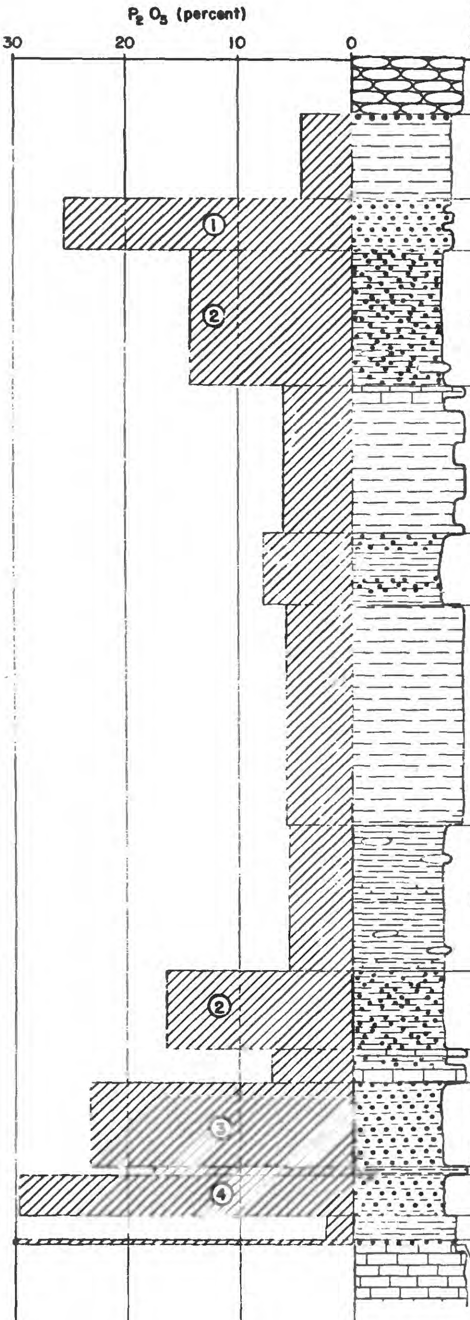
Fig. 6



Thickness (feet)	P_2O_5 (percent) Av.	P_2O_5 (percent) Range	Thickness (ft.) X P_2O_5 (percent)	Lithology
				REX CHERT MEMBER
				PHOSPHATIC SHALE MEMBER
15	4.4	3.0 - 4.8	66	Mudstone: medium hard, brownish gray, thick-bedded; persistent nodular phosphatic rock, 0.5 ft. thick at top.
9	25.4	22.6 - 27.0	229	Upper phosphate zone: coarsely oolitic, medium-hard, brownish-gray, thin- and thick-bedded phosphate rock; thin layers of phosphatic, oolitic, soft, brown mudstone interbedded.
24	14.6	12.0 - 20.5	351	Mudstone: phosphatic, soft, brownish black, thin-bedded; increasingly vanadiferous toward top; calcareous lenses, up to 1 foot in thickness, abundant in lower part.
26	6.1	4.5 - 7.8	159	Upper nodular zone: medium-hard and hard, moderate brown, thick-bedded, mudstone; and interbedded thin layers of nodular, soft to hard, grayish-black phosphate rock. Persistent hard, massive limestone, 2 ft. thick, at top. Dark yellowish-orange and strong brown stains generally abundant.
13	8.0	6.6 - 8.6	104	Mudstone and phosphatic mudstone: soft, brownish-gray, thin-bedded mudstone; contains some phosphatic layers.
39	6.0	4.4 - 8.4	234	Middle nodular zone: silty, hard, moderate brown, massive mudstone and interbedded thin layers of nodular, hard, grayish-black phosphate rock. Dark yellowish-orange and strong brown stains generally abundant.
26	5.9	4.6 - 6.5	153	Mudstone: soft, brownish-gray, thin-bedded mudstone; hard, brownish-gray massive limestone layers in middle and at base; limestone lenses abundant throughout.
14	16.9	15.0 - 18.5	236	Mudstone: phosphatic, soft, brownish gray, thin-bedded; contains a few limestone lenses.
6	7.3	4.3 - 10.0	44	Limestone and phosphatic mudstone: hard, gray, massive limestone at top and base (basal layer known as "false cap"); phosphatic, soft thin-bedded mudstone in middle.
15	23.5	21.9 - 25.1	357	Phosphatic rock: argillaceous, soft, brownish gray, thin-bedded. A parting, 2 ft. in thickness, contains only about 16 percent P_2O_5; remainder averages about 25 percent P_2O_5.
1	17.8	8.7 - 26.2	18	"Cap" limestone: phosphatic, argillaceous, hard, thick-bedded. Generally soft, clayey, and more phosphatic at the surface.
7	29.7	24.8 - 32.8	208	Lower phosphate bed: soft, brownish black, thin-bedded. Generally contains more than 31 percent P_2O_5 in operating mines.
4	2.4	2.0 - 3.0	10	Mudstone: clayey, soft, brown, thin-bedded.
1	30.6	29.9 - 34.0	31	Contact phosphate bed: crystalline in part, hard, grayish black, thick-bedded.
				WELLS FORMATION

① Contains 10.7 percent of total phosphate in member
② Contain 26.6 percent of total phosphate in member
③ Contains 16.2 percent of total phosphate in member
④ Contains 9.1 percent of total phosphate in member

GENERALIZED SECTION OF PHOSPHATIC SHALE MEMBER OF PHOSPHORIA FORMATION IN SLUG CREEK QUADRANGLE, IDAHO

Phosphate content based on analyses of samples collected from a cross-cut on the 300 level of the Conda Mine; and trenches in Trail Canyon and south Dry Valley

of minable thickness and grade at most places in western Wyoming and northern Utah.

The middle shale member of the Park City formation, which is the Utah equivalent of the phosphatic shale member of the Phosphoria formation, contains the principal phosphatic beds in Utah. None is as thick or highly phosphatic as in southeastern Idaho, but, at least in the Wasatch Mountains east of Provo, the thickest and richest beds are also near the base and top of the member.

In the central Wyoming area, near Lander,two thin, moderately phosphatic zones are present, one near the base and the other about 100 feet below the top (King). Neither zone has ever been mined.

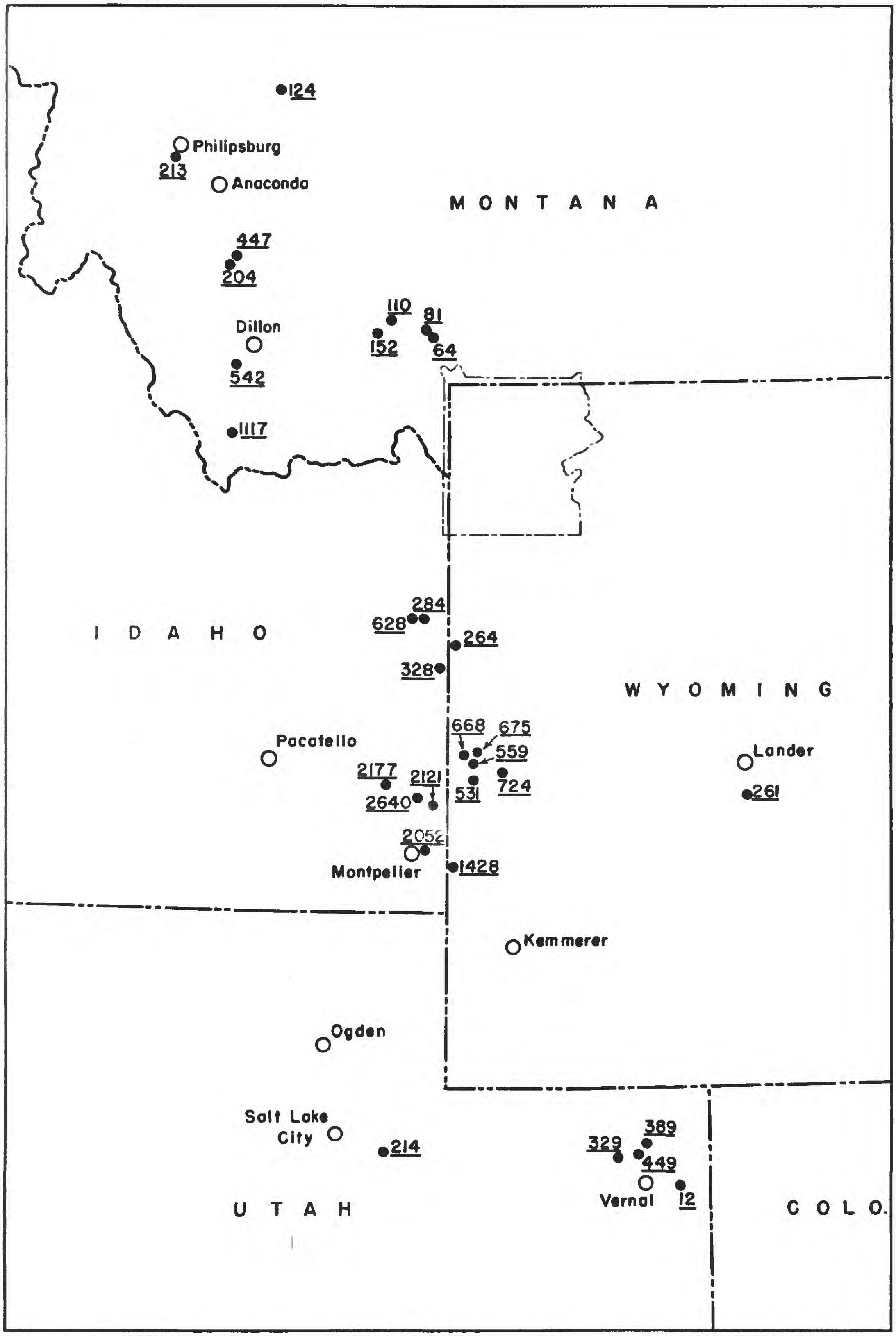
In Montana, phosphate is found at two principal horizons, one in Unit B, near the base of the formation, the other in Unit D, near the middle or top. As far as known, the lower zone is of commercial interest only in the Snowcrest and Centennial Ranges, where it is 4 to 6 feet thick and contains about 32 percent P_2O_5. Elsewhere it is too thin, as in the vicinity of Dillon, or too low in phosphate content, as in the vicinity of Dell, to be mined at present; or it is absent altogether, as in the Madison Range and the Melrose, Phillipsburg, and Garrison areas. The upper phosphate bed is about 4 feet thick and contains about 32 percent P_2O_5 in the Garrison area, and where the lower members are absent, it occurs at the base of the formation, but farther south in the Melrose, Dillon, and Dell areas the phosphate is so diluted by interbedded and admixed mudstone that no thick, highly phosphatic beds are present. The upper phosphate zone is present in the Madison and Centennial Ranges, but is too thin and too low in phosphate content to

be mined.

The general westward increase of phosphate content is shown by a comparison of the total amount of phosphate, in terms of thickness multiplied by percent P_2O_5, at various localities over the region (fig. 7). Thus, in the vicinity of Lander, the total feet-percent of phosphate in the phosphatic portions of the formation is about 260, and the total increases progressively westward to about 600 feet-percent in western Wyoming, 1,400 on the Wyoming-Idaho border, and 2,000-2,600 in southeastern Idaho. Though a similar trend exists in Utah and Montana, at no place yet known does the formation contain as much total phosphate as it does in southeastern Idaho.

Total phosphate alone, of course, is not a reliable means of evaluating the relative quality of the deposits over the region, for a total phosphate content can be dispersed over a large thickness of rock too low in P_2O_5 content to be minable, as it is in parts of southwestern Montana. Conversely, a relatively small total amount of phosphate, say 160 feet-percent, can be concentrated in one minable layer, as it is in the Garrison area and Centennial Range, where virtually all the phosphate in the formation is concentrated in one minable bed belonging to the middle and lower zones respectively. Over the remainder of the field, however, there is good correlation between the total amount of phosphate and the thickness of the high-grade beds. Thus, the Lander area contains no high-grade beds at all, and the grade increases westward to southeastern Idaho where 11 to 19 feet of beds contain 31 percent or more P_2O_5 (fig. 8). So it is too with beds of lower phosphate content. In the Lander area, about 3 feet of beds contain more than 25 percent P_2O_5, and in southeastern

Fig. 7



TOTAL PHOSPHATE (IN FEET X PERCENT P_2O_5) IN PHOSPHATIC PORTION OF PHOSPHORIA FORMATION

SCALE 0 20 40 60 80 100 MILES

Idaho, 20 to 32 feet of beds contain more than 25 percent P_2O_5 (fig. 9). Similarly, in the Lander area, only about 4 feet of beds contain more than 18 percent P_2O_5 whereas in southeastern Idaho, 43 to 62 feet of the section contain more than that amount (fig. 10).

Though regional variations in the stratigraphy must be considered in an appraisal of the potentialities of the field, they should not be emphasized so as to overshadow one of the most important features of the Phosphoria formation, namely, the remarkable lateral continuity of individual layers in particular areas. Thus, a distinctive phosphate bed at the very base of the phosphatic shale member is identifiable from the Crawford Mountains of Utah to Fort Hall, Idaho--a distance of more than 100 miles--though in no place is the bed more than a few inches thick. The lower phosphate bed is mined at various localities between Montpelier and Fort Hall, and over this distance it is relatively uniform in thickness and lithology. Many similar examples of great lateral continuity of individual layers could be given.

The lateral continuity of the beds is not great in the eastern and northern parts of the field, but even there it is sufficient at most places to greatly simplify evaluation of grade and tonnage of any particular layer. In contrast with most other types of mineral deposits, as few as 8 or 10 carefully cut samples are generally adequate to evaluate the phosphate content of any particular bed along an outcrop as much as a mile or two in length. A single sample, in fact, may be representative of the grade and thickness over an area of several tens of thousands of square miles, but it is not safe to depend upon it.

Origin

The origin of the Phosphoria and its minerals is by no means fully

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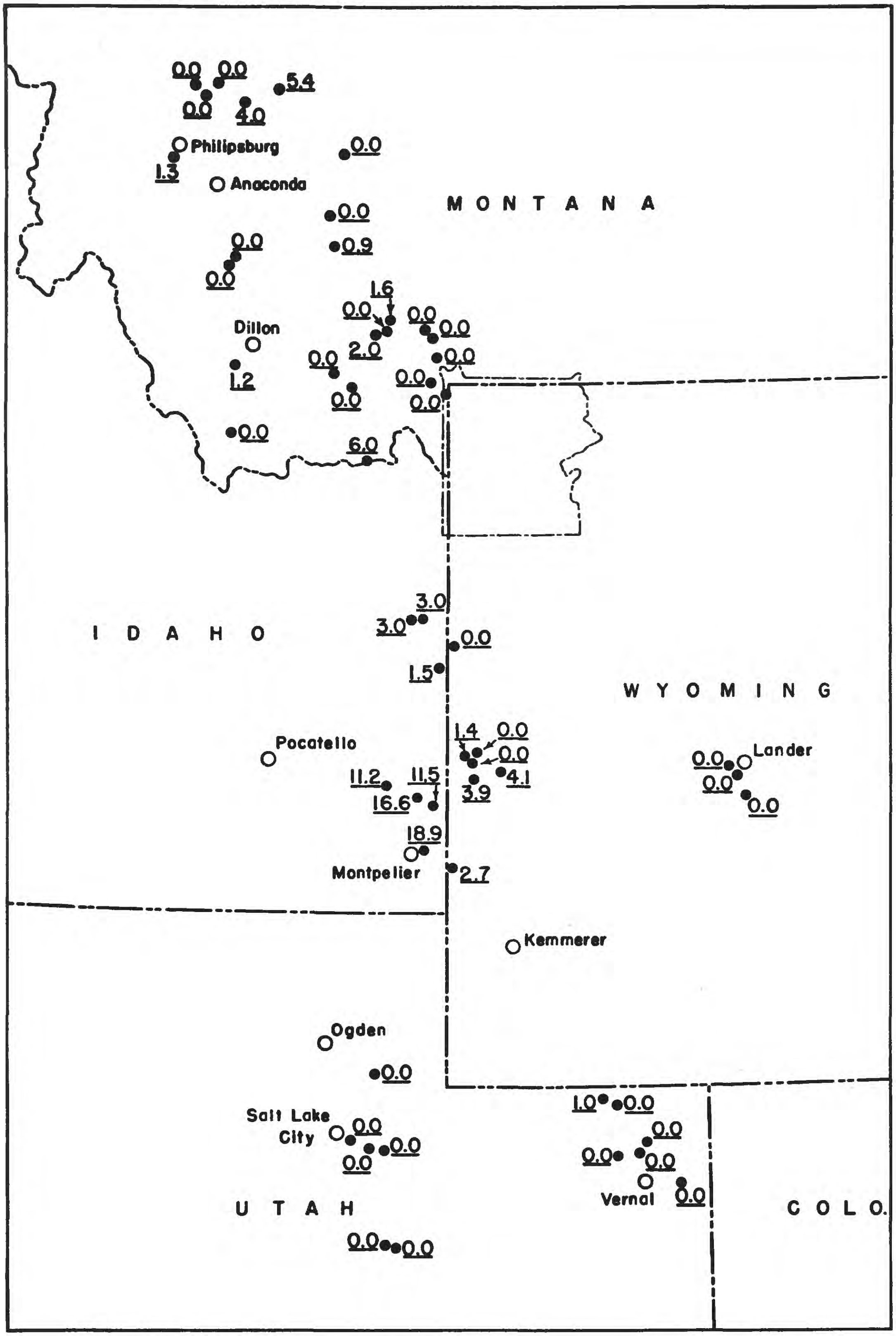
Fig. 8



TOTAL THICKNESS (IN FEET) OF ROCKS IN PHOSPHORIA FORMATION CONTAINING MORE THAN 31 PERCENT P_2O_5

SCALE 0 20 40 60 80 100 MILES

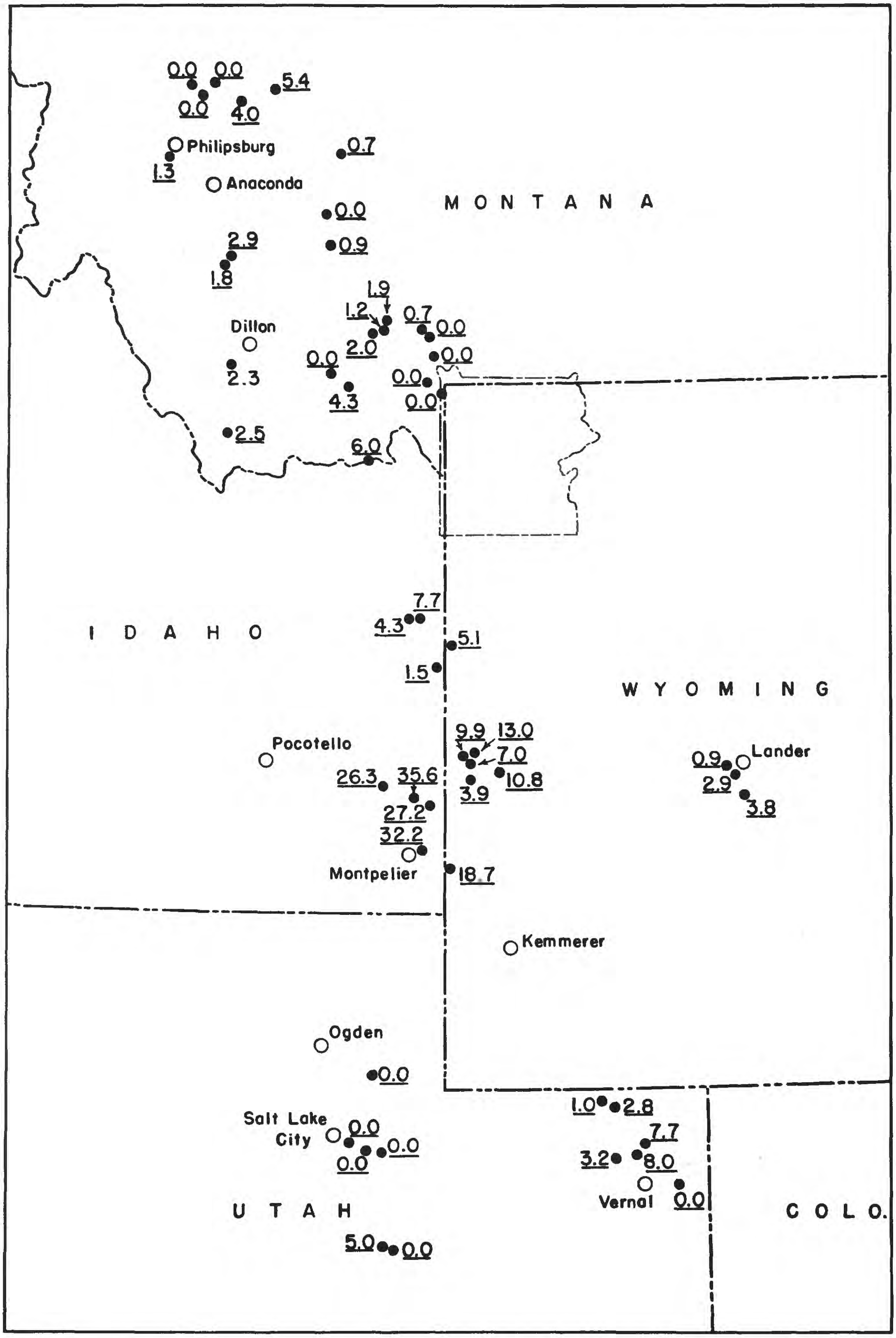
understood and, moreover, space does not permit full elucidation of such data and arguments as are pertinent to the problem. The following discussion is therefore merely a summary of views currently held by those working on the problem. Previous views are summarized ably by Mansfield (pp. 187-188, 1927; pp. 863-879, 1940a) and Pardee (pp. 151-166, 172-176, 1927).

Paleogeographic setting

The geography of the Northwestern States during Permian time is not known in detail, but the principal elements were: a) a low-lying land area to the east, bordering the Permian sea in central Montana, central Wyoming, and western Colorado; b) the shelf of the Permian sea, extending as far west as western Montana, western Wyoming, and central Utah; c) the miogeosynclinal basin, extending to eastern Nevada and central Idaho and separated in places (at least as far north as central Nevada) from the eugeosynclinal basin to the west by a geanticline (Nolan, 1943; Eardley, p. 315). A volcanic archipelago lay to the west, its eastern edge not far from the present eastern shore of the Pacific (Eardley, p. 311).

Although the phosphate deposits are restricted to an area of about 100,000 square miles, the Phosphoria sea was not a restricted or isolated body, but a part of the large Permian sea that covered much of the Cordilleran area. The principal marine facies correlative or at least partly correlative with the Phosphoria in the northwest are chemical sediments (carbonate and chert), clean quartz sandstone, and volcanic flows and pyroclastic rocks in the eugeosynclinal area of western Idaho, northern Nevada, and Oregon. It is noteworthy that thick sections of detritus, particularly of the graywacke type, are absent, not only in the region of Phosphoria facies, but in

Fig. 9



TOTAL THICKNESS (IN FEET) OF ROCKS IN PHOSPHORIA FORMATION CONTAINING MORE THAN 25 PERCENT P_2O_5

SCALE 0 20 40 60 80 100 MILES

adjacent areas as well.

The depth of the Phosphoria sea increased westward, as is shown by the westward decrease in grain size of the clastics. How deep the sea may have been at the edge of the shelf is not known, but the bottom there was at least below wave base, for ripple marks, cross-laminations, and other wave marks are lacking there; moreover, the large amount of organic matter in the sediments in western Wyoming and southeastern Idaho could hardly have been preserved under oxidizing conditions which certainly would have prevailed in a shallow sea of such wide extent. Even though the sea floor must have sloped gently westward, it must have been essentially flat in any given area, for individual layers are traceable over long distances and no unconformities have ever been recognized on physical evidence, either within the formation or at its base or top.

Time of deposition of the phosphate and minor elements

The deposition of the phosphate and minor elements coincided with the deposition of the matrix of the containing beds. This has never been questioned by those who have seen the rocks in the field, but, lest there be some skeptics who would be inclined to attribute the trace elements to replacement by later percolating solutions, a repetition of the evidence proving syngenetic origin seems justified.

1. Thin layers of various lithologic types and composition persist over areas of several square miles, and some layers, containing relatively uniform amounts of phosphate, vanadium, or other constitu-

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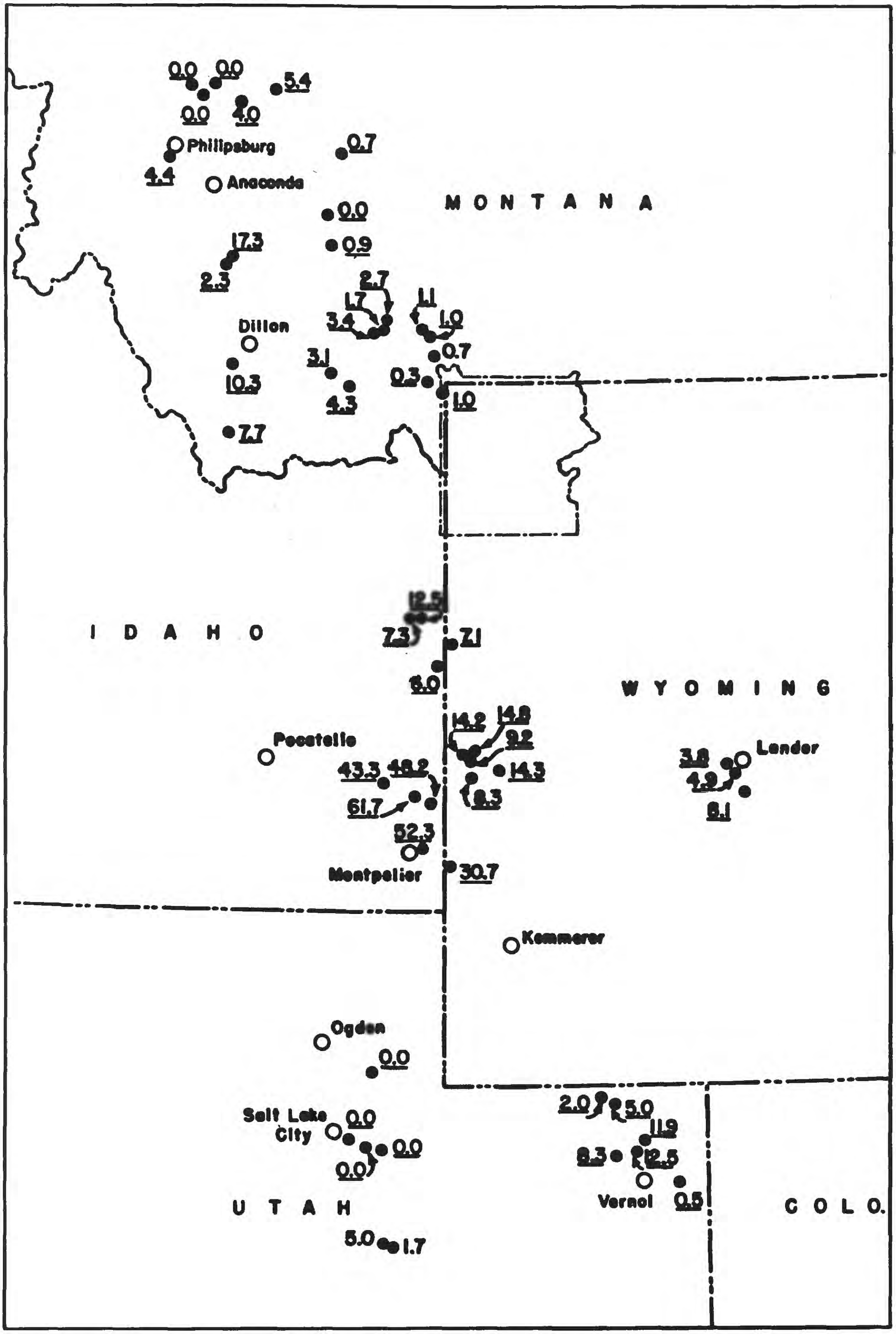
GEOLOGICAL SURVEY

Fig. 10



TOTAL THICKNESS (IN FEET) OF ROCKS IN PHOSPHORIA AND PARK CITY FORMATIONS CONTAINING MORE THAN 18 PERCENT P_2O_5

SCALE 0 20 40 60 80 100 MILES

ents, persist over areas of thousands of square miles.

2. Thin layers of markedly different composition, both in major and minor constituents, are interstratified.

3. Rocks which contain phosphate, vanadium, and uranium, and other trace elements are as diverse in texture, permeability, porosity, and composition as those which contain none of these constituents.

4. The mineral particles are very fine-grained.

Source of the Phosphoria sediments

Except for the detritus, which probably was derived from low-lying lands to the east, most of the elements in the Phosphoria formation were derived from the Phosphoria sea. All of the elements thus far reported from the Phosphoria formation, except antimony, are found in sea water today (Sverdrup, et. al., pp. 220, 229) and the sea is, in fact, the only "source rock" that could supply such opposing groups of elements as chromium, cobalt, and nickel, which are characteristic of ultrabasic rocks; vanadium and titanium, which, although found in rocks of diverse compositions, are comparatively abundant only in the gabbro family; copper, which is present in other rocks, but shows a preference for the subsilicic rocks; zinc, which is also found in other rocks, but which is most abundant in those that are slightly more siliceous; and molybdenum, tin, fluorine, and rare earths, all of which are generally most abundant in highly siliceous rocks (Clark, p. 40; Sandell and Goldich, p. 188).

Phosphatic sediments are accumulating on the sea floor today (Deitz, et. al.) and so are some of the other elements (Dana).

[illegible]

Although it has been suggested that the Phosphoria sea was richer in phosphate, fluorine, and possibly other elements than the sea today (Mansfield, 1940a), this postulate seems unwarranted. In fact, W. W. Rubey (unpublished investigations) has shown not only that the phosphate deposits of the Phosphoria type could accumulate from present day sea water, but that the Phosphoria sea was probably not much different in composition, with respect at least to phosphate content, CO_2, and pH, from that of the present day.

Factors leading to the concentration of phosphate and minor elements

The abnormally small deposition of carbonate and detritus was probably the most important factor in the concentration of the phosphate and minor elements of the Phosphoria formation. The Phosphoria is the product of deposition of half and possibly most of Permian time--an interval that is represented by several thousand feet of sediments in Texas and western Nevada--and yet is only 200 to 500 feet thick over most of the area. The notion that at least the phosphate was concentrated through slight or nondeposition of other constituents receives some support from occurrences in other rocks, where it is associated with unconformities and periods of nondeposition (Goldman; Pettijohn).

Absence of diluting carbonate and detritus is by no means the only factor effecting concentration of the phosphate and trace elements. As previously described, the total phosphate content of the formation increases westward, as the thickness of the formation increases, at least as far west as southeastern Idaho; evidently, therefore, other factors

beyond mere nondeposition of other constituents control the deposition of phosphate in one area and its nondeposition in another.

Kazakov (1937) and later more detailed investigations by Rubey (unpublished) have shown that precipitation of phosphate from the sea water is related primarily to the CO_2 content, pH, temperature, and pressure. By and large, the ocean is nearly saturated with phosphate (Dietz, Emery, and Shephard), but the phosphate content varies with depth, as does the temperature, partial pressure of CO_2, and pH. The following table is quoted from Kazakov (p. 111) and is based on conditions in the South Atlantic and the tropics.

Table 2

Depth, in meters	Temperature, centigrade	PCO_2 = x.10^{-4} atm	pH	P_2O_5 (mg/m^3)
0-50 zone of photosynthesis	22-20	about 3	8.15	From 0 to about 50 (oscillates seasonally)
50-500	20→7	3→11 (maximum)	8.1-7.7	Increase to 300 (maximum)
500-1,500	7→4	11→4	7.7→8.0	Fall to about 200
>1,500	<4	4.0	8.0	200
near-bottom water (up to 100 m above the bottom)	about 0.5	4.8	about 7.95	A slight increase

According to Kazakov "the deep waters of the sea basins are the chief resources of phosphorus," from which it is moved "by means of deep water currents." Phosphorus, along with calcium and carbon, is supplied from the continents and, by the solvent action of deep waters rich

in CO_2, from dead animal and vegetable organisms and the bottom sediments.

According to Kazakov, phosphate is precipitated when waters rich in P and CO_2 ascend from depths to shallower water near the shore line. Precipitation is promoted by diffusion of CO_2 into surface levels poor in carbon dioxide--the phytoplankton zone--and by escape of CO_2 resulting from higher temperature and lower pressure near the surface. The escape of CO_2 causes supersaturation and precipitation first of $CaCO_3$, and then of calcium phosphate. This chemical sedimentation of phosphate occurs at depths of not less than 200 meters, but intermediate between that of the zone of photosynthesis, where phosphate is assimilated by phytoplankton, and that of the deep sea where the high content of CO_2 keeps phosphate in solution. The following conditions are necessary: a) a direct connection of the shelf with the deep portions of the open ocean (not less than 200-500 m approximately); b) deep cold bottom streams ascending to the shelf as the principal source of phosphorus.

This mechanism would explain the confinement of phosphate facies to a position intermediate between the shore facies of the strand and the absence of phosphorite in continental fresh-water basins, in closed shallow sea-water basins, and in saline deposits.

Kazakov's explanation of the chemical precipitation of phosphate is, of course, incomplete, especially as it does not account for the precipitation of phosphate in the absence of the precipitation of calcium carbonate. Actually there are many phosphatic limestones, both in the Phosphoria formation and other phosphate deposits, but, as mentioned previously, the high-grade phosphates are developed only in the absence of calcium carbonate. Rubey's theoretical work has shown that there are

conditions, however, under which phosphate, but not carbonate, will be precipitated. Nevertheless, though it is incomplete, Kazakov's theory fits the observed and previously described facts of the distribution of phosphate in the Phosphoria formation. It does not, of course, explain the precipitation of the vanadium or other minor metals, except as their solution and precipitation may also be related to the CO_2 content.

In summary, the Phosphoria formation accumulated on the shelf of the Cordilleran sea during a long period of crustal stability when the height of the adjacent lands was so low that they contributed little debris to the sea. The phosphate deposits themselves accumulated in greatest thickness near the edge of the shelf, presumably where deep, cold waters, rich in CO_2 and phosphate, ascending from the depths of the sea, became more alkaline because of a decrease in partial pressure of CO_2 and an increase in temperature.

OCCURRENCE OF URANIUM IN THE PHOSPHORIA FORMATION

Composition and mineralogy of uraniferous rocks

Nearly all rocks of the Phosphoria formation contain traces of uranium, but the most uraniferous rocks are phosphatic. The relation to phosphate is by no means a direct one, however--many highly phosphatic rocks contain little or no uranium, a few strongly uraniferous rocks (though none containing .011 or more percent U) are only weakly phosphatic, and the most uraniferous rock yet discovered (0.034 percent U; 27 percent P_2O_5) is not the most phosphatic. The relation between uranium and phosphate in the 807 samples thus far analyzed for both constituents is shown graphically in figures 11, 12, and 13.

Despite the wide range in the U/P_2O_5 ratio, there is no mistaking a relationship between the two. As shown in figure 11, 50 percent of the samples containing less than 8 percent P_2O_5 contain less than 0.002 percent U; 50 percent of those containing less than about 19.5 percent P_2O_5 contain less than 0.004 percent U; and about 50 percent of those containing 27 percent P_2O_5 contain less than .009 percent U.

Significant amounts of uranium are not present in rocks containing more than a small amount of carbonate. Of 278 samples analyzed for both CO_2 and U, 44 contain more than 0.005 percent uranium and only 6 of these contain more than about 2 percent carbonate CO_2 (figures 14 and 15). Of the samples containing more than 0.01 percent U none contain more than about 2 percent carbonate CO_2.

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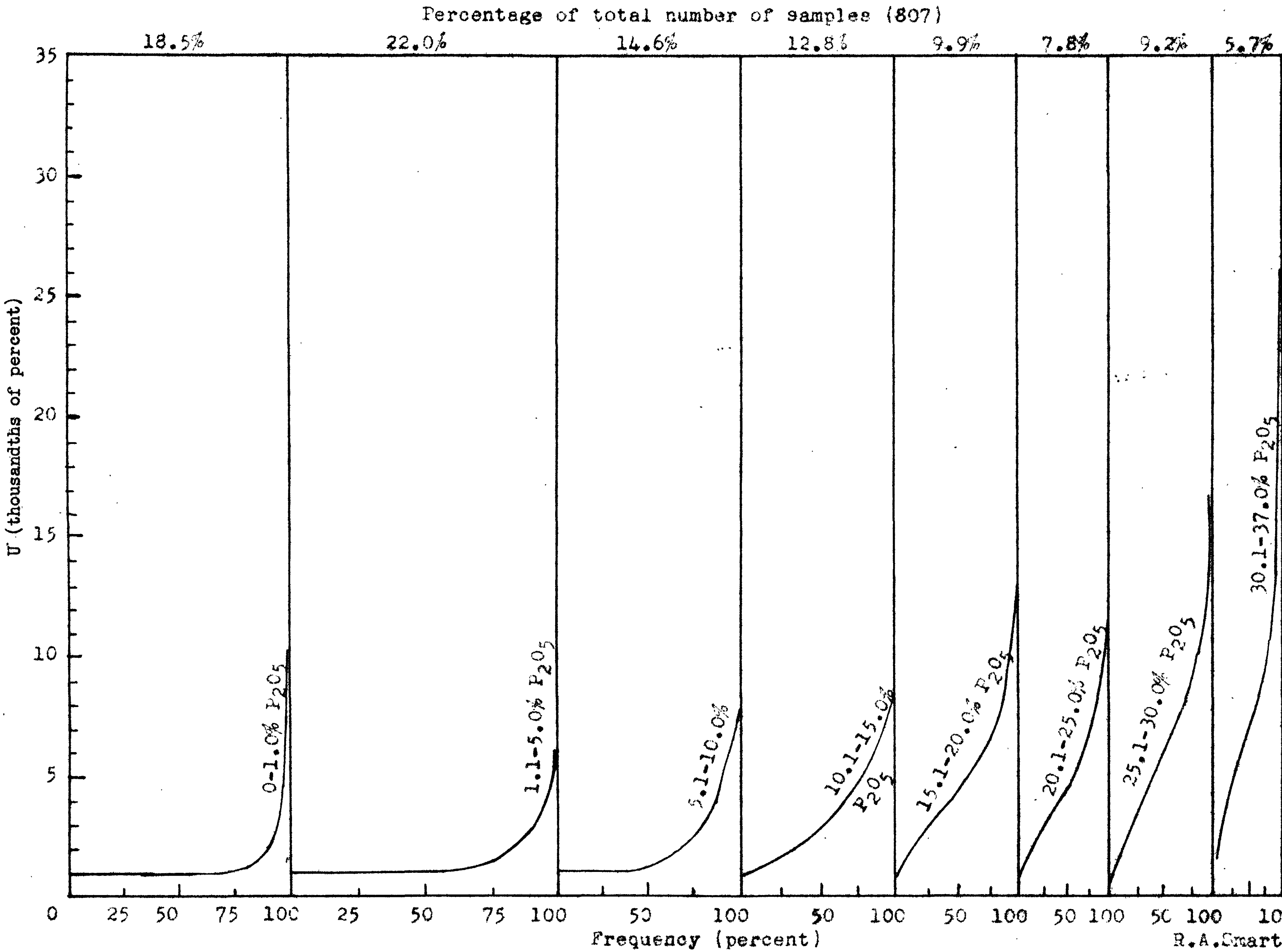
Fig. 12



R.A.Smart
May 1949

VARIATION IN URANIUM CONTENT OF ROCKS OF THE PHOSPHORIA FORMATION CONTAINING SPECIFIED AMOUNTS OF PHOSPHATE

Example: 7.3 percent of the samples analyzed contain more than 30.0% P_2O_5, and of these, 50 percent contain more than 0.0065% uranium

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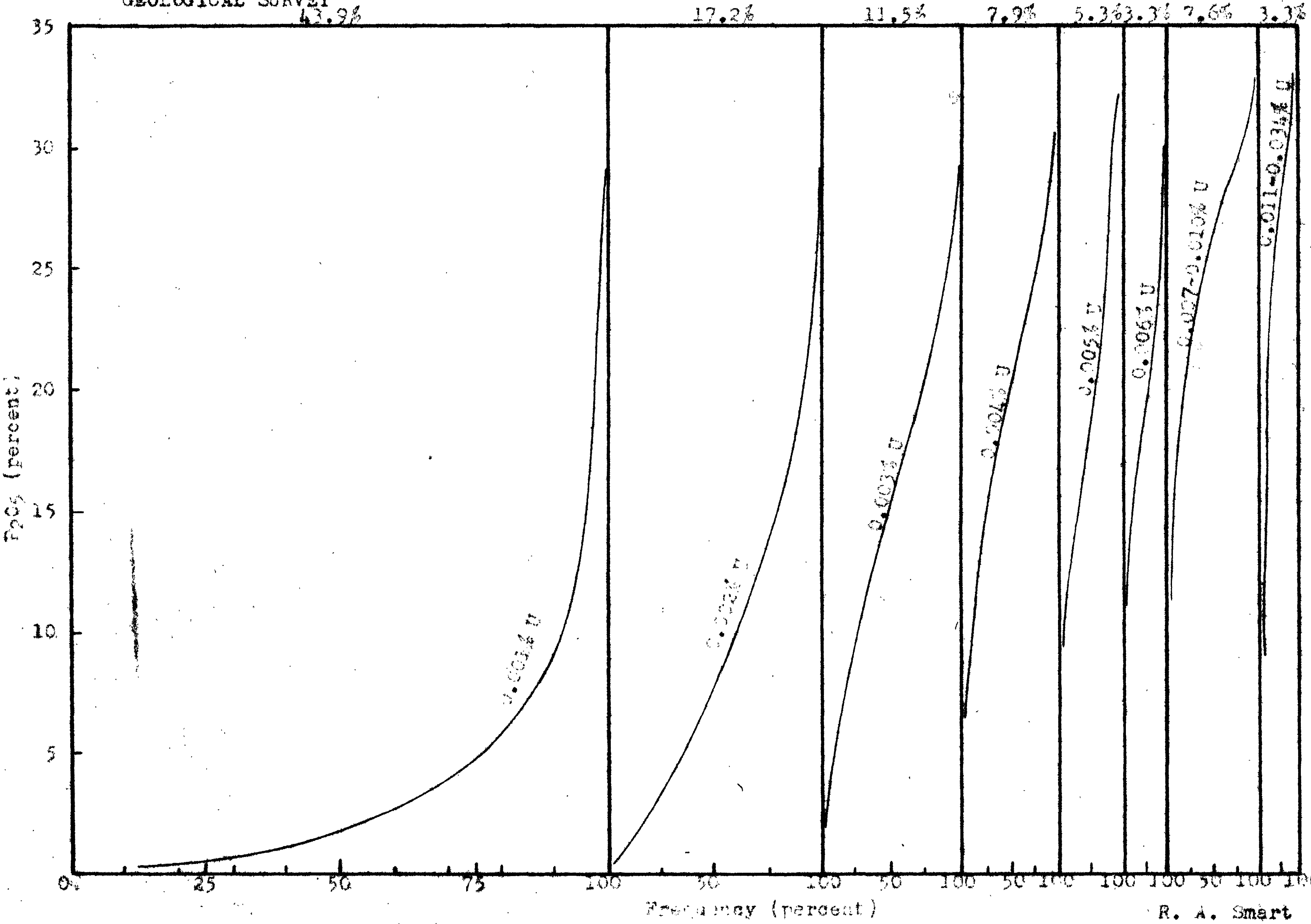
Fig. 13

Percentage of total number of samples (807)



R. A. Smart
May 1949

VARIATION IN PHOSPHATE CONTENT OF ROCKS OF THE PHOSPHORIA FORMATION CONTAINING SPECIFIED AMOUNTS OF URANIUM

Example: 43.9 percent of samples analyzed contain 0.001% Uranium, and of these 68 percent contain less than 10 percent P_2O_5.

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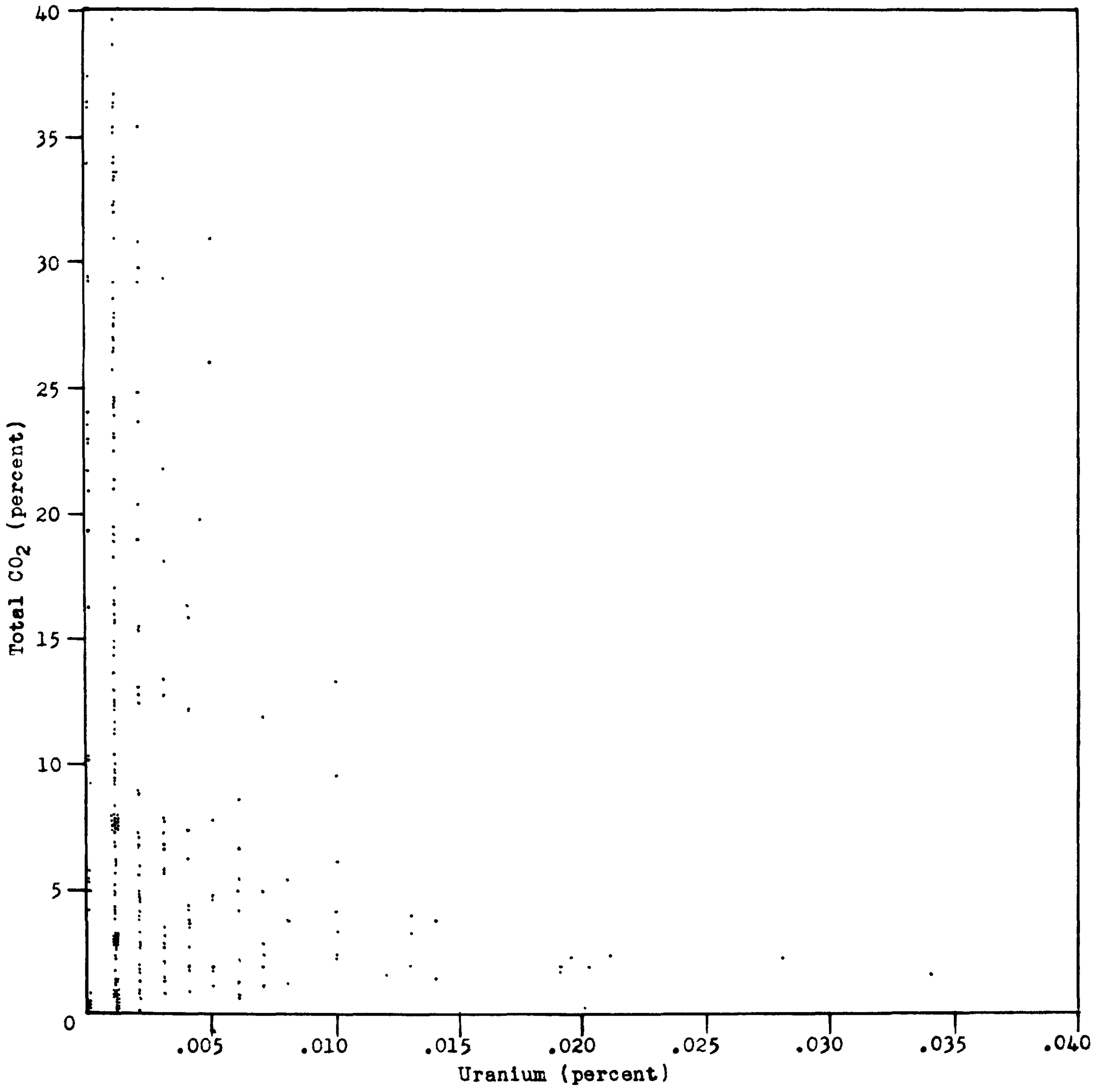
Fig. 14



Relation between uranium and total CO_2 in rocks of the phosphatic shale member at Coal Canyon, Wyoming, and Brazer Canyon, Utah.

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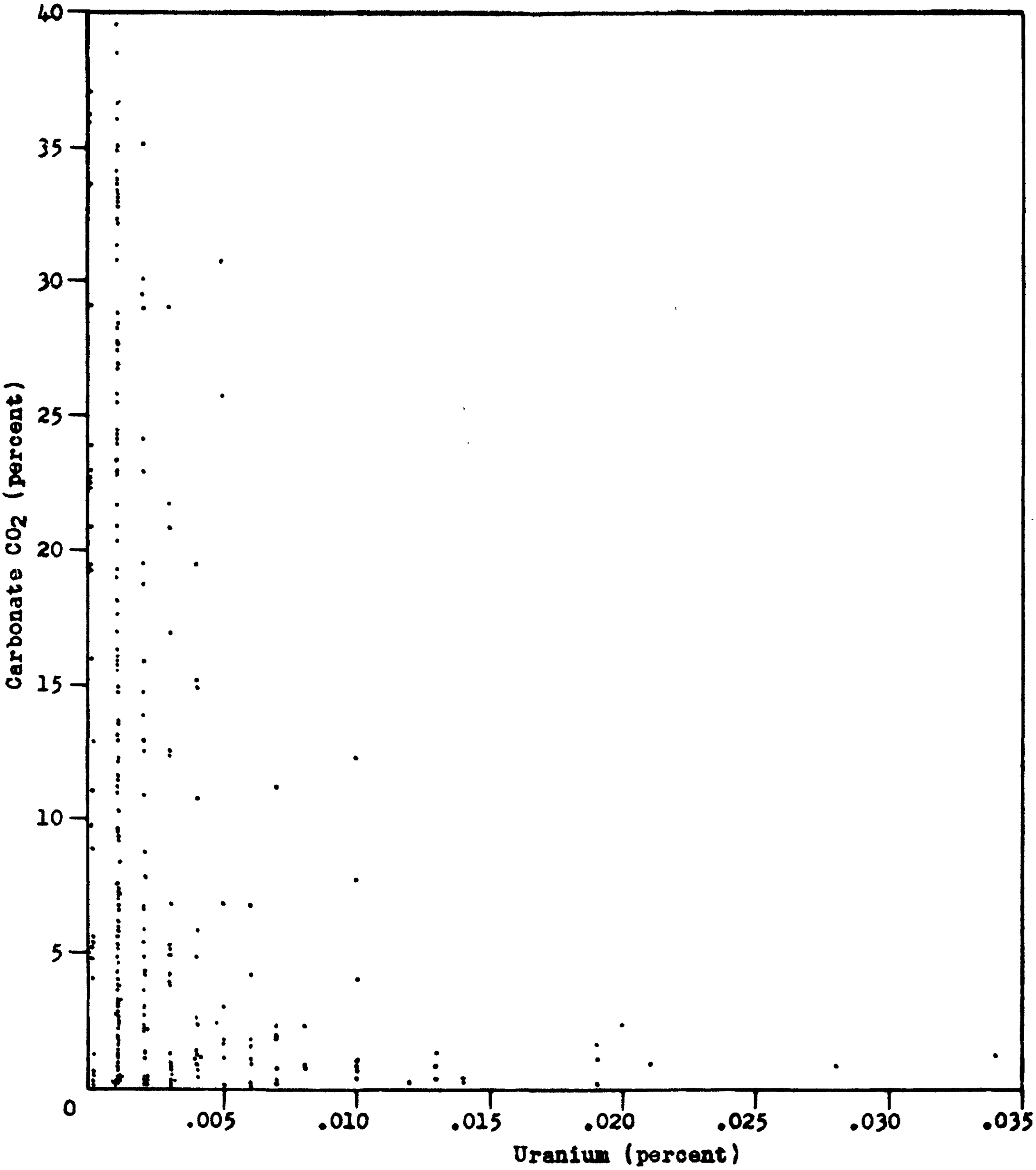
Fig. 15



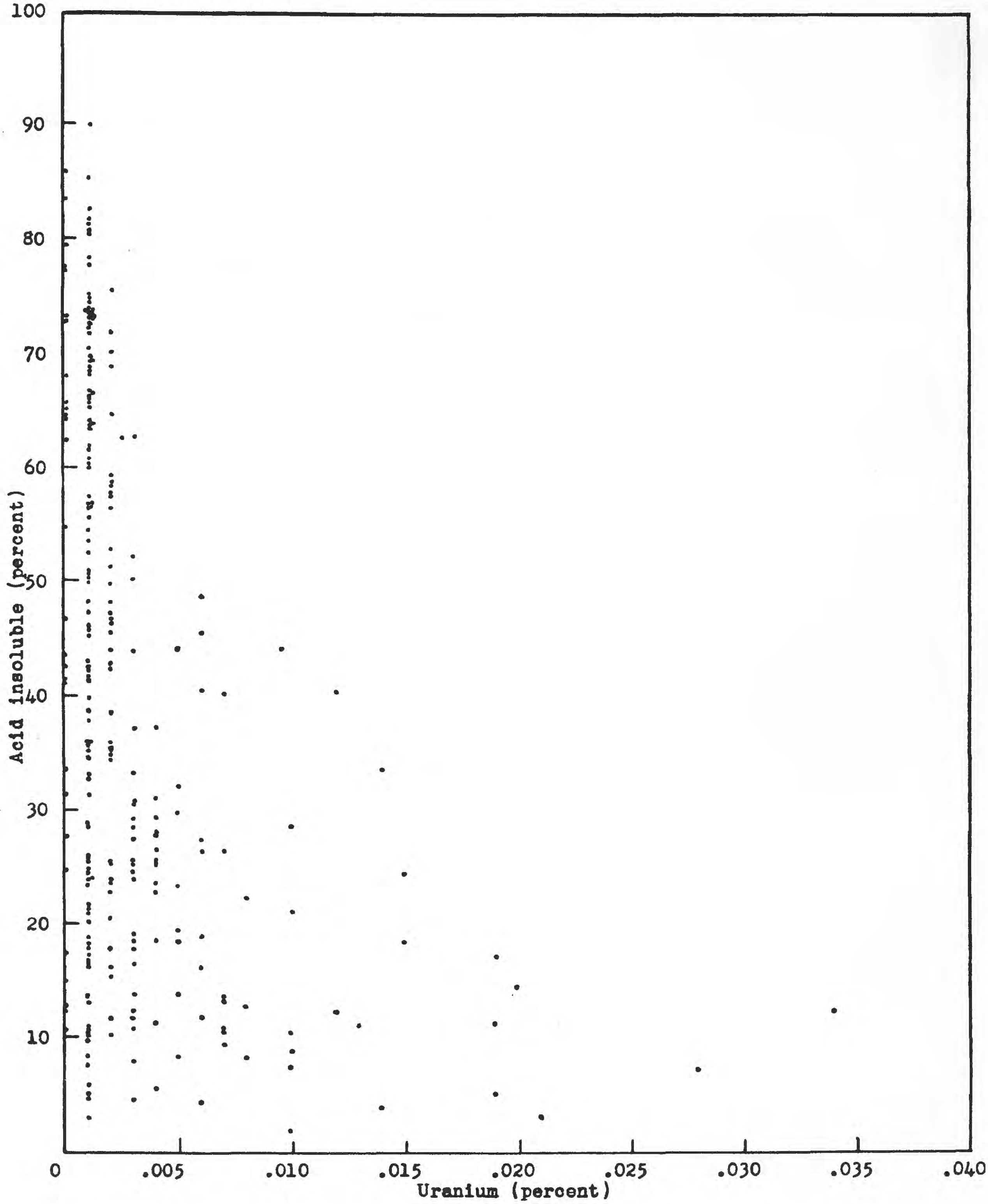
Relation between uranium and carbonate CO_2 in rocks of the phosphatic shale member at Coal Canyon, Wyoming, and Brazer Canyon, Utah. Carbonate CO_2 has been estimated (somewhat arbitrarily perhaps) as 0.1 x %P_2O_5 — total CO_2 (assuming phosphate mineral has the formula $10CaO. 3P_2O_5. CaF_2. CO_2$).

Uranium also varies inversely with acid insoluble (which may be taken as an approximate measure of the total amount of detritus in the samples) and with organic matter (as judged from loss on ignition, minus CO_2 and water). Unlike the CO_2, however, neither the organic matter nor acid insoluble seems to have any dampening effect on the uranium (figures 16 and 17). They decrease as the uranium increases merely because high concentrations of phosphate and organic matter and detritus are mutually exclusive.

That the uranium seems to be in the phosphate mineral is shown by the previously discussed positive relationship between U and P_2O_5 and, more convincingly, by the fact that the amount of uranium dissolved on acid treatment is proportional to the amount of phosphoritedissolved. The nature of the occurrence in the fluorapatite mineral is unknown, but the wide variation in the U/P_2O_5 ratio shows that uranium is not an essential part of the fluorapatite mineral. More likely uranium is held by chemical adsorption (that is, uranium ions are chemically bonded to anions on the surface of the phosphate mineral) or else it proxies for calcium, which has about the same ionic radius, in the fluorapatite lattice. Either mode of occurrence is difficult to prove and both fit the observed facts of the general relationship between uranium and phosphate.

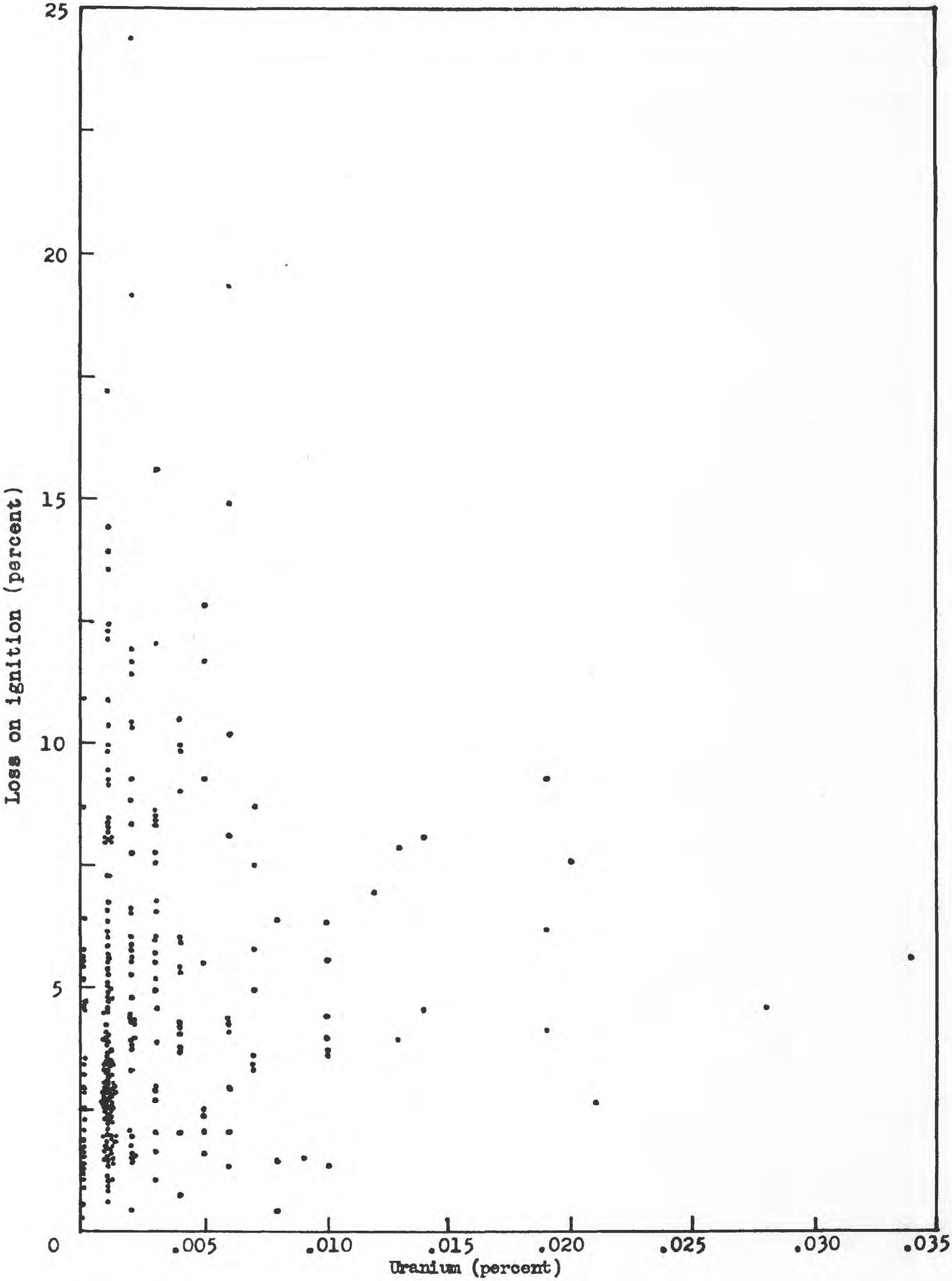
Areal variations in uranium content

In view of the general relation between uranium and phosphate, we would expect that the amount of uranium would increase westward as the phosphate increases (figs. 18 and 19). This is true, but in addition it appears also that the U/P_2O_5 ratio is greater in the western than in the



Relation between uranium and acid insoluble in rocks of the phosphatic shale member of the Phosphoria formation at Coal Canyon, Wyoming, and Brazer Canyon, Utah.

Fig. 17



Relation between uranium and organic matter (judged to be loss on ignition, minus CO_2 and water) in rocks of the phosphatic shale member of the Phosphoria formation in Coal Canyon, Wyoming, and Brazer Canyon, Utah.

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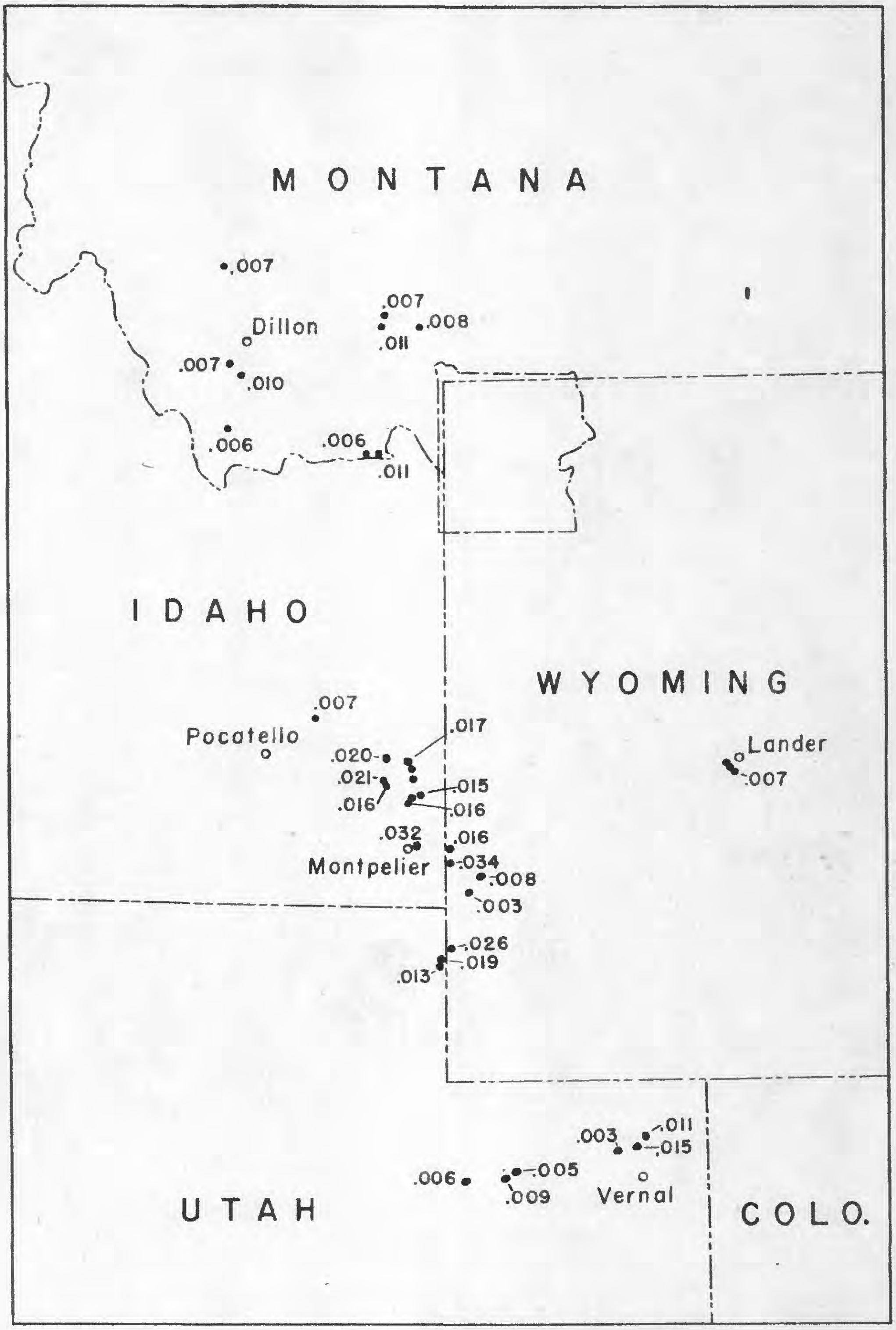
GEOLOGICAL SURVEY

Figure 18



MAXIMUM URANIUM CONTENT (PERCENT) THUS FAR REPORTED FROM THE PHOSPHORIA FORMATION AND ITS CLOSE STRATIGRAPHIC EQUIVALENTS

SCALE IN MILES
20 0 20 40 60 80

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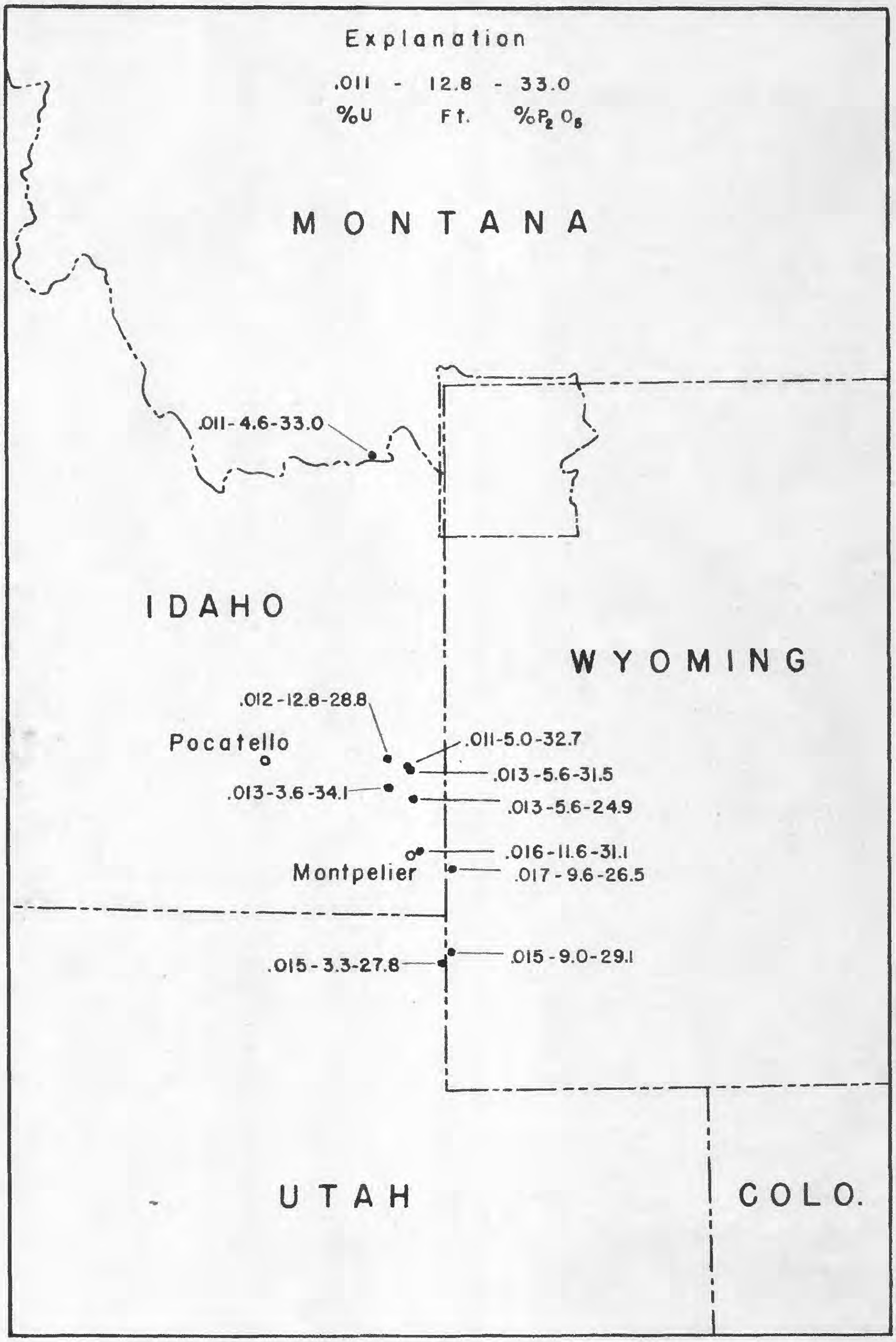
Figure 19



TOTAL THICKNESS, U, AND P_2O_5 CONTENT OF BEDS CONTAINING 0.01 PERCENT OR MORE U IN UNITS OF 3 OR MORE FEET IN THE PHOSPHORIA FORMATION AND ITS CLOSE STRATIGRAPHIC EQUIVALENTS

SCALE IN MILES

20 0 20 40 60 80

eastern part of the field. The data on which this generalization is based are very scant indeed. The trend, however, is illustrated by the following comparison of the U/P_2O_5 ratio in beds containing 20-25 percent P_2O_5 at specific localities (left to right = west to east).

Table 3

Average U/P_2O_5 ratio in beds containing 20-25 percent P_2O_5

Montpelier Canyon, Idaho	Coal Canyon, Wyoming	Near Vernal, Utah (3 localities)	Near Lander, Wyoming (10 localities)
0.00040	0.00018	0.00016	0.00010

Enough data are not yet available to show much about the local variation of uranium in specific beds. It appears that some, at least, are as uniform in their uranium content as are the phosphate beds themselves, but that the uranium content of other beds varies in ways not anticipated from the phosphate content. Thus, the lower phosphate bed in Caribou and Bear Lake Counties in southeastern Idaho contains an average of about 0.009 or 0.010 percent uranium and about 32 percent P_2O_5, but at the Simplot phosphate mine at Fort Hall the uranium content of the same bed is only about 0.006, though the phosphate content is about the same.

The vertical distribution of uranium within the section closely corresponds to that of the phosphate. It is noteworthy that, despite the wide variation in the U/P_2O_5 ratio, the most uraniferous beds are in the minable phosphate units. In southeastern Idaho and adjacent parts

of Wyoming and Utah, these beds lie near the base and top of the phosphatic shale member (fig. 20).

Origin

The uranium in the phosphates of the Phosphoria formation is of syngenetic origin. It seems certain that the immediate source of the uranium, like that of the phosphate and other minor elements, was the sea water, which now contains about 0.000002 grams per liter (Foyn, et. al.). The manner of its transportation and precipitation, however, are unknown, but the data available make possible some speculations which may be helpful in the search for other deposits.

The solubility products of the various uranium compounds that might be dissolved in sea water are unknown, but, judging from the water solubility of uranyl sulphate, phosphate, and especially carbonate (Dement and Dake, p. 100), together with the fact that the amount of uranium dissolved in the sea is small, it seems probable that their solubility products in the sea are higher than their ionic products and that the sea is therefore not saturated with uranium salts. If the sea were saturated with uranium salts, significant concentrations would be expected in sediments which accumulate slowly--not only in sediments like the marine phosphates and black shales, which do contain uranium, but also in the sediments of the deep sea. The deep sea sediments tested for uranium, however, contain only about 0.0005 to 0.001 percent uranium--an amount not nearly sufficient to account for their radium content (Urry, p. 203). In fact, Piggot and Urry (p. 85) have been led to the conclusion that "the ocean is a reservoir for most of the uranium

that is poured into it, while the ocean bottom is the repository for the transient radium." Both Goldschmidt (see also Sverdrup et. al. pp. 220-222) and Russell (p. 1483) have shown, on the other hand, that most of the uranium that could have been brought to the sea during all of geologic time is in the sediments rather than the sea water. It seems likely, however, that the uranium removed from the sea has been removed selectively, rather than by direct inorganic precipitation from a saturated solution.

Selective removal of uranium salts might have been brought about by organisms, or by various types of adsorption. Little is known about the part organisms might have played in the precipitation of uranium. The uranium content of marine organisms has not been determined, but some animals remove uranium from the bloodstream and concentrate it in body tissue and bone (Newman). Although marine organisms in great variety concentrate radium, Piggot and Urry (p. 88) doubt that this process explains the concentration of radium in the surface of the deep-sea sediments, because the animals extract only a small part of the radium from their environment, and "their remains mostly dissolve before reaching any profound depth." Even less is known about the role of marine organisms in concentrating uranium. Its concentration in phosphatic beds of the Phosphoria formation, rather than in beds rich in organic matter, make it doubtful, however, that organisms played a major role in the concentration of uranium there.

Several workers have suggested that uranium may be adsorbed by clay, organic matter, or other finely divided material (Beers and Goodman, p. 1251; Hoogteijling and Sisco; Tolmachev; and Frederickson), and it seems likely that uranium may also be adsorbed by phosphates. Adsorption is

the attraction of a foreign body to the surface of a given substance. Two general kinds have been recognized (Prutton and Maron, p. 232; Mantell, p. 3): (1) physical, or van der Waals adsorption, and (2) chemical adsorption. Physical adsorption is characterized by a loose bonding of the adsorbate to the adsorbent; it is probably of little importance in the concentration of uranium in phosphates, both because the amount of uranium adsorbed is apt to be very small, and because it is only loosely held. Chemical adsorption is characterized by firm bonding of the adsorbate to the adsorbent. It may involve the bonding of a foreign ion to open bonds at the surface of a substance, or it may involve the exchange or substitution of a foreign ion for an ion at the surface (even an interior one). The amount of adsorption and the selection of ions adsorbed is governed by a number of rules or laws, two of the most pertinent of which are (Hevesey and Paneth, p. 163): 1) The amount of adsorption of a given ion increases with decreasing solubility of the compound formed with the oppositely charged lattice ion; and 2) the adsorption of an ion is favored if the compound formed is isomorphous with the adsorbent and if the ion is similar in size to one of those of the crystal lattice (see Koltoff and Sandell, pp. 103-117).

In view of the similarity in ionic radius of uranium and calcium ions; the relative insolubility of the uranium in the phosphate mineral (though the uranium in the western phosphate rock is acid soluble, it is not leached out in the course of weathering, even where weathering has been so intense that the organic matter, carbonate, vanadium, and other minor elements have been removed); as well as the strong chemical affinity that exists between uranium and phosphate (shown by the many phosphate minerals and compounds; see DeMent and Dake, pp. 134-140), it seems probable that uranium could be adsorbed from the sea water by precipitated phosphate, and that it substitutes for calcium

in the fluorapatite structure. Whatever favors the adsorption of uranium, it seems certain that the presence of carbonate ion inhibits it. Piggot and Urry (p. 89) have pointed out that in the laboratory "the precipitation of uranium is inhibited by the presence of the carbonate ion." That such a relationship exists in nature is shown by the aforementioned negative correlation between uranium and carbonate.

The theory that uranium is precipitated by adsorption in the phosphate may explain the lack of a constant uranium-phosphate ratio. The amount of uranium in the phosphate mineral may be a function of the concentration of uranium in the sea at the time of deposition of the phosphate, the relative solubility of the uranium salts, as well as the length of time the phosphate mineral particle is exposed to the uranium-bearing solution. Phosphate precipitated at times or places where the sea contained subnormal amounts of uranium would contain less uranium than it could if the sea were more uraniferous. Similarly, precipitated phosphates exposed to the sea water only a short time, either because they were quickly deposited or buried after precipitation, would contain less uranium than those mineral particles that were exposed to the sea for a long time, either because they remained in suspension for a long time after their precipitation, or because they were exposed to sea water for long periods after their deposition. If, however, the uranium salt in the sea were highly soluble, the reverse might be true; phosphates quickly precipitated and buried might contain more uranium than those long exposed to the solution.

METHODS OF PROSPECTING FOR URANIUM

IN THE PHOSPHORIA FORMATION

Prospecting for uranium in the Phosphoria formation has consisted of systematic channel sampling of every lithologic unit of the phosphatic shale member of the formation, and, at some localities, the whole formation. Generally units less than 0.5 feet in thickness have been lumped together, but in some places units as thin as 0.2 feet have been sampled separately. This practice has been deemed advisable because:

1. Even with the general relationship between uranium and phosphate, there is no way of definitely predicting which beds are uraniferous and which are not, except by the use of chemical or radiometric analyses.

2. Even though the uraniferous beds generally can be distinguished from the non-uraniferous beds in the field by use of a Geiger counter, measurements so made are not accurate quantitatively, and are no substitute for laboratory determination.

3. Uranium is a minor constituent of the rocks and if it is ever recovered, it will be as a co-product of phosphate, and possibly other minor constituents such as fluorine, vanadium, nickel, or zinc. It is therefore necessary to know the content of all the rocks that might conceivably contain constituents of commercial interest; obviously the composition of the partings that might be mined with any particular unit, or might dilute it from the walls, must be known also.

4. Detailed stratigraphic studies, which must be based upon knowledge of the physical characteristics and chemical composition of individual layers, are required for estimation of reserves or deciphering the areal variations in and origin of the various layers.

Because of the great lateral continuity of individual layers, and the large area to be covered, it has been deemed sufficient to sample the complete thickness of the formation at intervals of 3 to 6 miles. As natural exposures are extremely rare, the rocks must be exposed artificially at most localities; this has been done generally by bulldozer-trenching, but in some places the beds have been sampled in underground workings. Diamond drilling has been attempted, but the poor core recovery obtained (30-85 percent) makes it unsatisfactory for sampling.

The beds exposed are described and measured, and, in addition to the channel samples cut from each, chip samples are collected from every bed, and fossils, which are an aid in correlation and hence in calculation of reserves, are collected wherever possible. Many of the logging and sampling techniques have been highly systematized, but as these would have to be modified for use on another formation, they need not be described here. The field use of the Geiger counter is adequately described elsewhere (Faul).

Both radiometric and chemical analyses have been made on each sample. Radiometric analyses are somewhat higher, but the agreement between the two methods is relatively close (fig. 21).

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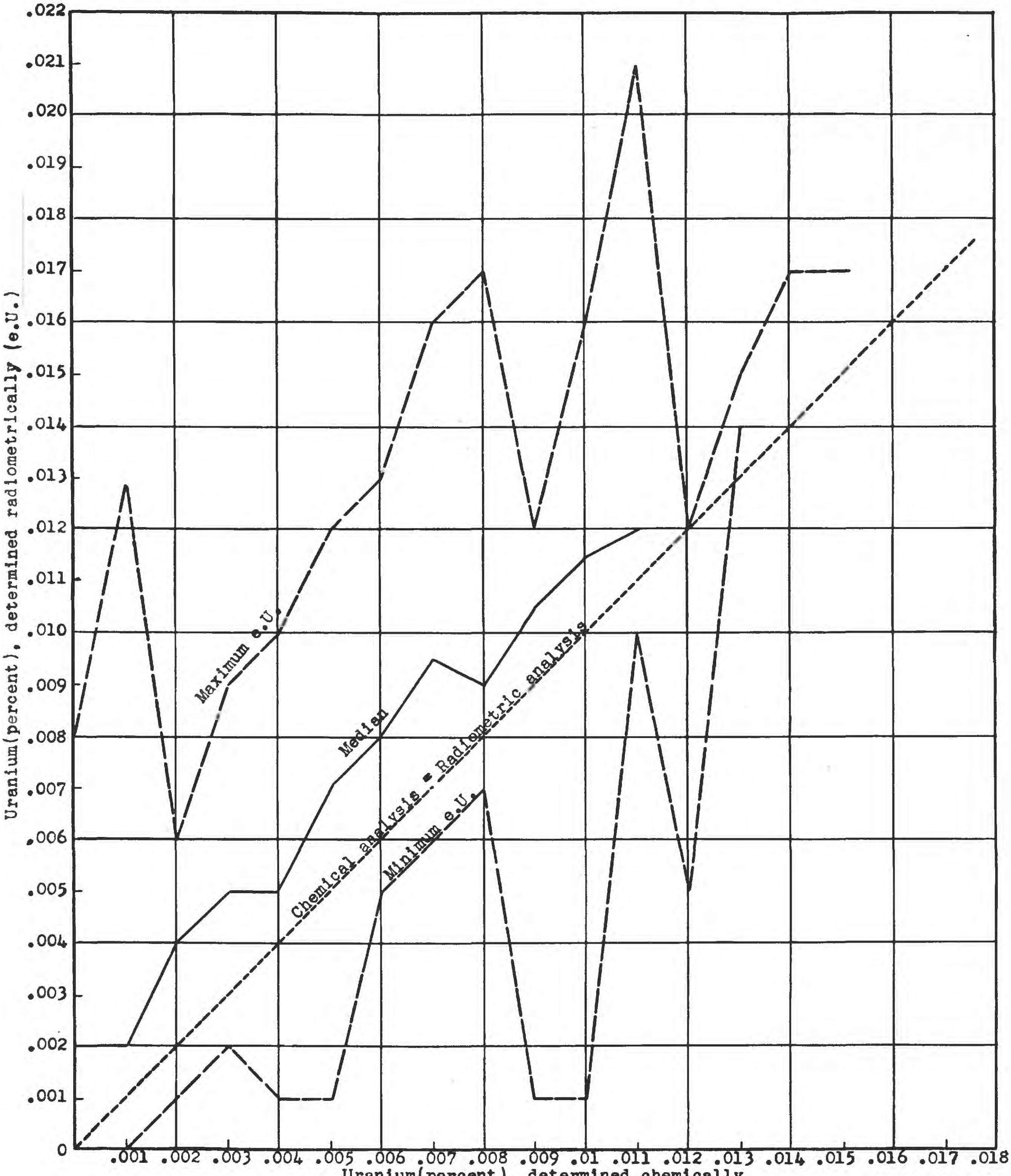
Fig. 21



R. A. Smart
May 1949

COMPARISON BETWEEN CHEMICAL AND RADIOMETRIC URANIUM ANALYSES

Long-dashed lines show extreme discrepancies. Solid line represents the median (i.e. 50 percent of the samples fall above and 50 percent fall below the median line). Line along which analyses would fall if both chemical and radiometric analyses were equal is short-dashed. Of the available analyses (667), 75 percent contain less then 0.005 percent Uranium. All analyses are of samples from the Phosphoria formation and its close stratigraphic equivalents.

SUGGESTIONS FOR PROSPECTING

FOR URANIFEROUS PHOSPHATE IN OTHER AREAS

Phosphate is concentrated in nature in a wide variety of rocks and by many different processes. The principal types of primary deposits are: (1) sedimentary "bedded deposits", (2) guano, and (3) apatite, in lenses, veins, or other igneous differentiates. Important secondary concentrations are formed from guano (phosphatized limestone) and sedimentary deposits (residual and reworked deposits).

Uranium, in amounts of 0.01 percent or more, thus far has been reported only from the marine sedimentary deposits, and not all of these contain such an amount of uranium. On the other hand, smaller amounts of uranium have been detected in non-sedimentary deposits. In view of the wide association of uranium with phosphate, not only in the bedded phosphate rock, but in primary and secondary vein minerals (e.g., autunite and torbernite), all phosphorite ought to be tested. Accordingly, the mode of occurrence of all the principal types of phosphate deposits is described briefly here.

Guano deposits

Guano, composed of the droppings of sea fowl, has been an important source of agricultural phosphate. Its value arises not only from the ease with which it can be mined and its favorable location with respect to tide water, but also from its content of available phosphate and nitrogen.

Guano deposits are found mainly on islands in the tropics, such as those off the coasts of Peru, Ecuador, Mexico, China, and Japan and

various Pacific islands; they are also found on the mainland, near the coast, in Peru, Ecuador, and Columbia. Some of these deposits are being actively built now, but other guano areas have been abandoned by the birds that made the deposits.

If the marine organisms (mostly fish) on which the birds feed, concentrate uranium, concentrations of uranium might be expected in the guano deposits. In view of the relatively low phosphate content of the guano deposits and the extent of their dilution by organic matter, it seems unlikely that any of the deposits will be found to contain as much as 0.01 percent uranium. Although known deposits should be tested, the results will be mainly of academic interest unless very large concentrations are found, for as the guano is applied to the soil without processing, it would be uneconomical to attempt to recover uranium in amounts such as are found in most phosphate rocks.

Guano (phosphatized) limestone

Downward migration of the relatively soluble guano phosphate has led to phosphatization of underlying bedrock on many tropical islands. Among the most important of these deposits are those of the Pacific on Angaur, Fais, Kita-daito, Makatea, Nauru, and Ocean Islands, but smaller deposits are found in many other places, especially the Indian Ocean (Rodgers, Mansfield, 1942). Most of the deposits are phosphatized limestones, but in some places where the underlying bedrock is non-calcareous, aluminum phosphate or ferrous aluminum phosphate is found. Examples of the latter are found in the deposits in the vicinity of Saldanha Bay, South Africa; Clipperton Atoll in the Northern Pacific; and Redonda in

the West Indies (du Toit).

Of the few specimens of guano limestone that have been tested for uranium by the Geological Survey, that from Makatea Island contained the most - 0.007 percent. The others (from Angaur, Nauru, and Ocean Islands) contained only negligible amounts. Whether or not any of these guano-limestone deposits contain significant amounts of uranium depends mainly on whether or not the guano itself is uraniferous, or whether the deposits have been exposed to sea water since their formation. Some of the deposits are found on elevated islands, which show evidence of repeated uplift, and it seems probable that phosphatization of the underlying rock can take place only above the water table (Rodgers, p. 407). If, however, any of these islands have been submerged for even short periods since the formation of the phosphatized limestone, the phosphate may have adsorbed some uranium from sea water. Even so, unless the deposits were actually reworked (and I know of none which show any of the characteristics of reworked deposits), it seems unlikely that the phosphate would be highly uraniferous because of the relatively small amount of surface that would have been exposed to the sea water.

The known reserves of insular phosphates are small and are not promising sources of uranium.

Apatite deposits

The largest and most important apatite deposits are late stage igneous differentiates, associated with alkaline rocks. The two most important apatite deposits are those at Kirovsk on the Kola Peninsula of Russia (Fiveg, 1937), where the apatite is associated with khibinite, foyaite,

nephelite syenite, and ijolite; and Uganda (Davies), where the apatite occurs with magnetite and phlogopite, associated with syenite, ijolite, pyroxenite, and carbonatite. Similar deposits (also associated with magnetite or titanium minerals) are found in northern Sweden and with titanium minerals at Magnet Cover, Arkansas; Nelson County, Virginia; Kragero and Bamle, in southern Norway; and many other localities over the world.

Only a few museum specimens of apatites have been tested by the Geological Survey for uranium, and none of these contained more than a trace. In view of the wide association of uranium with phosphate in other types of deposits, more extensive tests are needed before the apatites can be eliminated as possible sources of small quantities of uranium. Unlike the guano and phosphatized limestone deposits, some of the apatite deposits are very large (millions or even billions of tons) and as the phosphate rock must be processed before it can be used, significant quantities of uranium might be recovered as a by-product. The apatite deposits therefore deserve more consideration as possible sources of uranium than they have received to date.

Sedimentary deposits

Minor occurrences of phosphate in sedimentary rocks have been reported from scores of localities over the world, but known large, thick, high quality deposits are few indeed--the North African Cretaceous-Tertiary deposits are apparently the only deposits which compare in size and quality with those of the Phosphoria formation. Although the Florida

deposits are of smaller size and thickness and of lower quality, they are currently the most productive because they are easily mined and beneficiated.

Although small quantities of phosphates are concentrated in certain lacustrine and bog deposits, most sedimentary phosphates are marine. The largest deposits are associated with geosynclinal facies of which the preceding description of the Phosphoria may be taken as representative. It seems likely that few additional deposits of this type remain to be discovered, but they should be searched for geosyncline-wards from known deposits of the platform type. A clue as to the location of the most favorable ground for prospecting may be provided by the regional structure for, in both the Cordilleran and Appalachian areas, as well as many other geosynclinal areas over the world, the division between areas of simple, irregular structure and those of lineated, complex structure roughly approximates the division between platform and geosynclinal facies.

Most of the minor sedimentary deposits are associated with platform facies. Many of them are associated with unconformities or periods of slight or nondeposition, and some bear evidence of reworking (worn phosphate pebbles and worn and fragmented fossils). Glauconite, clean quartz sands, and clastic limestones containing well sorted and well worn fossils are common lithologic companions. The phosphate itself is generally nodular, and much of it is in the form of phosphatized fossil invertebrates, bones, or fish teeth. Examples of such deposits are those

of the Tertiary Hawthorn and the overlying Bone Valley formation in Florida (Mansfield, 1943; Matson) and beds of the same age in South Carolina (Rogers); the Devonian Bishop Brook formation in New York; the Devonian Oriskany formation in Pennsylvania (Ihlseng) and Virginia (Stose); the Devonian-Missippian Hardin sandstone member of the Chattanooga shale in Tennessee, commonly known as Tennessee blue rock (Mansfield, 1940b); the Lower Cambrian Yunnan type in China (Hsieh; and Hsieh and Chao); and many of the Russian deposits (Kazakov, p. 98; see also many of the other papers in the same volume).

Phosphatic nodules are also associated with many black shales, and some of those tested in this country are known to be highly uraniferous. Examples include those in shales of the Pennsylvanian Hogshooter limestone; the Checkerboard limestone, the Fort Scott limestone, and the Boggy formation; and the Devonian (?) Woodford chert in Oklahoma (Oakes).

Minor concentrations of phosphorus are also associated with many manganese and iron deposits of the platform or platform-miogeosynclinal type--not the eugeosynclinal type. Examples of these include the manganese deposits in the Ordovician Cason shale of Arkansas and the Devonian Oriskany formation of Virginia; and the iron deposits of the Silurian Clinton formation of the Appalachians and the Alsace-Lorraine of France.

Nonmarine residual phosphates

Inasmuch as most natural phosphates are insoluble except in acid or very weakly basic solutions, residual phosphates are rather common. Some of these, such as parts of the Bone Valley formation, are concentrated or reworked in submarine environments and, possibly because of this exposure to sea water (McKelvey and Nelson), are as uraniferous as some of the

primary deposits. But of those deposits that have been concentrated on land, such as the brown and white phosphates of Tennessee, all tested thus far have been found to be nearly barren of uranium. This may be because any uranium present in the phosphatic rocks (from which the secondary concentrations were derived) was leached out. Most of the parent rocks are phosphatic limestones and, in view of the strongly negative correlation observed between uranium and carbonate in the rocks of the Phosphoria formation, and in some of the black shales as well, it seems more likely that the parent phosphates were non-uraniferous.

Even though the nonmarine residual phosphates do not appear to be promising sources of uranium, they ought to be tested further.

CONCLUSION

The general origin of the various types of phosphate deposits is well enough known to guide exploration, not only for the phosphate deposits themselves, but for uranium in the phosphates. Of the various types currently mined, those that seem to deserve most attention as possible sources of uranium are the apatites and the geosynclinal phosphates, and in general, non-calcareous phosphates. In view of the fact that the expectable concentrations of uranium in the phosphates are low, further search for uraniferous phosphates seems best directed toward deposits which can be mined and beneficiated cheaply, like some of the nodular deposits, or to those which contain other valuable materials, such as oil, manganese, or iron.

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