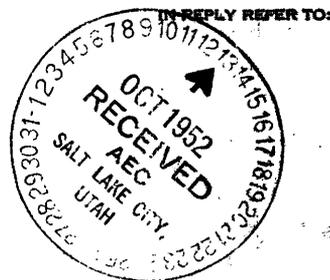




UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.



October 8, 1952

AEC - 386/3

Dr. Phillip L. Merritt, Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
P. O. Box 30, Ansonia Station
New York 23, New York

Dear Phil:

Transmitted herewith are six copies of Trace Elements Investigations Report 263, "The Permian phosphorite deposits of western United States," by V. E. McKelvey, R. W. Swanson, and R. P. Sheldon, October 1952.

This report was read at the 19th International Geological Congress in Algiers and probably will be published in the Proceedings of that group. Mr. J. C. Johnson approved the presentation and publication of the report, by letter dated August 1, 1952.

Sincerely yours,

W. H. Bradley
for W. H. Bradley
Chief Geologist

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UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

THE PERMIAN PHOSPHORITE DEPOSITS OF WESTERN UNITED STATES*

By

V. E. McKelvey, R. W. Swanson, and R. P. Sheldon

October 1952

Trace Elements Investigations Report 263

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

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THE PERMIAN PHOSPHORITE DEPOSITS OF WESTERN UNITED STATES

(Read at the 19th International Geological Congress, Algiers, September 1952)

By V. E. McKelvey, R. W. Swanson, and R. P. Sheldon

ABSTRACT

The Permian marine phosphorite deposits of the western United States were laid down in the Phosphoria formation and its partial stratigraphic equivalents over an area of about 135,000 square miles in Montana, Idaho, Wyoming, Utah, and Nevada. The deposits in the eastern part of the field lie on the western margin of the structurally simple North American craton. The rocks there consist of a few thin, locally glauconitic, nodular phosphorites, generally containing less than 30 percent P_2O_5 , interbedded with nodular limestones, calcareous mudstones, and sandstones. Eastward these marine beds tongue out into continental redbeds. The deposits in the western part of the field are a part of the complexly folded Cordilleran miogeosyncline. The facies there are of a deeper-water type and include thick phosphorite layers containing as much as 35 percent P_2O_5 , black phosphatic mudstones, limestones, and well-bedded black cherts.

The phosphorite deposits are composed chiefly of colloform carbonate-fluorapatite, quartz, and clay. In addition to phosphorus, they contain several minor elements that are of potential economic interest. The most important of these are fluorine, vanadium, chromium, nickel, rare earths, zinc, and uranium.

INTRODUCTION

Of the many phosphorite deposits over the world, Permian phosphorite deposits of western United States and the Kara Tau deposits of Russia are the only close analogue of the North African deposits in total volume of phosphatic materials, areal extent, and geologic relationships. With the splendid opportunity provided by this Congress to see the North African deposits first-hand and to learn of their characteristics from the geologists most familiar with them, a description of the deposits of western United States may be of value in focusing attention on features common to both deposits that are perhaps of critical significance in defining their origin.

GEOLOGIC SETTING

The Permian phosphorites of western United States were deposited over an area of about 135,000 square miles in the States of Montana, Idaho, Wyoming, Utah, and Nevada (fig. 1). The deposits in the western part of the field are part of the Cordilleran miogeosyncline (Kay; Eardley), a pile of sedimentary rocks 20,000 to 40,000 feet or more thick. The eastern part of the field is a part of the bordering stable platform, a positive area on which accumulated only a few thousand feet of sediments.

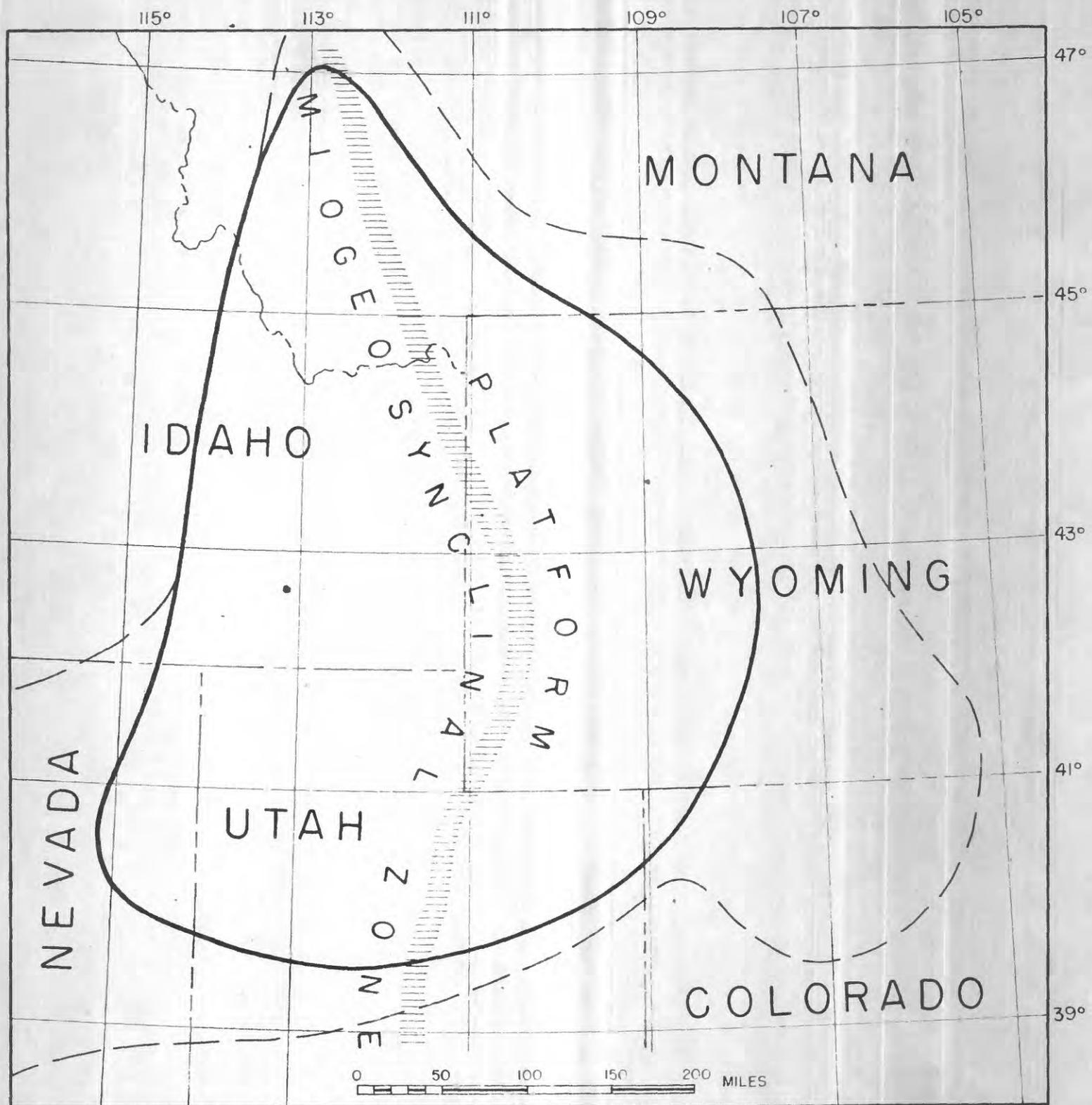


FIGURE 1. LIMITS OF THE PERMIAN PHOSPHORIA FORMATION AND ITS PARTIAL STRATIGRAPHIC EQUIVALENTS (DASHED LINE) AND THEIR PHOSPHATE DEPOSITS (SOLID LINE).



STRATIGRAPHY AND FACIES OF THE PHOSPHORIA FORMATION

Age and correlation

Most of the phosphorites in the western field are part of the Phosphoria formation and its partial correlative in Utah, the Park City formation. Its age limits are not yet established, but it certainly spans much of Permian time. The lower, phosphatic shale member is generally thought to be of Guadalupe (Kazanian) age and possibly Leonard (Artinskian and Kungurian) age as well (Miller and Cline; Newell; Thompson et al.; Licharew in Williams). Baker and Williams (1940) consider the lower part of the Park City formation, to be of Leonard age, and Frenzel and Mundorff (1942) class the lower part in Montana as Wolfcamp age. Diagnostic fossils have not yet been found in the upper part of the Phosphoria; its age can only be said now to be older than early Triassic (Otoceratan), the age Newell and Kummel (1942) assigned to the overlying Dinwoody formation in southeastern Idaho.

Regional variations in thickness and facies

At its type locality in southeastern Idaho, the Phosphoria formation consists of the phosphatic shale member, about 175 feet thick, overlain by the Rex chert member, about 240 feet thick (Richards and Mansfield; Mansfield, 1927). In nearby areas, a black shale unit, about 30 feet thick, overlies the Rex chert member. Individual layers of the formation persist with little change in lithology for miles or even tens of miles, particularly in a north-south direction. Over the field as a whole, however, the formation displays marked changes in facies. The facies may be divided roughly into a miogeosynclinal facies and a craton or platform facies. The boundary between them is not sharp, but over much of the field it corresponds in a general way to

the boundary between the miogeosyncline and craton as defined by other criteria.

These areal facies relationships may be illustrated by analysis of stratigraphic sections at a number of points from west to east across the field. As shown in the sections in figure 2 and table 1, the Phosphoria formation in south-central Idaho is about 680 feet thick and consists of about 3 percent carbonate-fluorapatite, 59 percent chert, and 38 percent carbonaceous mudstone. This is the typical geosynclinal facies. Calcareous rocks, as well as sandy layers, are absent altogether. Westward, in eastern Nevada, about 1,000 feet of cherty carbonate rocks appear, overlying about 160 feet of mudstone, chert, minor thickness of rather weakly phosphatic rocks (a few beds of which display disconformable contacts), and a thin redbed. Eastward from south-central Idaho, the Phosphoria formation thins to a thickness of about 300 feet in the vicinity of the Wyoming-Idaho border as it passes into the platform facies. Phosphatic rocks increase in thickness to a maximum of the equivalent of 73 feet of carbonate-fluorapatite in southeastern Idaho, then decrease sharply within a span of a few miles in western Wyoming. The phosphate also dwindles rather steadily eastward, and in central Wyoming it disappears altogether (fig. 3). Cherty mudstones in south-central Idaho give way to massive cherts that make up about half of the section in southeastern Idaho; these in turn become nodular and calcareous in western Wyoming, then pass to nodular, cherty limestones, some of which persist to east-central Wyoming. Carbonaceous mudstone, which makes up about a third of the formation in southeastern Idaho, likewise thins progressively eastward. Carbonate rocks first appear as discontinuous lenses or concretions in southeastern Idaho, are freely interbedded with the phosphatic beds in western Wyoming, and increase in thickness as phosphatic rocks decrease to form nearly 50 percent of the section in west-central Wyoming, then tongue out into redbeds in central and east-central Wyoming. Sandstone,

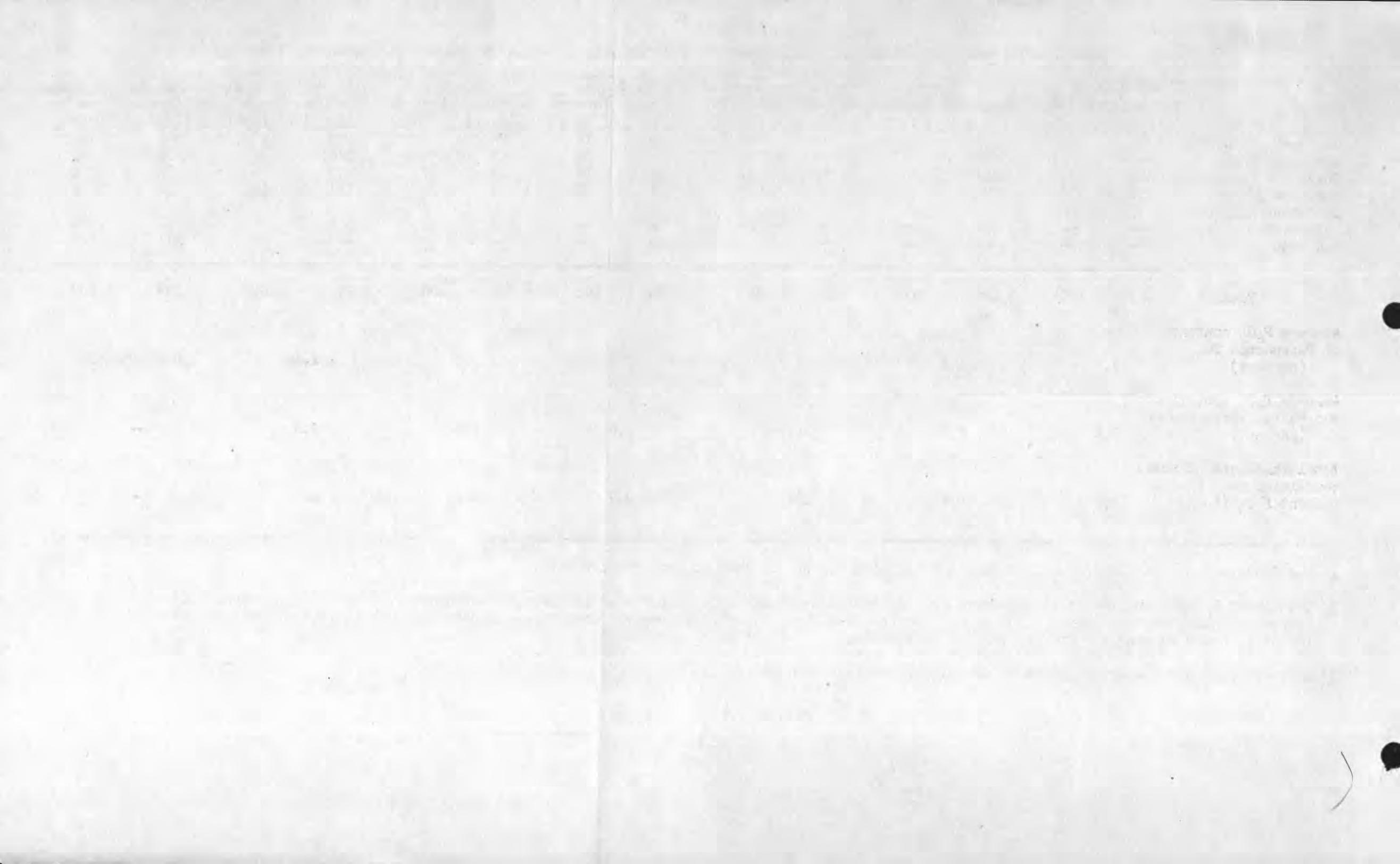
Table 1.--Thickness of principal rock components of Phosphoria formation at localities shown on figure 2 ^{1/}

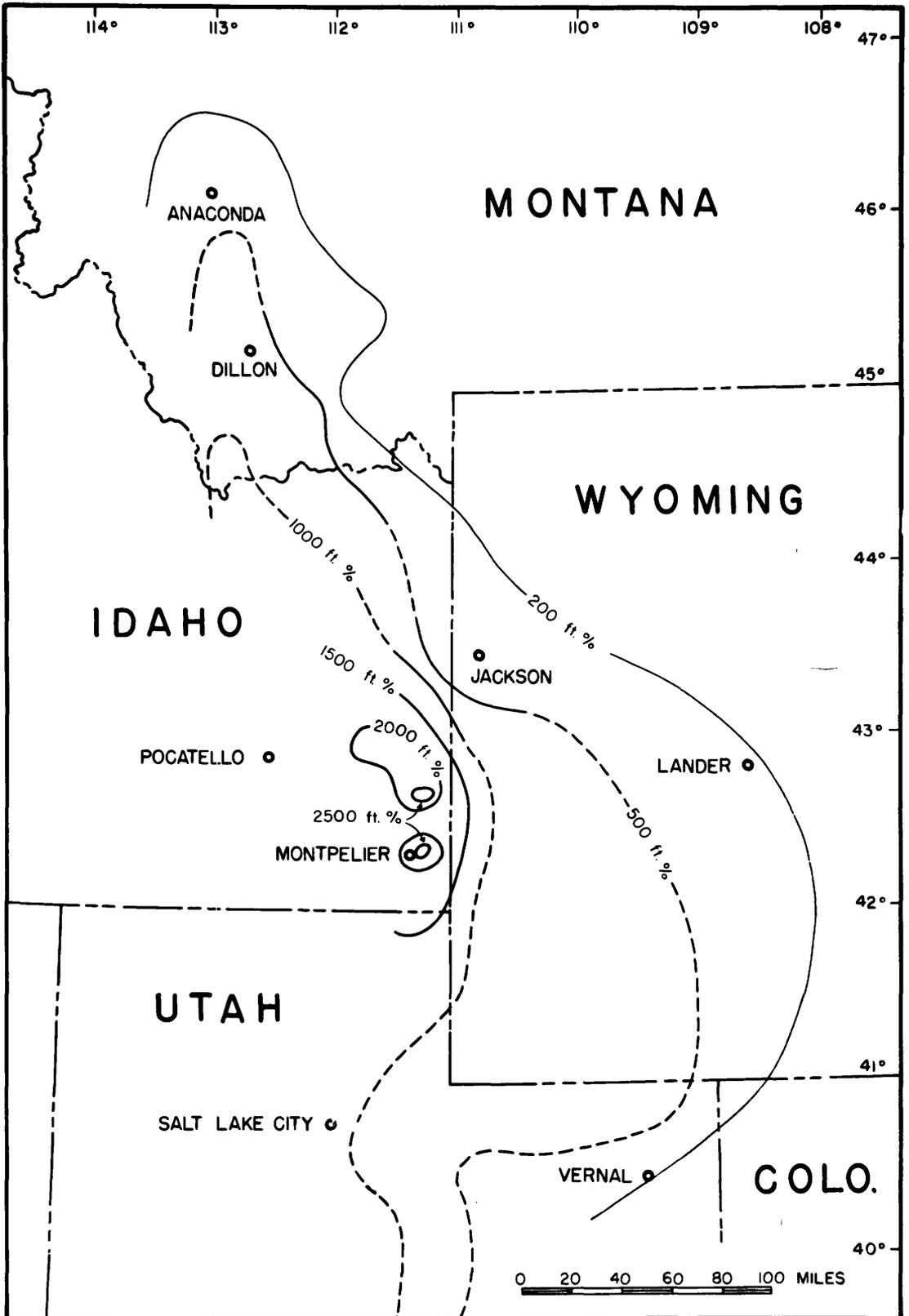
Rock component ^{2/}	Mud Springs ^{3/}		Paris		Montpelier Canyon		Coal Canyon		Poison Creek		Little Popo		Agie River		Rattlesnake Hills	
	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total	Thickness (feet)	Percent of total
Carbonate-fluorapatite	22	3	42	10	73	21	48	18	23	7	8	3	---	---	---	---
Carbonate rock	---	---	27	6	108	32	85	32	149	49	118	41	38	13	---	---
Chert	405	59	223	52	81	24	50	18	52	17	19	6	12	4	---	---
Mudstone ^{3/}	256	38	136	32	78	23	86	32	79	26	141	49	4	1	---	---
Sandstone and conglomerate	---	---	---	---	---	---	---	---	3	1	4	1	31	10	---	---
Red beds	---	---	---	---	---	---	---	---	---	---	---	---	214	72	---	---
Total	683	100	428	100	340	100	268	100	306	100	290	100	299	100	---	---
Average P ₂ O ₅ content of Phosphoria fm. (percent)	1.6		4.4		7.7		5.5		2.8		1.6		Not sampled			
Average P ₂ O ₅ content of phosphatic shale member (percent)	9.8		9.9		14.4		9.6		5.8		3.4		---			
Total thickness of rocks containing more than 31 percent P ₂ O ₅ (feet)	1.0		10.1		22.3		2.7		6.2		---		---			

^{1/} The Goshute Range section shown in figure 2 is omitted because of lack of quantitative data.

^{2/} Calculated by assuming that a thickness of rock described as phosphorite consists of 100 percent carbonate fluorapatite; one described as carbonatic phosphorite consists of 65 percent carbonate-fluorapatite and 35 percent carbonate mineral; etc. No correction has been made for differences in specific gravity of rock components.

^{3/} Includes silt and clay-size silicate minerals and organic matter.





TOTAL PHOSPHATE (IN FEET TIMES PERCENT P_2O_5) IN PHOSPHATIC PORTIONS OF PERMIAN FORMATIONS.

conglomerate, and traces of glauconite appear in west-central Wyoming but make up only 1 to 10 percent of the formation at most. The redbeds which largely displace these rocks in central and east-central Wyoming consist of even-bedded sandy siltstone, calcareous siltstone, and evaporites.

Although considerable progress has been made in the stratigraphic correlation of the component parts of the Phosphoria formation, the facies changes described, coupled with the scarcity of fossils diagnostic of specific ages within the Permian, make this problem difficult. It is not necessary, however, to discuss the details of the correlation problem. For the present purpose it will suffice to say that the rich phosphorites in the lower part of the phosphatic shale in the geosynclinal facies of Idaho are not present on the platform and that a transgressive relationship of the Phosphoria sea, from the west on to the platform is indicated. This relationship is perhaps even better demonstrated in Montana (Klepper in McKelvey, 1949a), where the lower units are present only in the southern part of the State, and in Utah, where the lower limestone member of the Park City formation wedges out on the platform (Thomas and Krueger).

THE PHOSPHORITES

With this picture of the distribution of the facies of the Phosphoria formation, it is appropriate now to examine briefly the mineralogy, chemical composition, and petrography of the phosphatic rocks as well as some of their important regional variations.

Mineral and chemical composition

The phosphorites of the Phosphoria formation are composed of colloform carbonate-fluorapatite (Altschuler and Cisney) mixed in varying proportions

with detrital silicates (chiefly quartz silt, clay minerals, and feldspar), calcite, dolomite, chert, carbonaceous matter, and glauconite. Purple fluorite, generally secondary, is common where the F/P_2O_5 ratio exceeds about 0.105 (W. W. Rubey, personal communication). Pyrite, generally oxidized at the surface to limonite, is present, particularly in the argillaceous rocks associated with the phosphorites.

The chief chemical constituents are phosphate, lime, fluorine, carbon dioxide, silica, alumina, ferric oxide, potash, soda, and sulfur. In addition, more than 35 metals are found in minor amounts in the Phosphoria formation (Hill et al., 1932; Jacob et al., 1933; Robinson). Of these, the rare earths and uranium, vanadium, chromium, nickel, zinc, molybdenum, silver, and selenium are most concentrated with respect to their relative abundance in the earth's crust. Uranium and the rare earths are most abundant in the phosphorites and probably occur in the carbonate-fluorapatite. Vanadium, chromium, selenium, and silver are found in both the phosphorites and the carbonaceous mudstones; they may occur in the carbonate-fluorapatite, but the most significant quantities probably occur in clay minerals. Although zinc, nickel, and molybdenum are trace constituents of the phosphate rocks, they are more highly concentrated in the more weakly phosphatic mudstones. Very likely they are tied up in clay minerals. Most of these metals are not abundant in limestones or even calcareous phosphorites and mudstones--in fact, uranium seems to decrease sharply in the phosphorites as the CO_2 content rises to as much as 4 percent (McKelvey and Nelson).

Petrography

Part of the carbonate-fluorapatite in the rocks is in the form of interstitial cement, and in a few layers most of the phosphate is in phosphatized

brachiopods and fish scales. The great bulk of the phosphatic particles, however, are conglomerated in pellets and nodules--in fact, almost no phosphorites are known that do not show at least a rude pelletal or nodular structure. The pellets and nodules are generally somewhat elliptical, with the long axis parallel to the bedding. They range in maximum diameter from 0.05 mm to more than 3 cm, and are generally well-sorted. Most of them are structureless but some of those in the range of 1 to 15 mm are concentrically laminated. Many, perhaps most, of the larger nodules are compound, i.e., are themselves composed of cemented, fine-grained pellets.

The phosphatic rocks are generally well-cemented with carbonate-fluorapatite, argillaceous matter, carbonaceous matter, chert, calcite, or dolomite. As the rocks of the Phosphoria formation are mixtures of these constituents, any one of them may be the dominant one. The phosphatic layers range in thickness from a millimeter to 2 meters. Most of them are a few millimeters thick and are interbedded with less phosphatic mudstones or carbonate rocks. Cross-bedding is rare and has been observed only in the eastern part of the field. Ripple marks and other wave marks have not been observed.

Although the P_2O_5 content of the rocks is as much as 38 percent, most beds of minable thickness do not contain more than about 32 percent P_2O_5 . The most phosphatic rocks are generally those in which the pellets are 1 to 15 mm in diameter; finer-grained rocks contain more carbonaceous and argillaceous matter; and because many of the coarser-grained nodules are compound, they also contain these impurities.

Areal variations in thickness and composition

The westward increase in the P_2O_5 content of the whole formation has already been described (fig. 3). A corresponding increase in the quality of

the phosphatic rocks also takes place to the west, as is shown by the westward increase in the thickness of rocks containing more than 31 percent P_2O_5 in figure 4. Although they are not reproduced here, maps showing the thickness of rocks containing more than 25 and 18 percent P_2O_5 at scores of localities indicate the same relationships (McKelvey, 1949a; Swanson et al.).

Carbonaceous matter also increases westward, both in the phosphorites and in the associated rocks. The carbonate content of the phosphorites decreases westward as it does in the associated rocks. Not only does the grain size of clastic constituents decrease westward, but the size of the phosphorite particles also decreases westward. Thus, nodules are more abundant in the platform facies than in the geosynclinal facies.

Two more subtle areal variations deserve notice. First, the F/P_2O_5 ratio decreases from about 0.13 or more in the platform facies in Wyoming, where fluorite is common, to 0.10 or less in the geosynclinal facies in southeastern Idaho where fluorite is rare (McKelvey, 1946). Second, some of the minor metals (vanadium, chromium, zinc, and uranium, for example) and perhaps most of them are, in contrast to fluorine, relatively less abundant in the platform facies than in the geosynclinal facies of southeastern Idaho and westernmost Wyoming.

ORIGIN OF THE PHOSPHORIA FORMATION AND ITS PHOSPHORITES

With this account of some of the important facts of the distribution of the Phosphoria formation, we may turn now to a discussion of their meaning. The problem of the origin of the phosphorites of the Phosphoria and similar formations has been vastly simplified by the remarkable work of Kazakov (1937). His analysis of the geological, oceanographic, and chemical data bearing on the problem is so penetrating and comprehensive that it deserves summary as a hypothesis to be modified rather than displaced.

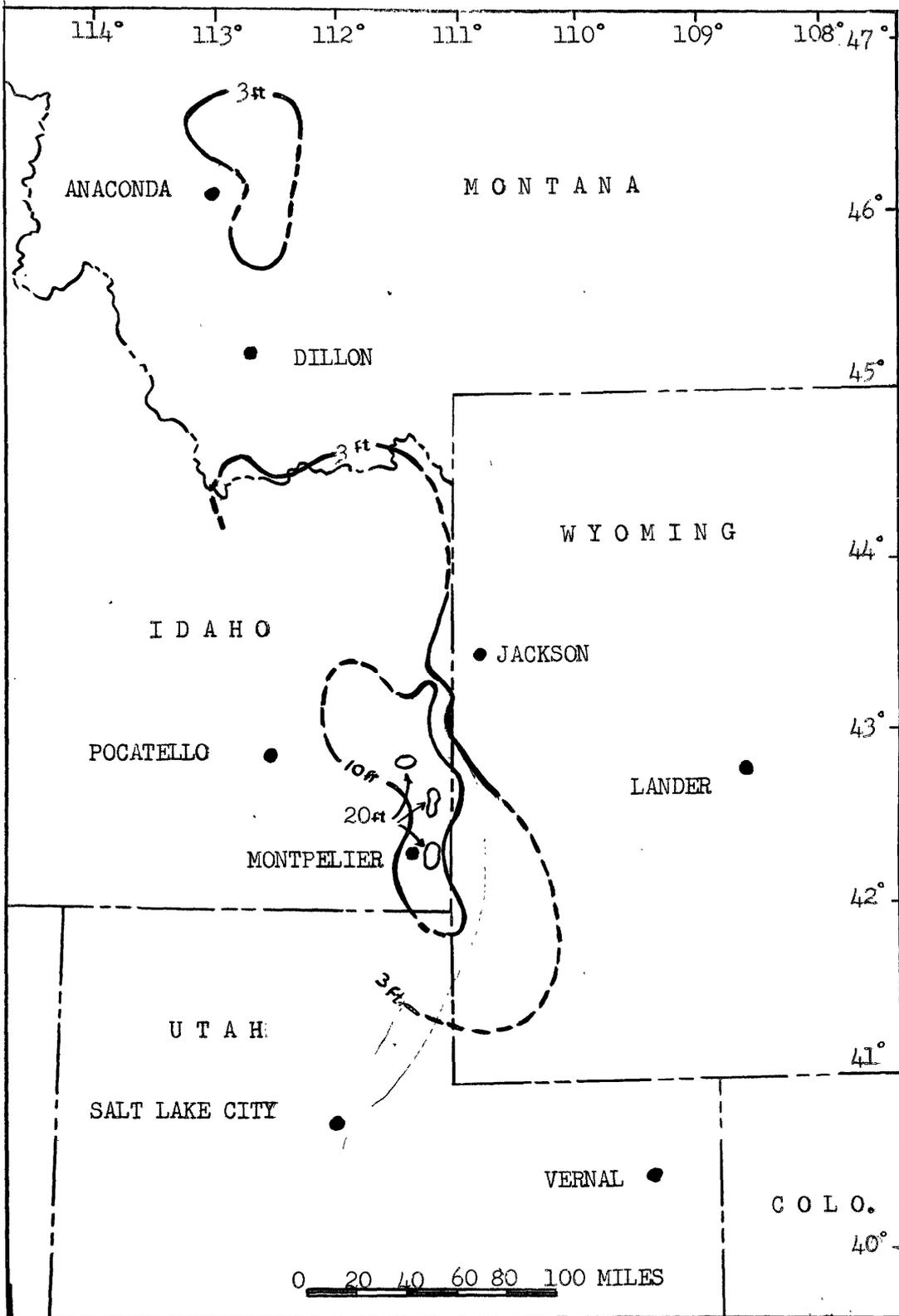


Figure 4. Thickness in feet of beds in the Phosphoria and Park City formations containing more than 31 percent P_2O_5 .

Kazakov's hypothesis

Kazakov recognized that the phosphorite facies are associated with marine limestones, sandstones, carbonaceous shales, and glauconites and are never associated with beds of lagoonal or fresh-water deposition; that phosphorite facies occupy a definite position with respect to synchronous shallow-water sediments on the one hand and deep-water sediments on the other (the paragenetic relationship of facies, as he calls it); that platform facies are distinguished by the nodular, pebbly habit of the phosphorites, their P_2O_5 content, and their association with glauconite and arenaceous materials; that the geosynclinal phosphorites are of bedded, plate, or flagstone type, high in P_2O_5 , and associated with limestones and shales; that the phosphorites increase in thickness and P_2O_5 content with increasing distance from the shore line and that thickness of phosphorites and their quality are interdependent; that the phosphorite columns typically consist of a basal conglomerate, overlain first by reworked, pre-phosphorite materials, then by the phosphate layer, and then by other materials that are derived from nearby terrigenous sources; that the quality of the phosphorites depends partly on the composition of the enclosing rocks, but mainly on the rate of sedimentation of terrigenous materials as compared with the rate of accumulation of phosphate; that phosphorites are generally associated with marine transgressions (he properly credits first mention of this to Cayeux); that the phosphorite facies may migrate across time lines; and finally that phosphorite facies are usually confined to the shelf on one side of a large, deep basin having ample connection with the ocean. Turning to oceanographic data collected by other workers, Kazakov noted that the P_2O_5 content of marine waters increases with depth from a minimum in the zone of photosynthesis to a maximum about 500

meters below the surface, as the pH and temperature decrease and the partial pressure of CO_2 increases. At greater depths the P_2O_5 content falls off slightly as the CO_2 content drops. Supplementing these data with information on the areal distribution of P_2O_5 in the sea and with observations of his own on phase equilibrium of $\text{CaO-P}_2\text{O}_5\text{-HF-CO}_2\text{-H}_2\text{O}$ in low-concentration fields (analogous to sea water) he discarded the classical biolith theory for the origin of phosphorites and presented the hypothesis that phosphate is chemically precipitated on shelving bottoms between depths of 50 and 200 meters where the pH of ascending cold waters rises as their temperature increases and the partial pressure of CO_2 decreases. The water first becomes saturated with calcium carbonate, which he said is precipitated first, and later with calcium phosphate. He emphasized that phosphate cannot be precipitated either in the zone of photosynthesis, where available phosphorus is assimilated by phytoplankton, or at depths below 200 meters, where the high CO_2 content prevents conditions of supersaturation. In this circulating system (which he patterns from actual conditions in the South Atlantic) the deep waters upwelling on one side of a basin are largely depleted of phosphorus by chemical precipitation and phytoplankton assimilation; these waters, circulating back in the upper levels of the sea, yield no phosphate when they reach the other side of the basin.

Kazakov's hypothesis represents an excellent synthesis of the geologic, oceanographic, and physical chemical data on phosphate that fits the observed facts better than any other hypothesis. It is interesting to note that W. W. Rubey, of the U. S. Geological Survey, working without knowledge of Kazakov's paper, developed much the same hypothesis about 1940. Dietz, Emory, and Shepard (1942) have also presented data on sea-water solubility of tricalcium phosphate in support of a hypothesis of chemical precipitation of phosphorites on the banks off the coast of southern California.

Supplementary and modifying evidenceSource of phosphate and associated constituents
in the Phosphoria formation

Kazakov postulated that the phosphate in marine phosphorites is derived from cold waters upwelling from the ocean basin and thus indicated that oceanic circulation is a prerequisite to the formation of phosphorites. Data on the Phosphoria formation further emphasize its importance. Assuming that the Phosphoria formation contains an average of about 550 feet-percent P_2O_5 over an area of about 135,000 square miles, it contains about 1.7×10^{12} metric tons of P_2O_5 . This is more than five times the 0.32×10^{12} tons of P_2O_5 in the ocean now, calculated on the assumption that the ocean contains 0.23 mg/kg in a volume of 137×10^{12} km³ (Sverdrup et al., pp. 15, 220). These rough calculations, revised from earlier ones by Rubey and by McKelvey (1946) to conform with new data on the P_2O_5 content of the formation, indicate that the Phosphoria must have drawn on the resources of a major part of the ocean over a long period. In fact, at first glance it might appear that the phosphate in the ocean is not adequate to produce the phosphate deposits of the Phosphoria. Calculations based on Clarke's (p. 118) and Conway's (p. 119) estimates of the total dissolved solids brought to the oceans, however, indicate that about 4.5 million tons of P_2O_5 are brought to the sea annually; in a later paper, Kazakov (1950) gives an estimate of 1 million tons annually. At this rate, over a period of 15 million years, equivalent to about half of Permian time, between 15×10^{12} and 70×10^{12} tons of P_2O_5 would be brought to the sea. The time required for the sediments of the Phosphoria formation to accumulate may have been less than 15 million years and the amount of land surface exposed in the Permian probably was not nearly as large as now, but even if the time of

accumulation and the volume received from the lands are cut in half, 3.8×10^{12} to 16×10^{12} tons would be available for the accumulation of the Phosphoria deposits as well as the smaller amounts that are found in other Permian rocks.

Mansfield (1940) suggested that the fluorine in the Phosphoria might have been derived from Permian volcanic activity to the west. Some might have originated locally, but both Rubey (personal communication) and Kazakov (1950) have called attention to the fact that the amount of fluorine in sea water now is much greater than the amount of phosphate (1.4 mg/kg compared to 0.23 mg/kg). No unusual local source, therefore, seems required to account for the fluorine. In further support of the concept that the phosphate and associated elements were derived from normal sea water rather than from special sources, it may be pointed out (McKelvey, 1946) that the assemblage of elements in the Phosphoria, including the minor metals, is essentially the same as that found in sea water now; and, moreover, sea water is the only source that could be expected to yield elements of such diverse petrogenic affinities as, for example, chromium, vanadium, and the rare earths.

While on the subject of the source of the Phosphoria sediments, it should be mentioned that one of the important prerequisites in the concentration of the phosphorites in the Phosphoria and similar deposits is the lack of a source of a large amount of clastics that might have so diluted the phosphorites as to make them of little value. For example, if the 5,000 feet of Permian sedimentary rocks in Texas contained about 0.15 percent P_2O_5 (the average in sedimentary rocks) the section would contain about 750 feet-percent P_2O_5 --an amount similar to that in the Phosphoria formation (McKelvey, 1946).

Size, shape, and depth of the Phosphoria sea

Kazakov (1937) emphasized that the most favorable site for the accumulation of phosphorite is at depths between 50 and 200 meters on a shelving bottom on

one side of a large basin that has free access to the open sea. Other writers, most recently Krumbein and Garrels (1952), believe that phosphorites accumulate in restricted basins. Beyond the data already presented on the volume of P_2O_5 in the formation and its implications regarding marine circulation, the Phosphoria data cast light on these topics.

The outline of the Phosphoria sea is difficult to reconstruct. Mansfield (1927, p. 185) pictures it as open to the north, to the southwest, and possibly to the south, primarily because of faunal affinities with rocks in Alaska, California, and Texas. The new data do not modify this picture greatly except that facies changes and pinch-outs in Montana suggest that the basin might have been closed to the north. Little is known of the formation in the western part of the area but the redbed, nodular phosphate, and disconformities in the Goshute Range section suggest that the western margin of the basin there was close by.

The redbed facies in Wyoming and Utah have been interpreted by many writers as of non-marine deposition, but the even bedding and great lateral continuity of individual layers suggest a marine environment. The presence of evaporites and absence of fossils suggest, however, that the sea water was not of normal composition and that marine circulation was impeded locally. The bulk of the redbeds are of terrigenous origin, however, and they indicate the direction in which the land lay, even though it may have been tens or scores of miles from their seaward margin.

The area of the Phosphoria sea in which normal marine facies were deposited was about 225,000 square miles and possibly greater at times. The marginal sea may have covered 25,000 to 75,000 square miles in addition.

The overlap of Phosphoria sedimentary rocks to the east and north, the eastward and westward intertonguing with redbeds, the eastward and northward

coarsening in grain size, all suggest a basin, deepest in central Idaho and western Utah and shelving to the west, north, and east. Phosphorites were deposited at intermediate depths in this basin on three sides, rather than one, as Kazakov supposed. This does not diminish the force or logic of Kazakov's argument but merely indicates that the source of the upwelling cold waters was probably to the south or southwest.

As regards the depth at which the phosphorite was concentrated, the even, fine lamination of the rocks; the absence of ripple or scour marks and near-absence of cross-bedding; and the association of the phosphorite with fine-grained clastics and carbonaceous matter indicate that the bottom was below wave base (McKelvey, 1946). The sorting of the deposits, on the other hand, suggests some gentle current action. In a sea of this size, storm waves might be expected to affect the bottom at depths greater than 50 meters and probably even greater than 200 meters, at least to the extent of aerating the bottom sufficiently to oxidize carbonaceous matter exposed for long periods. This, together with the fact that most of the phosphorites on the present sea bottom at various localities over the world are found at depths of 400 to 1,000 meters or more (Twenhofel), leads us to suggest that the zone of phosphorite formation may have been somewhat deeper than Kazakov reasoned, possibly between 200 and 1,000 meters, depending partly on the local climate.

Precipitation of phosphorite, carbonate, chert,
and carbonaceous matter

The paragenetic relationships of the phosphorite facies of the Phosphoria indicate that the waters ascending the shelf of the Phosphoria sea became saturated first with carbonate-fluorapatite and then with calcium carbonate, rather the reverse as Kazakov thought (Kazakov, 1937, p. 112). The facts show

also that although the sea may have been simultaneously supersaturated with respect to both apatite and carbonate, resulting in a phosphatic limestone, this condition was not the prevailing one. Generally the areas of supersaturation with respect to apatite and carbonate are different, and, contrary to Kazakov's report, most of the phosphorites do not necessarily contain calcium carbonate. This phase of the problem, as well as the relation of MgO to the system, has been studied by Rubey. It is not appropriate to anticipate his account of these studies, but he permits us to say that the solubility pH curves of apatite and carbonate in the sea are roughly similar in form but do not coincide precisely. This lack of precise coincidence, of course, is most significant - were it not true carbonate-fluorapatite and calcite would be precipitated together and in about the same proportions as they are found in sea water. Phosphate would be found only in slightly phosphatic limestones, and concentrations of phosphate could be formed only by weathering.

The general increase in carbonaceous matter with increase in phosphate over the western field suggests a genetic relationship between the two constituents, a relationship that has been discussed by many of the early investigators. Rather than a direct cause-and-effect relationship, it seems likely that both the organic matter and the phosphate are the product of the phosphate-rich waters upwelling from the ocean basins. Sverdrup et al., (p. 784) summarize the work of several investigators, particularly Hentschel (1928) and Hentschel and Wattenburg (1930), which shows that the production of phytoplankton in the sea is controlled by the availability of phosphate and nitrates and is greatest in areas of upwelling of cold, phosphate-rich waters. Phytoplankton is the chief source of organic matter such as is found in the Phosphoria formation (Trask, 1939), and it seems safe to say that the abundance of organic matter in the Phosphoria reflects abundant growth of

phytoplankton, nourished by the same phosphate-rich waters from which the carbonate-apatite itself was derived. This phytoplankton growth need not have been most luxuriant in the waters directly above the areas in which it is found now. Organic matter derived from phytoplankton behaves much like finer fractions of solid material (Trask) and may thus have been carried from shallower to deeper waters along with the fine-grained clastics with which in truth it is found in the Phosphoria formation.

In repudiating the classical biolith theory of the genesis of phosphorites, Kazakov implies that organisms play little part in the precipitation of phosphate. We sympathize with the view that the origin of chemical sediments like the phosphorites is best thought of in terms of the inorganic chemistry and physics of the sea water---even though an organism may extract a compound from the water, it will be resorbed on the death and decay of the organism unless the water is essentially saturated with that compound. Nevertheless, it seems probable that much of the phosphate in the sediments has been derived through the decay of organic remains, the existence of which is so well shown by the carbonaceous matter. Ordinarily, the phosphate derived from decaying plankton is resorbed by the sea in winter (Harvey), but if the sea is already essentially saturated the phosphate would accumulate as part of the sediment. In addition, some phosphate might be released from organic matter after its burial through bacterial decay of proteins (Zobell, 1939).

Internal evidence from which to judge the relative importance of biologic versus inorganic precipitation is obscure. As previously mentioned, the bulk of the phosphorite is in the form of pellets and nodules, the origin of which might cast some light on the problem. Most investigators have considered these and similar pellets to be of inorganic origin (Mansfield, 1927, p. 364) but Branner and Newsom (1902), Moore (1939), Dietz et al., and others favor

a faecal origin. As is evident from both natural phenomena and industrial pelletizing processes, fine-grained particles may be aggregated in many ways, and it is difficult to tell how those of the Phosphoria were formed. Their wide range in size, good sorting in individual layers, regional trends in average size, the compound nature of many of the larger ones and the oolitic or pisolitic structure of others does not favor organic origin. Even if they were formed by excretion, however, the fact that only deposit-eating animals generally form pellets firm enough to persist for any length of time (Moore), particularly long enough to be sorted by currents, suggests that the organisms may merely have shaped pre-existing bottom sediment and that the pellets are not an index of the role organisms may have played in the precipitation of phosphate.

Another significant relationship evident from the facies of the Phosphoria is that the areas of bedded chert correspond in a general way to the areas in which phosphorites are found. This association, not reported by Kazakov, is a common one in the geosynclinal phosphorites. Its significance is not known to us now, but the areal variations in the cherty facies may cast some light on it. The total volume of chert increases westward as carbonates and sand decrease; and in the deepest part of the basin the cherty facies pass into thin-bedded, thick, cherty mudstones. The mutually exclusive distribution of quartzite and chert, particularly evident in Montana, and the westerly increase in argillaceous matter in the cherty beds suggest that the chert is formed from diagenetic recrystallization of silt-sized quartz, which is most abundant in a zone intermediate between near-shore sandy detritus and deep-water argillaceous detritus. Correns (1950) has reported that precipitation of silica in fresh water is controlled by pH, and investigations by M. A. Warner, one of our co-workers who is studying the origin of the cherts, suggest that the pH may

control the precipitation of silica from sea water. It is possible, too, that organisms played an important role in the precipitation of fine-grained silica, as they may have with the phosphate.

Little is known about the precipitation control of the minor metals in the Phosphoria formation and related deposits. Recent experiments made by Krauskopf indicate that the sea is not saturated with respect to the minor metals and suggest that their precipitation is effected by coprecipitation or chemical adsorption. Areal variations in the ratios of these metals to phosphate and other compounds, however, indicate that their precipitation must be controlled not only by the formation of a given coprecipitant but by additional chemical factors.

SUMMARY

With these modifications to Kazakov's hypothesis, as applied to the origin of the Phosphoria, we can summarize our present understanding of its origin as follows:

The Phosphoria formation accumulated in a large shelving embayment bordered by lands of low relief that contributed little detritus to the sea. Cold, phosphate-rich waters upwelled into this basin from the ocean reservoir to the south or southwest. Phosphorite was deposited from these ascending waters, probably in depths of 1,000 to 200 meters, as their pH increased along with increase in temperature and decrease in partial pressure of CO_2 . Carbonates were precipitated from these waters when they reached more shallow depths, at a somewhat higher pH. The phosphate-rich waters nurtured a luxuriant growth of phytoplankton, as well as higher forms of plant and animal life, some remains of which were concentrated with fine-grained materials in deeper waters away from shore. Part of the phosphate and probably some of the fine-grained silica in

the formation was concentrated by these organisms. Finally, these conditions persisted over much of Permian time.

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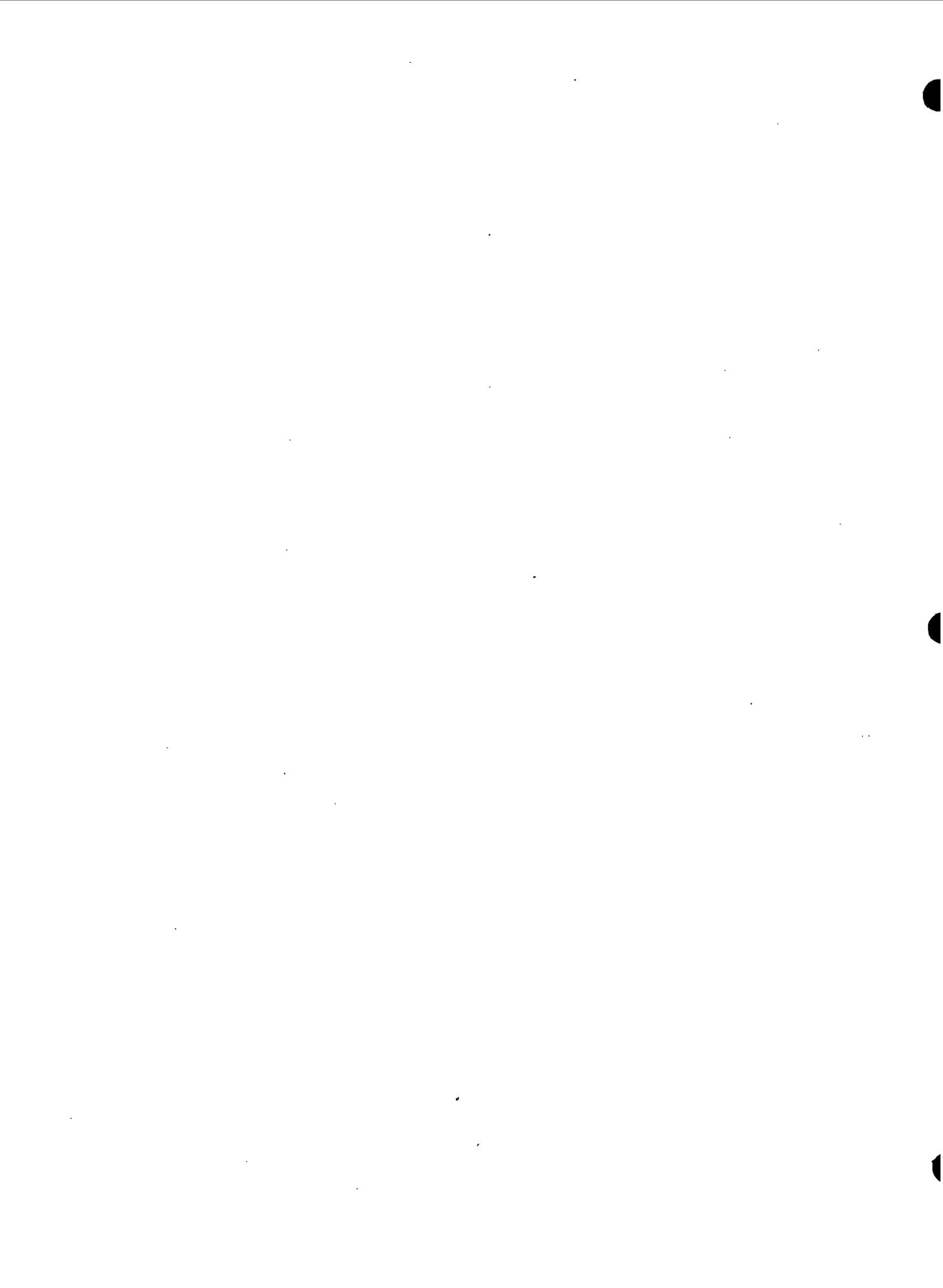
Many geologists of the U. S. Geological Survey have participated in the recent investigations of the Phosphoria formation. It is not possible to mention them all, but we are particularly indebted to James Steele Williams, K. B. Krauskopf, R. A. Gulbrandsen, M. A. Warner, and E. R. Cressman for information they have supplied. Most of all, however, we wish to acknowledge the stimulating leadership provided during the formative years of these investigations by W. W. Rubey as well as the facts and ideas he uncovered during his own research on the problem in the period of 1937-1943.

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