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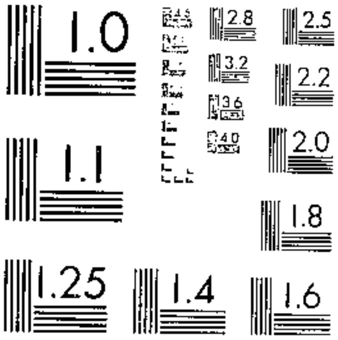

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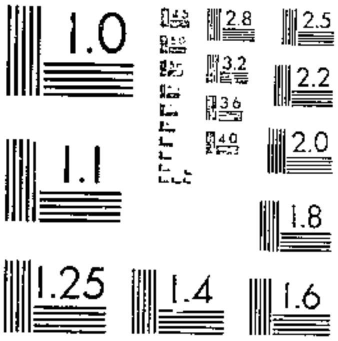

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TECHNICAL BULLETIN No. 364 JUNE 1933

UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C

THE COMPOSITION AND DISTRIBUTION OF PHOSPHATE ROCK WITH SPECIAL REFERENCE TO THE UNITED STATES

By K. D. JACOB, *Chemist*, and W. L. HILL, H. L. MARSHALL, and D. S. REYNOLDS, *Assistant Chemists, Division of Fertilizer Technology, Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils*.[1]

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INTRODUCTION

Phosphate rock is the most important of the mineral fertilizer materials, in annual tonnage handled.

The domestic phosphate-rock industry dates from 1867, when mining of the South Carolina deposits began. Since then the annual produc-

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[1] The authors express to L. F. Rader, Jr., their appreciation for assistance in the chemical analyses; to S. B. Hendricks and M. E. Jefferson, of the physics and physical chemistry division, for the X-ray and microscopical examinations of the samples; to L. T. Alexander and Hubert Lakin, of the soil chemistry and physics division, and to Mrs. Dorotha M. Darnell, formerly of the same division, for the mechanical analyses and the preparation of the mechanical separates; to G. R. Mansfield, United States Geological Survey, and to B. L. Johnson, United States Bureau of Mines, for criticism of the manuscript; and to the phosphate mining companies and fertilizer manufacturers, who furnished the majority of the samples used in this investigation.

tion has increased, more or less steadily, to an average of approximately 3,000,000 long tons at present. During this more than half a century phosphate-mining activities have shifted from the comparatively low-grade South Carolina deposits to the richer Florida and Tennessee deposits. Comparatively small tonnages are also produced annually from the deposits in Idaho, Montana, and Wyoming, which perhaps constitute the largest known reserve of high-grade phosphate rock in the world. From time to time small quantities of phosphate have been mined in other States, notably Alabama, Arkansas, Kentucky, Pennsylvania, and Utah. Deposits of limited extent are also known to occur elsewhere in the United States.

Aside from the part played by phosphate mining in contributing to the wealth of the United States, phosphate rock has formed the basis of the domestic chemical-fertilizer industry from the time of its establishment (about 1850). This industry now consumes approximately 2,000,000 long tons of phosphate rock annually in the manufacture of approximately 4,000,000 short tons of phosphate fertilizers, principally superphosphate. In addition to this approximately 300,000 long tons of rock are used annually in the manufacture of elemental phosphorus, phosphate chemicals, and blast-furnace products; as an ingredient in livestock and poultry feeds; and for direct application to the soil as a fertilizer. The annual exports of phosphate rock amount to approximately 700,000 long tons.

Although phosphate rock is valued primarily for its content of phosphoric acid, the commercial desirability of a particular grade or type of rock may be affected to a certain extent by the presence of admixed impurities such as silica, carbonates, aluminum, iron, etc. Phosphate rock containing more than about 5 to 6 percent of total oxides of iron and aluminum is not considered desirable for the manufacture of superphosphate, principally because of the poor mechanical condition of the resulting product. Rock of very high iron content is also undesirable for the manufacture of phosphoric acid by furnace processes because of the formation of iron phosphide, a material for which there is only a limited demand and which is relatively difficult to convert into other phosphate products.

In the manufacture of superphosphate, the presence of about 1 to 3 percent of carbon dioxide in the phosphate rock is desirable because the liberated carbon dioxide renders the superphosphate porous and spongy, and thereby facilitates drying. Larger percentages of carbon dioxide are not desirable, however, because of the increase in the amount of sulphuric acid required to obtain satisfactory conversion of the phosphoric acid into available forms.

Other than its action as a diluent, silica has no harmful effect on the use of phosphate rock for the manufacture of superphosphate and other products. On the other hand, high-silica rock may possess some advantage in the manufacture of phosphoric acid by furnace processes, inasmuch as a certain ratio of lime to silica must be maintained in the furnace charge in order to produce a slag which may readily be tapped from the furnace.

As shown by recent investigations *(64)*,[2] fluorine is an essential component of the complex phosphates occurring in all types of domestic phosphate rock, and in nearly all commercially important types

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[2] Italic numbers in parentheses refer to Literature Cited, p. 79.

of rock from foreign deposits. Sufficient evidence is now available to justify the conclusion that the conversion of the phosphoric acid of phosphate rock into a condition that will permit its ready utilization as plant food is dependent upon the extent to which the complex phosphate-fluorine compound is decomposed by the processing treatment. From the standpoint of the fertilizer manufacturer, fluorine was formerly considered an undesirable constituent of phosphate rock, because the fluorine-bearing gases generated during the manufacture of superphosphate created a nuisance in the vicinity of the factories. Today, however, many superphosphate plants are utilizing these gases for the production of hydrofluosilicic acid and fluosilicates. Because of the deleterious effect of fluorine on the health of animals (*7, 107, 147*), its presence in phosphate rock has prevented the general use of this cheap source of calcium and phosphorus in mineral mixtures for livestock feeding.

Among the constituents of phosphate rock, calcium is next in importance to phosphoric acid. Recent investigations (*52*) have shown that normal growth of tobacco cannot be obtained on certain soils, particularly sandy and sandy loam soils, without the application of calcium compounds. The compounds present in superphosphate and in double or triple superphosphate are effective sources of calcium for such soils. The fertilizers used on these soils in the past always contained calcium in the form of superphosphate, and evidence of calcium deficiency was not obtained until the new types of calcium-free fertilizers were used.

During recent years considerable attention has been given to the effect on plant growth of the so-called less common elements, such as manganese, copper, zinc, chromium, vanadium, arsenic, iodine, etc. (*103, 171*). Certain of these elements occur in phosphate rock and, aside from their possible effect on plant growth, may have an important bearing on the use of the rock in the manufacture of phosphates for food and technical purposes, so far as they impart undesirable properties to the finished products. If the phosphates are to be used in the manufacture of food products, it is also important that the content of certain impurities, such as arsenic and lead, shall not exceed the limits prescribed by the various State and Federal pure-food regulations.

It is evident from the foregoing that a thorough knowledge of the complete chemical composition of the various commercial types of phosphate rock occurring in the United States is an aid in their rational use for the manufacture of fertilizers and phosphate chemicals and for other purposes. This information is also valuable in the study of the chemical structure of phosphate rock, a thorough knowledge of which is essential to an understanding of the reactions occurring during processes in the manufacture of available phosphates. Despite their importance, comprehensive data on the chemical composition of domestic phosphate rock are not available. Except for occasional incomplete analyses of isolated samples, usually selected materials or prospect samples, the sparse data recorded in the literature before the beginning of the present investigation relate principally to the occurrence of phosphoric acid, calcium, aluminum, and iron.

The results presented in this bulletin comprise more or less complete chemical analyses of all the domestic types of phosphate rock which are of commercial interest at present. Special attention is given to the occurrence of fluorine, iodine, and the so-called less-common metallic elements, such as manganese, chromium, vanadium, copper, zinc, and arsenic; to the chemical composition of the mechanical fractions separated from natural phosphates; and to the solubility of natural phosphates in ammonium-citrate and citric-acid solutions.

In order to present a comprehensive picture of the phosphates of the United States, it is important to give a brief review of the deposits and the production and reserves of rock before discussing the results of the chemical analyses.

REVIEW OF PHOSPHATE DEPOSITS OF THE UNITED STATES

ALABAMA

Deposits of phosphatic greensand and phosphatic nodules and shell casts occur in Alabama in a belt extending southward 20 to 50 miles from a line drawn from Columbus, Ga., westward through Tuskegee, Montgomery, Marion, Greensboro, and Eutaw, Ala., on to Columbus, Miss. (*137*, *183*, *184*, *192*). Deposits of phosphate also occur in Limestone County, just south of the Tennessee line, along Elk River, Sugar Creek, and Little Shoal Creek (*105*, *165*; *185*, *p. 64*). According to Phalen (*138*), a deposit of aluminum phosphate (wavellite) is reported to exist near Mitchell Mountain, on the Coosa River, 6 miles east of Coal City, St. Clair County. In general, the Alabama phosphates are comparatively low in phosphoric acid and occur in small, irregular deposits. Consequently, the deposits have not been worked on a large scale, although before 1901 small quantities of rock were mined in certain localities.

ARKANSAS

Deposits of phosphate rock extend over a considerable area in north-central Arkansas (*11*, *12*, *140*, *146*, *196*), and the phosphate horizon has been recognized in Independence, Stone, Izard, Searcy, Marion, Baxter, and Newton Counties. The only deposits that have been developed commercially are those on Lafferty Creek, Independence County, near the junction of East Lafferty and West Lafferty Creeks, about 4 miles southwest of Cushman. These deposits have not been worked, however, since 1915. In general, the Arkansas phosphates contain less phosphoric acid and more iron and aluminum than the Tennessee phosphates, and many of the deposits are located at some distance from railroad lines. These factors have operated against their commercial development, but the deposits constitute an important phosphate reserve for the Middle-Western agricultural region.

FLORIDA

Since 1890 the Florida phosphate deposits (*93*, *113*, *122*, *126*, *140*, *176*, *177*, *195*, *208*, *209*) have been of great importance to agriculture, not only in the United States but in European and other foreign countries.

Four principal varieties of phosphate occur in Florida. In the order of their present importance these are land-pebble phosphate; hard-rock phosphate; claylike phosphates, including the soft and waste-pond phosphates; and river-pebble phosphate. Phosphatized limestone and phosphatic marl also occur in certain localities (*122*).

The land-pebble phosphate deposits are by far the most important in Florida, and, from the standpoint of production, they have been the most important in the United States since 1905. The deposits cover a considerable area in the eastern and western portions of Hillsborough and Polk Counties, respectively, and extend southward into the northeastern corner of Manatee County and the northwestern corner of Hardee County. At present the principal producing mines are located near Bartow, Brewster, Coronet, Lakeland, Mulberry, Nichols, and Pierce.

The hard-rock phosphate deposits occur in a belt that extends southward from Suwannee and Columbia Counties, through portions of Gilchrist, Alachua, Levy, Marion, Citrus, Sumter, and Hernando Counties, to Pasco County—over 100 miles. Deposits are also known in Lafayette, Taylor, Jefferson, Wakulla, and Liberty Counties. Deposits of plate rock, a variety of hard-rock phosphate, occur in central Marion County near Sparr, Anthony, and Ocala. Mines have been operated in nearly all sections of the hard-rock phosphate region, but since 1925 only certain deposits near the towns of Dunnellon, Inverness, and Hernando have been worked.

For the purpose of this bulletin, the claylike phosphates of Florida are divided into two classes, namely, soft phosphate and waste-pond phosphate (*71, 85, 122*). Soft phosphate is commonly closely associated with both the land-pebble and hard-rock phosphates, but it occurs to a greater extent in the hard-rock deposits. It is not only present in the matrix of the hard-rock and land-pebble phosphates, but Mansfield (*113*) states that soft phosphate occurs in more or less isolated pockets in the Vicksburg limestone and in larger areas scattered over several square miles northwest of Ocala, Marion County, and in Pasco County, south of Greer and southwest of Richland. Since 1889 small quantities of soft phosphate have been mined from time to time and sold principally for direct application to the soil.

During the process of preparing hard-rock phosphate for the market the soft phosphate in the matrix is washed into waste ponds, where it settles out with the clay and other impurities, the finer particles concentrating at points farthest from the entrance to the ponds. The abandoned waste ponds in the hard-rock district contain a considerable tonnage of this material, which analyzes as high as 25 percent phosphoric acid. The waste ponds in the land-pebble district contain smaller percentages of finely divided phosphate than do the hard-rock waste ponds. In this publication the finely divided phosphate deposited in the hard-rock phosphate waste ponds will be referred to as waste-pond phosphate in order to distinguish it from the soft phosphate obtained directly from the original deposits. For the last several years, small tonnages of waste-pond phosphate have been recovered annually from abandoned waste ponds in the hard-rock district, principally near the town of Dunnellon, and sold for direct application to the soil.

According to Matson (*122*), river-pebble phosphate was first mined in 1888 on Peace River near Arcadia, De Soto County, and later along Peace River from Mulberry, Polk County, southward. Mining was also done near Fort Ogden and Hull, De Soto County, on

Alafia River, and in Clay County on Black Creek, a tributary of St. Johns River. River-pebble deposits have also been reported on Manatee, Miakka, Kissimmee, and Caloosahatchee Rivers and at the mouth of Fisheating Creek. No river-pebble phosphate has been mined since 1914.

GEORGIA

According to McCallie (*106*), deposits of phosphatic marl in Georgia are widely distributed in the counties lying along the Georgia-Florida State line. Deposits of phosphate rock have been discovered in Thomas County, near the towns of Boston and Thomasville, and, according to Day (*41*), in Glynn County at the headwaters of the Little Satilla River. Because of the limited quantity of phosphate and the high mining costs, the deposits were worked only at irregular intervals before 1900. Phosphatic nodules, of no economic importance, occur in Floyd and Chattooga Counties, embedded in the Chattanooga shale (*60*).

IDAHO

The Idaho deposits constitute one of the largest known reserves of high-grade phosphate rock in the world. The known deposits lie in the southeastern part of the State in Bear Lake, Bannock, Caribou, Bingham, Bonneville, Madison, Teton, Fremont, and Clark Counties (*51, 113, 114, 118, 119, 154, 155, 173, 175, 194*). Those thus far studied in detail are located in the Montpelier, Crow Creek, Freedom, Slug Creek, Lanes Creek, Henry, Crane's Flat, and Portneuf quadrangles, and in the Fort Hall Indian Reservation. In 1930, deposits were being worked near Conda, Caribou County, and Paris, Bear Lake County. Phosphate rock has also been mined near Montpelier, Bear Lake County.

ILLINOIS

Phosphate deposits in Illinois occur immediately above the Maquoketa shale in the southern portion of Calhoun County (*97, 205*). Although these deposits have not been investigated, it is quite probable that they are not commercially valuable at the present time.

KENTUCKY

Phosphate deposits are known to occur in Kentucky in the vicinities of Midway, Versailles, and Wallace, Woodford County; Lexington, Fayette County; Georgetown, Scott County; near the Forks of Elkhorn, Franklin County; and near Pine Grove Station, Clark County (*49, 139, 140, 196*). Deposits of phosphatic limestone occur directly below the phosphate rock horizon. The richest deposits of phosphate rock, which occur in the area around Wallace and Midway, were worked for several years prior to 1927.

MASSACHUSETTS

In Massachusetts, phosphate nodules of no commercial importance occur in the tertiary greensand beds exposed in the cliffs at Gay Head, Martha's Vineyard (*137, 178*). Small quantities of apatite are said to occur at Bolton, Worcester County (*206*).

MISSISSIPPI

Deposits of phosphatic marl in Mississippi occur in Tippah, Tishomingo, Pontotoc, Itawamba, Chickasaw, Monroe, Oktibbeha, Lowndes, Noxubee, Kemper, Hinds, and Lauderdale Counties (*41*), but none of these deposits is of commercial importance at present. Beds of phosphatic nodules, similar to those in Alabama, are said to occur in Mississippi.

MONTANA

The known Montana phosphate deposits (*35, 50, 113, 133, 134, 135, 156, 189*) occur in the vicinities of Philipsburg and Maxville, Granite County; Elliston and Garrison, Powell County; and Melrose, Silver Bow County. Deposits are also known in Deer Lodge, Beaverhead, Gallatin, Madison, and Lewis and Clark Counties. The most important deposits are located in the Elliston, Garrison, and Philipsburg districts. In 1930, mining operations were started near Garrison and Philipsburg. A small quantity of phosphate has also been mined from the Maxville deposits.

NEVADA

According to Stone (*188*), deposits of phosphate rock have been reported in Nevada. Specimens of low-grade rock have been found near Ely and Osceola, White Pine County, and near Ocala and Huxley, at the south end of Humboldt Lake, Churchill County.

NEW JERSEY

Small deposits of massive apatite are said to occur at Hurdtown, Sussex County, N.J. According to Wilber (*206*), these deposits were mined to a small extent prior to 1882.

NEW MEXICO

No phosphate-rock deposits have been discovered in New Mexico, but deposits of bat guano occur in the southern part of the State and shipments have been made from those near Lava, Socorro County (*142*).

NEW YORK

According to Wilber (*206*), a deposit of massive apatite occurs in New York at Crown Point, Essex County. This deposit was mined to a small extent prior to 1882. Apatite also occurs in St. Lawrence County. Unsuccessful attempts have been made to separate, on a commercial scale, the apatite that is associated with the magnetite in deposits at Mineville, Essex County (*140*).

NORTH CAROLINA

The phosphate-rock deposits of North Carolina (*27, 37, 38, 40, 113, 137, 141*) lie in a belt 15 to 20 miles wide, extending from the South Carolina line northeastward with the trend of the coast to the Neuse River, and with its southeastern boundary 20 to 25 miles from the coast line. The belt runs through the counties of Columbus, Bladen, Sampson, a corner of Pender, and through Duplin, and includes a small part of Lenoir, Jones, and Onslow Counties. Deposits of a conglomerate of phosphatic nodules and marl lie just below the phosphate-rock deposits and extend southward through Pender and New Hanover Counties nearly to the coast. The conglomerate deposits near Castle Hayne in New Hanover County, were worked for several years during the latter part of the nineteenth century. The scattered nature of the deposits and the high mining costs have prevented their extensive development. No phosphate rock has been mined in North Carolina since 1903.

OKLAHOMA

A small deposit of phosphate nodules has been discovered in Oklahoma in the extreme southeastern corner of Cotton County, just west of the Cotton-Jefferson County line (*179*, *180*). Also, Reeds (*148*) reports the occurrence of phosphatic nodules in the Woodford shale and chert of the Arbuckle Mountains.

PENNSYLVANIA

Deposits of low-grade phosphate rock have been found in Pennsylvania at various points within 12 miles of Reeds Gap, Juniata County (*83*). The entire mass of detritus occurring in these localities between the Oriskany sandstone and the Onondaga limestone has been phosphatized to an extent varying from 3 to 12 percent of phosphoric acid. Deposits of aluminum phosphate (wavellite) occur at the foot of South Mountain, in the vicinity of Mount Holly Springs, 20 miles southwest of Harrisburg (*190*). These deposits were worked about 1905, and the ore was used for the manufacture of elemental phosphorus.

SOUTH CAROLINA

Production of phosphate rock from the South Carolina deposits, which were the first to be discovered in the United States, began in 1867, and for more than 50 years important quantities of phosphate were mined annually from these deposits (*80*, *113*, *126*, *127*, *137*, *145*, *163*, *181*, *197*, *208*, *209*). The South Carolina phosphates are usually divided into two classes, land rock and river rock, the first being the most important. The land rock occurs in a more or less irregular bed which represents the undisturbed phosphatized Edisto marl. The river rock probably consists in part of the original phosphatized Edisto marl and in part of fragments derived from the land deposits and concentrated on the river bottoms. Phosphate deposits occur in Berkeley, Dorchester, Charleston, Colleton, and Beaufort Counties in a seaboard zone, most of which is less than 30 miles wide, extending from the Broad River, Beaufort County, northward to a point about 20 miles beyond Charleston. Production of river rock ceased in 1910 and that of land rock in 1925.

TENNESSEE

From the standpoint of production, the Tennessee phosphate deposits rank second in importance in the United States, being exceeded only by the Florida deposits. Three distinct commercial varieties of phosphate rock are recognized in Tennessee. These are known as the brown-rock, blue-rock, and white-rock phosphates. All the important deposits of these varieties are in the western part of the central basin of Tennessee and in the valleys of the western part of the highland rim surrounding the basin. Deposits of another variety, ranging in color from white to brownish black, are found in Johnson County (*90*). This rock is characterized by a relatively high content of manganese, but it usually contains less than 30 percent of phosphoric acid, and, at present, is not of commercial importance. Phosphatic limestones, usually containing less than 20 percent of phosphoric acid, are widely distributed in Tennessee, usually in close association with the phosphate-rock deposits.

The principal deposits of brown-rock phosphate, the most important of the Tennessee phosphates, occur in Sumner, Davidson, Williamson, Hickman, Maury, Lewis, and Giles Counties (*62a, 81, 113, 140, 186, 196*). In 1930, mines were being operated in the vicinity of Mountpleasant, Spring Hill, Columbia, Century, Ridley, and Southport, in Maury County; Nashville, Davidson County; Wales, Giles County; and Twomey, Hickman County.

Two types of blue-rock phosphate, formerly known as black phosphate, are recognized. These are the bedded phosphates and the nodular or kidney phosphates. The deposits of bedded phosphate are the most important, although kidney phosphate has been mined in certain localities, notably near Boma, Putnam County (*129*). Blue-rock deposits are known in the western part of Maury County; the eastern part of Lewis County; along Duck River and on both sides of Swan Creek in Hickman County; near Fernvale Springs in the western part of Williamson County; and in the southern and northern parts of Perry and Wayne Counties, respectively (*60, 61, 62a, 81, 140, 186, 196*).

White-rock phosphate occurs in several widely separated localities in Perry and Decatur Counties (*60, 61, 62, 62a, 82, 123, 196*). Mines have been operated at Tomscreek, Perry County, and along the tributaries of Beech River, between Parsons and Decaturville, Decatur County. Although many of the deposits contain high-grade phosphate, they occur mostly in pockets, and the high cost of mining has prevented extensive development. No production of white-rock phosphate has been reported since 1915.

At least two geological formations of phosphatic limestone are recognized in Tennessee, namely, the Leipers formation and the Bigby formation. The Leipers limestone has been a factor of considerable importance in the formation of blue-rock phosphate and in many places it directly underlies these phosphate deposits. Bigby phosphatic limestone is widely distributed in the brown-rock phosphate area, and is the source of much of the brown rock, though some of the latter is also derived from the Leipers limestone. Although no ecomonical method has been devised for the manufacture of fertilizers from phosphatic limestone, it is used to some extent in the preparation of mineral feeds for poultry and stock.

TEXAS

Phosphate rock deposits have not been discovered in Texas, but the investigations of Shead (*179, 180*) indicate that deposits may occur in the Permian red beds of the Wichita formation, in northern Texas, and Schoch (*170*) reports the occurrence of phosphatic rocks in Bexar and Brewster Counties. According to Phillips (*142*), there are deposits of bat guano in caves distributed along a line extending southwest from Lampasas County to Uvalde and Edwards Counties. Guano deposits have been found in Lampasas, Burnet, Llano, Mason, Williamson, Blanco, Gillespie, Hays, Comal, Kerr, Medina, Uvalde, and Edwards Counties. Some of these deposits have been worked at various times.

UTAH

Phosphate rock is widely distributed in northeastern Utah (*8, 51, 113, 174, 194*). Deposits are known in the Crawford Mountains, Laketown, and Woodruff areas of Rich County; and the Weber River Canyon, Sheepherd Valley, and Beaver Creek areas, near Ogden, Weber County. On the north side of the Uinta Mountain Range, deposits occur in the Weber-Bear River and Henrys Fork areas of Summit County. On the south side of the range, deposits occur in the Provo-Duchesne River area of Wasatch and Duchesne Counties, and the Whiterock River-Brush Creek area of Duchesne and Uintah Counties. Deposits also occur in Morgan County. Small quantities of phosphate rock have been mined in Utah, principally in Rich County, but no production has been reported since 1920.

VIRGINIA

Deposits of low-grade phosphate have been observed in two localities in southwestern Virginia (*191*), namely, at the foot of the southeast slope of Clinch Mountain, 5 miles west of Saltville, and in Walker Valley at the east end of Brushy Mountain, 5 miles west of Marion. Nelsonite, a name given to a group of high titanium-phosphorus-bearing ores, occurs in Amherst and Nelson Counties, and, to a less extent, on the northwest slope of the Blue Ridge in Roanoke County (*140, 191, 204*). The phosphorus is present in these ores in the form of coarsely crystalline apatite. A large deposit of ilmenite nelsonite, the normal and most abundant variety, occurs in Amherst County, near Piney River, and is being worked for the recovery of titanium compounds and apatite (*1*).

WYOMING

Phosphate rock is widely distributed in the western part of Wyoming (*9, 34, 51, 112, 113, 173, 194*). Deposits are known in the Wind River, Owl Creek, and Shoshone Mountains; the Hoback, Gros Ventre, Teton, and Salt River Ranges; the Sublette Ridge, Beckwith Hills, and Cokeville areas; and in Snake River Canyon. Since 1906 phosphate rock has been mined from some of the deposits, principally those near Cokeville, Lincoln County.

PRODUCTION OF PHOSPHATE ROCK IN THE UNITED STATES

Data on the marketed production of phosphate rock in the United States, as of December 31, 1930, are given in table 1. The figures include rock used by the producers.

TABLE I.—*Total marketed production and reserves of phosphate rock in the United States, as of December 31, 1930*

Source and type of phosphate	Marketed production, including rock used by producers	First and last years of commercial production	Estimated reserves[1]
Florida:	*Long tons*		*Long tons*
Land pebble	[2] 52,262,745	1891 [3]	[4] >269,000,000
River pebble	1,310,075	1888, 1914	(5)
Hard rock	[6] 12,175,066	1889 [3]	8,200,000
Soft rock	94,807	1890 [3]	(5)
Total	65,842,693		>277,200,000
South Carolina:			
Land rock	[7] 9,253,412	1867, 1925	8,798,000
River rock	4,105,205	1870, 1910	(5)
Total	13,358,617		>8,798,000
Tennessee:			
Brown rock	[8] 10,803,286	1896 [3]	[4] 10,000,000
Blue rock	[8] 1,279,650	1894 [3]	83,340,000
White rock	[8] 8,617	1898 [9], 1916	(5)
Total	15,282,432		>93,340,000
Western States:			
Idaho	474,584	1906 [3]	4,997,380,000
Montana	6,713	1921 [3]	391,316,000
Utah	18,047	1907, 1920	326,727,000
Wyoming	60,271	1907 [3]	115,694,000
Total	559,615		5,831,117,000
Alabama	844	1887 [9], 1900	(5)
Arkansas	31,753	1900, 1915	20,000,000
Kentucky	113,661	1911, 1926	863,000
North Carolina	56,585	1885 [9], 1903	(5)
Pennsylvania	3,993	1899, 1904	(5)
Other States	70		(5)
Grand total	95,250,263		>6,231,318,000

[1] Containing the equivalent of approximately 55 percent or more of tricalcium phosphate.
[2] Includes a small quantity of river-pebble and soft phosphate.
[3] Under production in 1930.
[4] This figure can be approximately doubled by the use of flotation, according to a private communication from James A. Barr, of the International Agricultural Corporation.
[5] Estimate not available.
[6] Includes a small quantity of soft phosphate.
[7] Includes a small quantity of river rock.
[8] This figure is low because separate data on the production of the different types of Tennessee phosphate are not available for the years prior to 1905.
[9] Approximate year of first production.

In the case of the Florida phosphates, the figures were compiled from the data given by Wright (*208*) for the years 1888 to 1891; from those given by Johnson (*91*) for the years 1900 to 1928; and from the various volumes of Mineral Resources of the United States for the other years. It should be pointed out that the figures for the different types of rock are only approximate owing to the fact that in some years they include small quantities of other types. For example, the figure for land-pebble phosphate includes a small quantity of river-pebble and soft phosphate, and the figure for hard rock includes a small quantity of soft phosphate.

The figures for South Carolina phosphate were compiled from data given by Johnson (*91*) and in Mineral Resources of the United States. An insignificant quantity of river rock is included with the land rock.

The figures for the Tennessee brown- and blue-rock phosphates were furnished by the United States Bureau of Mines.[3] Since separate

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[3] The authors are indebted to B. H. Stoddard and B. L. Johnson for the compilation of these and other data furnished by the Bureau of Mines.

data on the various types of Tennessee phosphate for the years prior to 1905 are not available, the figure for the total Tennessee production, which is compiled from Mineral Resources of the United States, is greater than the sum of the totals for the different types. The figure for white rock represents the production in 1905 to 1908, inclusive. The quantity of white rock mined prior to 1905 is not known, but with the exception of a small tonnage (amount unknown) in 1915, this type of phosphate has not been produced since 1908.

The figures for the western phosphates[3a] were compiled from data furnished by the Bureau of Mines and from those given in Mineral Resources of the United States. The figures for Arkansas and Kentucky were compiled from data given by Johnson (*91*) and in Mineral Resources of the United States, the last publication also furnishing the figures for Alabama and Pennsylvania.

With the exception of a production of 700 tons in 1892, as reported by Wright (*208*), the figure for North Carolina was compiled from data given in Mineral Resources of the United States. It should be pointed out, however, that the figure includes 40,400 tons of low-grade phosphatic conglomerate, of which 35,000 tons were sold for use in building streets and roads.

RESERVES OF PHOSPHATE ROCK IN THE UNITED STATES

Data relating to the estimated reserves of phosphate rock in the United States, as of December 31, 1930, are given in table 1. It is believed that these estimates are, as a general rule, very conservative, since they do not take into account the use of the flotation process for the recovery of marketable phosphate from low-grade materials which cannot be treated successfully by the ordinary methods of concentration.

In 1923, G. W. Holland, of the United States Geological Survey, investigated the reserves of Florida land-pebble phosphate and estimated that the field contained at that time more than 288,000,000 long tons of minable phosphate (*116, p. 250*). Approximately 19,000,000 long tons of land pebble were mined during 1924–30. Consequently, it is estimated that the reserves of this material amounted to more than 269,000,000 long tons, as of December 31, 1930. James A. Barr,[4] chief engineer of the International Agricultural Corporation, estimates that the reserves of land pebble have been further increased at least 100 percent by the development of the flotation process for the treatment of low-grade phosphate ores.

In arriving at the figure for reserves of Florida hard-rock phosphate, the estimate made by Phalen (*140*) in 1915 has been revised to allow for the rock mined since that time, the figure on mined production being supplied by the United States Bureau of Mines. Estimates on the reserves of river-pebble and soft phosphate are not available.

Based on an estimate made originally by Chazal (*29, p. 18*) in 1904, Mansfield (*117, p. 88*) estimated that the reserves of South Carolina land-rock phosphate amounted to 8,800,000 long tons as of December 31, 1924. Corrected for the amount of rock mined since that time, the figure becomes 8,798,000 long tons as of December 31, 1930. No estimate of the reserves of river rock is available.

[3a] The term "western phosphates", as used in this publication, refers to phosphate from Idaho, Montana, Utah, and Wyoming.

[4] Private communication.

In 1915, Phalen (*140*) estimated that the reserves of brown-rock phosphate remaining in middle Tennessee amounted to approximately 4,000,000 long tons. According to figures furnished by the United States Bureau of Mines, however, approximately 6,500,000 tons of brown rock were mined from this region in 1916–30. The estimate of reserves of brown rock was made by James A. Barr, who writes as follows:[5]

> The following figures were compiled from available prospecting data and adding thereto probable tonnages in other phosphate areas.
>
> It is generally conceded that the quantity of commercial grade phosphate outside of contiguous blocks now being exploited, is quite limited and found mostly in scattered areas too small to justify economical mining unless we consider the lately developed flotation process. This, we estimate, more than doubles the tonnages.
>
> Without flotation, the brown phosphate reserves will probably not exceed 10,000,000 tons, but with beneficiation we estimate a total from 20,000,000 to 24,000,000 tons.

The estimate of reserves of Tennessee blue-rock phosphate is that made by Phalen (*140*), from which has been deducted the mined production of rock as reported by the Bureau of Mines for the period 1916–30. An estimate of the reserves of white-rock phosphate is not available, and no figures have been compiled to show the quantity of phosphate occurring in Tennessee in the form of phosphatic limestone.

In 1927, Mansfield (*119, p. 292*) published revised estimates of the phosphate rock available in the Western States. These estimates, which do not take into consideration the rock mined in the individual States, have been changed to allow for the marketed production of rock from the beginning of commercial operations through the year 1930. The figures on marketed production, most of which were furnished by the Bureau of Mines, approximate very closely those on mined production.

The figure on reserves of Arkansas phosphate is that given by Waggaman (*198*) in 1914, no later estimate being available. The estimate of reserves of Kentucky phosphate given by Mansfield in 1922 (*115, p. 116*) has been revised to allow for the phosphate mined since that year. Estimates of the phosphate reserves in Alabama, North Carolina, and Pennsylvania are not available, but the reserves in these States are, no doubt, comparatively insignificant.

FLOTATION OF PHOSPHATE ROCK

The use of flotation methods for recovering marketable phosphate from low-grade ores has been mentioned in the preceding paragraphs, with special reference to its effect on the reserve supply of phosphate rock in the United States.

The results of experimental investigations in the United States Bureau of Mines (*102*) have shown that by means of flotation Florida land-pebble phosphate washer waste, containing approximately 4.5 percent phosphoric acid and 85 percent insoluble material, principally silica, can be concentrated to yield a product containing approximately 32 percent phosphoric acid and 6 percent insoluble material, 83 percent of the phosphoric acid being recovered in the concentrate. Charles E. Heinrichs, of the Phosphate Recovery Corporation, states[5]

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[5] Private communication.

that in a typical 30-day period of commercial operation of the flotation process, concentrates averaging approximately 35.5 percent phosphoric acid and 6.5 percent insoluble material were produced from Florida land-pebble washer waste containing approximately 7.5 percent phosphoric acid.

Although flotation in the phosphate industry has thus far been used principally in the recovery of phosphate from high-silica Florida land-pebble washer waste, a commercial unit for treating Tennessee brown-rock phosphate has recently been erected. The concentration of this type of phosphate involves the removal of iron and aluminum compounds, as well as silica. Data furnished by Heinrichs (table 2) indicate the extent to which a commercial grade of Tennessee brown-rock phosphate sand can be improved by flotation. It will be noted that the treatment has resulted in the removal of a very considerable portion of the iron, aluminum, and silica but has had no significant effect on the carbon dioxide and fluorine. It is said, however, that carbonate not combined with the phosphate molecule can be removed by flotation. Attempts to remove fluorine have not been successful, since this element is present, as a general rule, only in combination with the phosphate molecule.

TABLE 2.—*Effect of flotation on the composition of Tennessee brown-rock phosphate sand*

Item	P_2O_5	Fe_2O_3	Al_2O_3	CO_2	F	SiO_2
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Composition before flotation [1]	32.32	3.34	2.20	1.30	3.15	10.21
Composition after flotation [1]	35.82	2.28	.84	1.42	3.47	4.56

[1] Data furnished by Charles E. Heinrichs, of the Phosphate Recovery Corporation.

The flotation process seems destined to play an important part in conserving the supplies of Florida land-pebble and Tennessee brown-rock phosphates. When the occasion arises, the process can, no doubt, be applied also to all other types of domestic phosphate rock.

DESCRIPTION OF SAMPLES

More or less complete analyses of 46 samples of mineral phosphate were made. The samples represented nearly all of the more important types and sources of this material in the United States. Similar analyses of samples of bone ash, chlorapatite, fluorapatite, and foreign phosphate rocks were made. Brief descriptions of these samples are given in the following paragraphs. Partial analyses of a large number of additional samples from deposits in the United States and foreign countries were made.

Florida land-pebble phosphate.—All samples of land-pebble phosphate were taken from materials that had been subjected to the washing and screening processes (*199*) customarily used in preparing this type of phosphate for the market. Unless stated otherwise, the samples were taken from commercial, kiln-dried materials.

Samples 439, 910, and 912. Deposits near Mulberry, Polk County. Sample 439 was representative of a shipment of 2,218 tons. Samples 910 and 912 were taken from 100-pound quantities of air-dried material.

Samples 617 and 947. Deposits near Brewster, Polk County. These samples represented shipments of 4,700 tons and 150 pounds, respectively.

Sample 618. Deposit near Pierce, Polk County. Representative of a large shipment.

Samples 619 and 622. Deposits near Nichols, Polk County. Representative of large shipments.

Samples 627 and 898. Deposits near Lakeland, Polk County. Representative of large shipments.

Sample 790. The location of the deposit from which this sample came is unknown, but it was in either Polk County or Hillsborough County. The sample was taken from about 25 tons of material.

Florida hard-rock phosphate.—Unless stated otherwise, the samples of hard-rock phosphate were taken from washed, screened, and kiln-dried materials.

Sample 434. Deposits near Dunnellon, Marion County. This sample was a composite of several samples representing large shipments.

Sample 589. Deposit near Floral City, Citrus County. Representative of a 3,500-ton shipment.

Sample 771. The location of the deposit from which this sample came is unknown. Nor is it known whether the sample was taken from commercial, washed and screened material, or from unwashed material.

Sample 932. Deposit near Dunnellon, Marion County. Representative of a 200-pound quantity of air-dried material.

Florida soft phosphate.—The term soft phosphate is used to designate the claylike phosphate obtained directly from the original deposits (p. 5). Unless stated otherwise, the samples were taken from noncommercial air-dried materials.

Sample 443. Deposit in Gilchrist County, about 7 miles west of Fort White and 3 miles south of the Santa Fe River.

Sample 580. Deposit in the hard-rock phosphate district. The location of the deposit is not known.

Sample 728. Deposit near Juliette, Marion County.

Sample 1091. Deposit near Bartow, Polk County. Representative of a 100-pound quantity of commercial kiln-dried material, which had not been subjected to washing and screening operations. Soft phosphate has been produced from this deposit on a commercial scale for several years.

Florida waste-pond phosphate.—The term waste-pond phosphate is used to designate the very finely divided claylike phosphatic material obtained from the waste ponds of hard-rock phosphate-washing plants (p. 5). Unless stated otherwise, the samples were taken from air-dried materials.

Sample 726. Abandoned waste pond near Felicia, Citrus County.

Sample 727. Abandoned waste pond near Dunnellon, Marion County. This sample and no. 726 came from waste ponds from which comparatively small quantities of material have been marketed in recent years.

Sample 915. Abandoned waste pond near Dunnellon. Representative of a 100-pound quantity of commercial kiln-dried material.

Tennessee brown-rock phosphate.—Unless stated otherwise, the samples of brown-rock phosphate were taken from commercial, washed and kiln-dried materials.

Sample 56. Location of deposit unknown. This material is Bureau of Standards standard sample no. 56, which is widely used as a reference standard in the determination of calcium, phosphorus, aluminum, and iron in phosphate rock.

Samples 564, 587, and 906. Deposits near Wales, Giles County. The material from which no. 587 was taken is known as "cone sand", one of the finer sizes of rock obtained during the washing process. No. 906 was taken from a 100-pound quantity of air-dried material.

Samples 762 and 908. Deposits near Mountpleasant, Maury County. No. 908 was taken from a 100-pound quantity of air-dried material.

Tennessee blue-rock phosphate.—Unless stated otherwise, the samples of blue rock used in this investigation came from deposits of the bedded variety of phosphate (p. 9).

Samples 448 and 772. Deposit at Glover, Lewis County. Commercial air-dried materials.

Samples 449 and 930. Deposit near Gordonsburg, Lewis County. No. 449 was taken from commercial kiln-dried material. No. 930 was representative of a 200-pound quantity of air-dried material.

Sample 1049. Air-dried kidney phosphate from a deposit near Boma, Putnam County. Kidney phosphate was formerly mined in this locality.

Tennessee white-rock phosphate.—The two samples of air-dried materials used in this investigation came from deposits which were formerly worked.

Sample 1031. Deposit near Godwin, Maury County.

Sample 1048. Deposit near Tomscreek, Perry County.

Tennessee phosphatic limestone.—Sample 916. Bigby phosphatic limestone from a brown-rock phosphate mine near Mountpleasant, Maury County. Representative of a 100-pound quantity of air-dried material.

Sample 917. Leipers phosphatic limestone from a blue-rock phosphate mine near Gordonsburg, Lewis County. Representative of a 100-pound quantity of air-dried material.

South Carolina land-rock phosphate.—The samples were representative of the commercial material formerly produced from the deposits.

Sample 1138. Lamb's Mine, about 15 miles from Charleston.

Sample 1139. Bulow Mines, Johns Island, Charleston County. Representative of a 150-pound quantity of material.

Idaho, Montana, and Wyoming phosphates.—Samples 454 and 973. Deposit at Conda, Caribou County, Idaho. Commercial kiln-dried materials.

Sample 550. Commercial material from a deposit near Paris, Bear Lake County, Idaho.

Samples 1009, 1010, and 1011. Prospect samples from a deposit near Garrison, Powell County, Mont.

Sample 948. Deposit near Cokeville, Lincoln County, Wyo. Representative of a 200-pound quantity of commercial air-dried material.

Morocco phosphate.—Sample 1162. Commercial material from either the Boujniba or the Kourigha deposits, probably the latter.

Tunisian phosphate.—Sample 552. Commercial material from the Gafsa deposits.

Christmas Island phosphate.—Sample 452. Commercial material from Christmas Island in the Malay Archipelago.

Connetable Islands phosphate.—Sample 904 was taken from a quantity of material which had lain for many years in the factory yard of a chemical company in New Jersey. The material, which consists principally of hydrated aluminum phosphate, was formerly used in the manufacture of sodium phosphate by alkali treatment processes. The two small Connetable Islands are 13 miles off the coast of French Guiana in approximately latitude 4°54′ north and longitude 51°57′ west.

Curacao Island phosphate.—Sample 943 was taken from a few selected lumps of commercial material, whereas no. 985 was taken from a 200-pound quantity representative of a large commercial shipment from Curacao Island in the Dutch West Indies.

Nauru Island phosphate.—Sample 450. Commercial material from Nauru Island, in the Pacific Ocean in longitude 165°55′ east, 26 miles south of the Equator and about 2,200 miles north by east from Sydney, Australia.

Ocean Island phosphate.—Sample 451. Commercial material from Ocean Island, in the Pacific Ocean 165 miles east of Nauru Island and 52 miles south of the Equator. Geographically, Ocean Island belongs to no particular group of islands, but is assigned to the Gilbert group for administrative purposes.

Fluorapatite.—Sample 905. Selected material from a deposit in Quebec Province, Canada.

Chlorapatite.—Sample 634. Deposit at Kragerö, Norway.

Bone ash.—Sample 971. High-grade commercial material.

METHODS OF CHEMICAL ANALYSIS

Methods for the complete chemical analysis of phosphate rock have not been compiled into a single publication. The methods used in this investigation were selected from the literature, so far as they were available and were known to give accurate results. Published methods for the determination of certain elements in other substances were so modified as to make them applicable to phosphate rock. Since an extended discussion of analytical methods would be out of place here, only such information as is necessary to identify the methods used is given in the following paragraphs.

TOTAL PHOSPHORIC ACID

The sample was brought into solution by the method recommended by Lundell and Hoffman (*104*), and the phosphoric acid was determined by the gravimetric method of the Association of Official Agricultural Chemists (*6, p. 14*). As was recommended by Lundell and Hoffman (*104*), the yellow precipitate of ammonium phosphomolybdate was dissolved in a solution of ammonium hydroxide and ammonium citrate, and the filter paper was washed finally with dilute hydrochloric acid in order to dissolve any iron phosphate that may have been precipitated along with the ammonium phosphomolybdate.

TOTAL CALCIUM, IRON, AND ALUMINUM

The sample was brought into solution by the method recommended by Lundell and Hoffman (*104*). In determining the calcium it was first precipitated as the sulphate in the presence of alcohol, in order to effect its separation from magnesium, and after reprecipitation as the oxalate it was weighed as the oxide. Total aluminum was determined by the routine method of Lundell and Hoffman (*104*), and the results were corrected for the presence of titanium, chromium, and, when necessary, vanadium. Total iron was determined by reducing with stannous chloride and titrating with potassium dichromate, according to the method of Knop (*94*).

MAGNESIUM, MANGANESE, TITANIUM, SODIUM, POTASSIUM, CHROMIUM, VANADIUM, COPPER, ZINC, AND ARSENIC

These elements were determined by the methods briefly outlined by Hill, Marshall, and Jacob (*73*).

SILICA

Total silica was determined by the Berzelius method as modified by Hoffman and Lundell (*77, p. 805; 79*). Hill and Jacob (*69*) have shown that this method is applicable to the determination of silica in phosphate rock, whereas the method of digestion with hydrochloric acid, ordinarily used in rock analysis, gives low results because of the presence of fluorine in phosphate rock. The ordinary method for determining silica (*69*) was used on the samples of mechanical fractions separated from finely divided phosphates.

CARBON DIOXIDE

Carbon dioxide was determined by the acid evolution method, using Knorr's apparatus.

FLUORINE

Unless stated otherwise, the fluorine determinations were made by the volatilization method outlined by Wagner and Ross (*201*) and modified by Reynolds, Ross, and Jacob (*77, p. 600; 153*). This method accounts for an average of about 93.5 percent of the fluorine present in phosphate rock. The results so obtained have, therefore, been calculated to 100 percent recovery of the fluorine on the basis of an actual recovery of 93.5 percent. The method gives, however, very low and erratic results on materials, such as the Florida waste-pond phosphates, which contain appreciable quantities of silicates decomposable by sulphuric acid (*151*). Fluorine in these materials was determined by the method of Hoffman and Lundell (*79*) as modified by Reynolds and Jacob (*150*). This modification of the Hoffman-Lundell method will hereinafter be referred to as the fusion-acid extraction method.

CHLORINE, IODINE, AND BROMINE

Chlorine was determined gravimetrically according to Hillebrand's method for silicate rocks (*76, p. 220*). Iodine was determined by the furnace method as outlined by McHargue (*109*) and applied by Hill and Jacob (*70*) to the analysis of phosphate rock. Several samples were tested for bromine by treating the aqueous layer from the iodine determination with saturated chlorine water, extracting the liberated bromine with carbon tetrachloride, and determining it colorimetrically by comparison with a standard solution.

SULPHUR, ORGANIC MATTER, WATER, AND IGNITION LOSS

The methods used for these determinations have been outlined by Hill, Marshall, and Jacob (*74*).

RESULTS OF CHEMICAL ANALYSES

The principal data obtained on the samples described on pages 14 to 17 are given in tables 3 to 6. Data on the composition of phosphates from certain domestic deposits not included in the present investigation are summarized in table 7.

TABLE 3.—*Chemical composition of Florida phosphates*

LAND-PEBBLE PHOSPHATE

Sample no.	Location of deposit	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3 [1]	TiO_2	Na_2O	K_2O	MnO	Cr_2O_3	V_2O_3	SiO_2 [2]	CO_2	F [3]	Cl	SO_3 [4]	Total water, organic carbon, and nitrogen [5]	Total	
																			Uncorrected	Corrected [6]
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
618	Pierce	30.53	46.16	0.53	0.89	1.51	0.01	0.46	0.18	0.020	0.000	0.00	9.80	3.69	3.92	0.01	1.34	[7] 2.41	101.49	99.84
617	Brewster	30.70	46.48	.33	.71	2.14	.05	.62	.20	.020	.000	.00	8.52	2.10	4.01	.01	1.32	[7] 4.25	101.46	99.77
619	Nichols	30.98	47.27	.10	.71	1.63	.04	.53	.18	.020	.010	.01	8.11	4.38	3.98	.01	1.13	2.62	101.71	100.03
910	Mulberry	31.09	46.57	.25	1.11	2.59	.072	.57	.14	.042	.013	.02	7.28	3.76	3.94	.01	.98	2.91	101.35	99.69
947	Brewster	31.28	47.20	.20	.97	1.69	.064	.59	.19	.012	.009	<.01	7.59	3.70	4.04	.01	1.14	2.70	101.48	99.78
790	Not known	31.40	47.37	.14	.90	1.62	.06	.41	.45	.025	.012	.01	8.92	3.63	3.97	.03	1.19	[7] 1.12	101.35	99.68
430	Mulberry	33.22	47.68	.21	1.01	1.90	.05	.42	.15	.050	.013	.01	7.66	2.63	3.87	.02	[8] .67	2.13	101.69	100.06
622	Nichols	33.56	48.25	.17	.99	.86	.03	.58	.18	.002	.011	.01	8.30	2.67	3.96	(9)	[8] .84	[7] 1.75	102.35	100.68
627	Lakeland	33.70	47.07	.12	.81	1.56	.03	.60	.25	.005	.000	.00	7.51	1.84	3.90	(9)	.86	[7] 2.22	101.37	99.73
912	Mulberry	35.37	49.05	.08	1.05	.70	.060	.15	.11	.017	.009	.01	7.48	1.48	3.95	.003	.20	1.74	101.46	99.80
898	Lakeland	35.55	49.77	.01	.87	.68	.03	.07	.09	.005	.000	.00	7.38	1.74	3.95	(9)	[8] .42	[7] 1.28	101.88	100.22
	HARD-ROCK PHOSPHATE																			
771	Not known	31.25	42.52	0.21	2.61	1.83	0.06	0.09	0.06	0.020	0.010	0.01	12.95	2.41	3.35	<.005	[8] 0.16	3.94	101.48	100.07
589	Floral City	34.68	49.10	.05	1.38	1.20	.01	.41	.33	.034	.009	.02	6.39	1.82	3.79	.00	[8] .14	[7] 1.46	100.91	99.31
434	Dunnellon	35.33	50.19	.03	1.19	.88	.03	.42	.26	.036	.009	.02	4.32	2.78	3.76	.00	[8] .12	[7] 1.32	100.70	99.12
932	do.	35.09	51.08	.05	.52	.60	.039	.10	.06	.014	.004	.01	5.01	2.19	3.91	.008	.01	1.67	101.36	99.71
	SOFT PHOSPHATE																			
1091	Bartow	25.47	30.89	0.34	10.49	3.26	0.17	0.00	0.21	Trace	0.038	0.02	21.46	1.24	[10] 2.23	(9)	0.00	[7] 5.22	101.04	100.10
580	Not known	29.40	16.67	.08	23.05	3.28	.19	.67	.13	.020	.040	.005	13.60	.37	1.23	.12	.00	[7] 11.83	100.75	100.23
728	Juliette	31.80	41.61	.22	5.82	1.54	.11	.26	.14	.014	.018	.00	10.67	1.87	3.33	Trace	[8] .17	4.03	101.60	100.20
443	Gilchrist County	34.04	48.40	.00	2.08	.80	.05	.17	.05	.032	.012	.00	5.23	2.69	3.79	.02	.00	[7] 3.05	101.40	99.86
	WASTE-POND PHOSPHATE																			
727	Dunnellon	21.63	28.70	0.84	13.73	2.57	0.22	0.00	0.53	0.020	0.030	0.01	23.27	1.00	[10] 1.91	(9)	0.00	[7] 5.80	100.35	99.53
726	Felicia	23.48	30.89	.55	11.49	3.01	.36	.20	.47	.022	.028	.02	19.78	1.70	[10] 2.08	.005	[8] .14	6.05	101.18	100.30
915	Dunnellon	23.03	25.20	.21	16.67	4.25	.36	.40	.36	.013	.038	.01	16.80	1.26	[10] 1.84	.01	.00	8.69	99.74	98.97

[1] Total Fe.

[2] Total Si.

[3] Determined by the volatilization method (*153*), except as stated otherwise.

[4] Total sulphates, except as stated otherwise.

[5] Including water derived from combustion of organic matter but exclusive of water driven off at 105° C.

[6] Corrected for O equivalent of F and Cl.

[7] Ignition loss, constant weight at 1000° C., corrected for total CO_2.

[8] Total S.

[9] Not determined.

[10] Determined by the fusion-acid extraction method (*150*).

TABLE 4.—*Chemical composition of Tennessee phosphates*

Sample no.	Location of deposit	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	Na_2O	K_2O	MnO	Cr_2O_3	V_2O_3	SiO_2[2]	CO_2	F	Cl	SO_3[3]	S[4]	Total water, organic carbon, and nitrogen[5]	Total	
																				Uncorrected	Corrected[6]
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
BROWN-ROCK PHOSPHATE																					
587	Wales	30.17	41.87	0.16	2.72	3.43	0.16	0.27	0.64	0.23	0.003	0.00	14.38	1.05	3.24	0.01	[7] 0.63	(8)	[9] 1.75	100.71	99.35
[10] 56	Not known	31.28	44.85	.31	3.06	3.30	.08	.32	.62	.21	.007	.00	8.58	1.91	3.56	.07	1.21	0.48	1.93	101.87	100.17
564	Wales	32.85	45.31	.15	2.22	3.34	.08	.28	.42	.20	.005	.00	8.12	1.11	3.62	.01	[7] .77	(8)	[9] 3.05	102.13	100.61
762	Mountpleasant	33.73	47.02	.06	1.78	2.25	.05	.14	.31	.27	.007	.00	7.40	1.71	3.87	.005	.75	.00	1.70	101.74	100.11
906	Wales	34.39	47.61	.10	1.17	3.42	.05	.22	.37	.060	.005	.00	7.11	1.31	3.77	.01	.61	.09	1.39	101.60	100.01
908	Mountpleasant	34.44	49.19	.02	1.16	2.52	.07	.19	.26	.13	.006	.00	5.92	1.96	3.81	.01	.70	.00	1.42	101.81	100.21
BLUE-ROCK PHOSPHATE																					
772	Glover	30.45	44.51	0.30	0.72	3.54	0.05	0.16	0.30	0.020	0.006	0.00	9.06	2.00	3.49	0.007	4.08	1.09	2.23	102.01	100.13
930	Gordonsburg	30.97	45.38	.36	1.22	3.42	.089	.37	.43	.015	.005	<.005	9.13	2.59	3.80	.01	1.27	2.09	1.28	102.43	100.05
[11] 1049	Boma	31.22	43.51	.07	1.19	1.70	.081	.22	.55	<.003	.005	<.005	12.36	.91	3.09	.01	2.00	.81	4.14	101.96	100.30
448	Glover	32.03	46.33	.12	.61	3.30	.05	.13	.04	.025	.005	.005	7.68	1.48	3.67	.01	2.45	.55	[9] 3.60	102.09	100.34
449	Gordonsburg	33.65	48.71	.11	.99	2.35	.06	.21	.06	.024	.007	.007	4.80	2.09	3.95	.02	1.06	1.28	[9] 3.57	103.04	100.90
WHITE-ROCK PHOSPHATE																					
1048	Tomscreek	30.20	42.90	0.06	1.39	1.75	0.075	0.13	0.42	<0.003	<0.005	<0.005	16.82	2.36	3.06	Trace	[7] 0.02	(8)	1.66	100.85	99.56
1031	Godwin	35.80	50.79	.06	1.45	.92	.054	.20	.18	.045	<.005	.01	1.91	3.05	3.30	0.01	[7] .35	(8)	2.82	101.45	99.85
PHOSPHATIC LIMESTONE																					
[12] 916	Mountpleasant	11.22	52.08	0.55	0.39	1.27	0.043	0.28	0.18	0.25	<0.005	<0.005	2.43	28.22	1.12	0.01	1.55	0.30	[9] 0.65	100.64	100.02
[13] 917	Gordonsburg	11.68	49.80	.42	.27	1.05	.038	.28	.21	.10	<.005	<.005	5.53	25.57	1.05	.01	2.27	1.01	[9] .21	100.50	99.68

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[1] Total Fe.

[2] Total Si.

[3] Total sulphates, except as stated otherwise.

[4] Acid-insoluble sulphide; considered as pyrite, FeS_2.

[5] Including water derived from combustion of organic matter, but exclusive of water driven off at 105° C.

[6] Corrected for O equivalent of F, Cl, and pyritic S.

[7] Total sulphur.

[8] Not determined.

[9] Ignition loss, constant weight at 1000° C., corrected for total CO_2 and for oxidation of pyritic sulphur, when present.

[10] Bureau of Standards standard sample no. 56.

[11] Kidney phosphate; other blue-rock samples are bedded phosphates.

[12] Bigby formation.

[13] Leipers formation.

TABLE 5.—*Chemical composition of South Carolina and western phosphates*

Sample no.	Location of deposit	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	Na_2O	K_2O	MnO	Cr_2O_3	V_2O_5	SiO_2[2]	CO_2	F	Cl	SO_3[3]	S[4]	Total water, organic carbon, and nitrogen[5]	Total: Uncorrected	Total: Corrected[6]
	SOUTH CAROLINA LAND-ROCK PHOSPHATE																				
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1139	Bulow mines, Johns Island, S.C.	26.92	43.19	0.28	0.99	1.56	0.08	1.19	0.23	0.090	0.028	0.00	13.30	5.06	3.58	0.02	1.74	0.19	[7] 3.77	102.22	100.65
1138	Lamb's mine, near Charleston, S.C.	27.85	44.88	.33	1.06	1.49	.07	.97	.27	.030	.028	.00	10.04	5.11	3.77	.02	1.97	.18	3.87	101.97	100.32
	IDAHO PHOSPHATE																				
550	Paris, Idaho	32.21	45.27	0.17	1.90	0.97	0.09	0.64	0.46	0.005	0.13	0.15	10.36	1.77	3.43	0.03	1.43	0.00	[7] 1.88	100.90	99.46
454	Conda, Idaho	32.24	45.96	.22	.96	.80	.07	.78	.40	.002	.13	.35	7.50	1.80	3.40	.03	1.36	.00	4.34	100.64	99.21
973	do	32.53	45.99	.31	1.16	.87	.06	.65	.45	.002	.13	.40	8.15	1.72	3.33	.03	1.74	.00	4.35	101.87	100.47
	MONTANA PHOSPHATE																				
1011	Garrison, Mont.	27.63	44.65	0.00	0.96	2.16	(8)	0.16	0.22	(8)	(8)	(8)	17.30	0.75	6.98	0.01	0.13	(8)	[7] 1.40	102.38	99.44
1009	do	31.39	43.74	.22	1.91	2.11	0.07	.28	.58	0.042	0.07	0.05	15.29	1.00	3.19	.01	.14	0.01	1.25	101.35	100.01
1010	do	37.47	52.02	.03	.54	.56	.04	.40	.26	.028	.05	.04	4.90	1.18	3.83	.01	.28	.01	.70	102.35	100.74
	WYOMING PHOSPHATE																				
948	Cokeville, Wyo.	30.19	46.22	0.08	1.19	0.87	0.10	0.64	0.35	0.004	0.12	0.12	7.19	4.13	3.54	0.03	1.35	0.52	4.30	100.94	99.25

[1] Total Fe.

[2] Total Si.

[3] Total sulphates.

[4] Acid-insoluble sulphide.

[5] Including water derived from combustion of organic matter, but exclusive of water driven off at 105° C.

[6] Corrected for O equivalent of F, Cl, and pyritic S.

[7] Ignition loss, constant weight at 1000° C., corrected for total CO_2 and for oxidation of pyritic sulphur, when present.

[8] Not determined.

TABLE 6.—*Chemical composition of foreign phosphate rocks, apatites, and bone ash*

Sample no.	Type or source of phosphate	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	Na_2O	K_2O	MnO	Cr_2O_3	V_2O_3	SiO_2[2]	CO_2	F	Cl	SO_3[3]	Total water, organic carbon, and nitrogen[4]	Total	
																			Uncorrected	Corrected[5]
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1162	Morocco	35.11	53.00	0.16	0.45	0.12	0.025	1.19	0.16	0.0025	0.045	0.00	0.86	4.12	4.24	<0.005	1.40	1.63	102.52	100.74
552	Tunis: Gafsa	27.55	45.93	.45	1.44	.65	.050	1.25	.44	.003	.042	.00	7.76	5.96	3.46	<.005	2.94	3.96	101.89	100.43
452	Christmas Island	39.46	52.50	.10	[6] .80	-------	(7)	.53	.05	(7)	(7)	(7)	.60	2.28	1.32	.02	.00	[8] 2.05	99.71	99.15
943	Curacao Island	40.66	49.50	1.70	[6] .45	-------	(7)	1.23	.04	(7)	(7)	(7)	.50	2.73	.38	.14	.72	[8] 2.46	100.51	100.32
985	do	38.59	49.96	1.23	.40	.61	.024	.88	.09	<.003	<.005	.01	.39	3.90	.70	.16	.61	2.47	100.03	99.70
450	Nauru Island	38.92	54.42	.00	[6] .30	-------	(7)	.45	Trace	(7)	(7)	(7)	.20	2.04	2.62	.01	.00	[9] 2.78	101.74	100.64
451	Ocean Island	40.32	54.08	.00	[6] .20	-------	(7)	.49	Trace	(7)	(7)	(7)	.40	1.06	2.97	.01	.00	[9] 1.88	101.41	100.16
905	Fluorapatite	40.30	52.40	.46	[6] .60	-------	(7)	.00	.00	(7)	(7)	(7)	3.08	1.51	3.26	.16	.00	[9] .44	102.21	100.80
634	Chlorapatite	40.50	52.97	.29	.98	.18	(7)	.22	.10	(7)	(7)	(7)	1.16	.00	.17	4.13	.00	[9] .48	101.18	100.18
971	Bone ash	40.36	54.04	1.07	.00	.24	.015	.96	.09	<.003	<.005	<.005	.45	.70	.054	.03	.40	[10] .63	99.05	99.02
904	Connetable Islands	54.51	.60	.31	30.92	4.43	.16	.07	.06	<.003	.017	.005	1.82	.00	.06	Trace	.10	[11] 2.01	100.48	100.45

[1] Total Fe.
[2] Total Si.
[3] Sulphates only.
[4] Including water derived from combustion of organic matter, but exclusive of water driven off at 105° C.
[5] Corrected for O equivalent of F and Cl.
[6] Al_2O_3 plus Fe_2O_3.
[7] Not determined.
[8] Ignition loss, constant weight at 1100° C., corrected for total CO_2 from carbonate.
[9] Ignition loss, constant weight at 1000° C., corrected for total CO_2 from carbonate.
[10] This sample gave an ignition loss, corrected for total CO_2 from carbonates, of 1.50 percent when heated to constant weight at 1250° C. in a tube furnace in a current of air dried by sulphuric acid.
[11] This sample lost 22.58 percent of water of hydration when heated to constant weight at 105° C.

TABLE 7.—*Chemical composition of phosphates from domestic deposits not included in the present investigation*

Source and type of phosphate	Literature reference	Samples analyzed	Average composition												
			P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SiO_2	CO_2	F	SO_3	Insoluble material	Other constituents
		Number	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Alabama; phosphatic nodules and shell casts from Dallas, Greene, Hale, and Perry Counties	(*192*)	10	19.40	34.99	----	----	----	----	----	----	----	----	----	22.28	----
Alabama; phosphate rock from Elk River Valley, Limestone County	(*165*)	27	26.83	----	----	----	----	----	----	----	----	----	----	----	----
Arkansas; samples from deposits in the northern part of the State	(*12*)	85	26.62	----	----	[1] 8.59	----	----	----	----	----	----	----	----	----
Florida; river pebble from Peace and Caloosahatchee Rivers	(*44*)	2	28.41	44.22	0.61	1.69	0.94	----	----	----	5.13	2.46	----	9.12	----
Florida; mine-run land pebble from Fort Meade, Polk County	(*200*)	1	15.38	22.79	----	[1] 7.50	----	----	----	45.09	1.53	1.58	----	----	----
Florida; mine-run hard rock from Newberry, Alachua County	(*200*)	1	30.69	42.07	----	[1] 5.03	----	----	----	14.37	2.22	3.68	----	----	----
Georgia; lumps, nodules, and pebbles from Decatur, Echols, Glynn, and Thomas Counties	(*106*)	7	32.08	46.97	----	[1] 2.62	----	----	----	----	----	----	----	7.42	----
Kentucky; samples from Clark, Fayette, Franklin, Harrison, Scott, and Woodford Counties	(*49*)	40	29.16	----	----	[1] 5.93	----	----	----	----	----	----	----	----	----
Montana; Melrose, Silver Bow County	(*50*)	2	34.94	51.27	----	1.50	.46	----	----	----	----	----	----	4.06	----
North Carolina; samples from Duplin, Onslow, and Sampson Counties	(*87*)	40	19.00	----	----	----	----	----	----	----	1.82	----	----	43.17	----
Oklahoma; nodules from Cotton County	(*179, 180*)	1	24.00	39.76	Tr.	5.11	3.23	0.43	0.72	16.83	3.07	4.31	Tr.	----	MnO-0.176 TiO_2-.35
Pennsylvania; white and blue rocks and red nodules from Juniata County	(*89*)	----	13.7-24.7	----	----	[1] 5.0-18.0	----	----	----	----	----	----	----	30.0-50.0	----
South Carolina; samples of river rock	(*163*)	8	25.15	----	----	----	----	----	----	----	3.50	----	----	15.87	----
Tennessee; samples from various localities in Johnson County	(*60*)	6	23.87	32.56	1.09	6.71	2.68	[2] 2.40	----	19.20	2.19	1.20	0.23	----	MnO-3.89
Utah; Dunnellon claim, Crawford Mountains	(*119, p. 210*)	1	36.35	50.97	.22	.50	.26	2.00	.47	.30	1.72	.40	2.98	1.82	----
Utah; Elsinore claim, Tunnel Hollow, Morgan County	(*119, p. 210*)	1	32.05	46.80	.26	.90	.33	2.08	.58	----	2.14	.66	2.34	9.40	----
Utah; Woodruff Creek, Rich County	(*92*)	1	32.44	43.02	.83	[1] 1.52	----	----	----	----	.85	1.36	[3] 2.24	----	----
Virginia; phosphate pebbles from Clifton Forge, Alleghany County	(*202, p. 302*)	1	27.62	30.86	.27	1.04	1.21	----	----	----	----	----	----	25.26	----
Virginia; ilmenite nelsonite from Nelson County	(*204, p. 109*)	4	10.01	12.44	.71	----	[4] 8.43	----	----	[5] .97	Tr.	.60	(6)	----	MnO-0.21 TiO_2-39.74
Virginia; rutile nelsonite from Nelson County	(*204, p. 120*)	2	8.78	11.65	.20	----	[7] 3.26	----	----	.81	Tr.	.52	(5)	----	[9] MnO-0.26 TiO_2-67.70
Virginia; apatite separated from ilmenite nelsonite	(*204, p. 108*)	1	41.30	54.37	.53	----	.61	----	----	----	----	[8] 2.50	----	.33	Cl-0.10 TiO_2-0.20
Wyoming; Wind River Mountains near Lander, Fremont County	(*84*)	9	21.45	37.91	----	[1] 1.94	----	----	----	----	----	----	----	----	----

[1] Al_2O_3 plus Fe_2O_3.

[2] Na_2O plus K_2O. 3 samples contained an average of 0.45 percent Na_2O and 1.86 percent K_2O.

[3] Also contained 0.92 percent S as FeS_2.

[4] Also contained 26.79 percent FeO.

[5] 3 samples.

[6] 2 samples contained an average of 1.31 percent total S.

[7] Also contained 6.5 percent FeO.

[8] Contained 0.98 percent total S.

[9] 1 sample.

All figures given in the principal tables of results and nearly all of those in the other tables are the average of duplicate determinations. Unless stated otherwise, all results have been calculated to the moisture-free basis (105° C.). In these tables, the omission of a significant figure indicates that a positive test for the element was not obtained, whereas a faintly positive test is indicated by the inequality sign (<).

PHOSPHORIC ACID

The results of analyses for phosphoric acid (P_2O_5) in the present commercial grades and types of domestic phosphate rock (tables 3–5) range from approximately 30 to 37 percent, roughly equivalent to 65.5 to 81 percent B.P.L.[7] Additional data on the phosphoric acid content of these materials are given in tables 9 to 11.

Four samples of Florida soft phosphate contained 25.47 to 34.94 percent phosphoric acid (table 3). It should be noted, however, that only one of these samples (no. 1091) was taken from commercial material, and that this material is not used for the manufacture of phosphate fertilizers by chemical processes but for direct application to the soil and for other purposes. The samples of Florida waste-pond phosphate contained 15.34 to 25.31 percent phosphoric acid (tables 3 and 9). As sold at the present time, this material usually contains approximately 20 to 24 percent phosphoric acid.

The phosphoric acid content of 10 samples of Tennessee phosphatic limestone ranged from 10.09 to 19.13 percent, the average being12.43 percent (tables 4 and 10). These samples contained 14.86 to 28.91 percent carbon dioxide with an average of 25.31 percent, those highest in phosphoric acid containing the smallest quantities of carbon dioxide.

The phosphoric acid in 13 prospect samples from the Garrison, Mont., deposits ranged from 27.63 to 37.47 percent (tables 5 and 11), whereas a sample of commercial material (no. 1252, table 11) contained 36.38 percent phosphoric acid. Five samples of commercial material from a deposit at Cokeville, Wyo., contained 26.60 to 30.19 percent phosphoric acid (tables 5 and 11). The phosphate from this deposit is sold principally for direct application to the soil.

The results, 26.92 and 27.85 percent phosphoric acid, obtained on two samples of South Carolina land-rock phosphate (table 5) fall within the range, 25 to 28 percent phosphoric acid, reported by Shepard (*182*) on several hundred samples of commercial material mined in the early days of the industry.

Figures on the phosphoric acid content of a few samples of Arkansas, Kentucky, Oklahoma, and South Carolina phosphates are given in table 12.

The results given in tables 6 and 13 show that the north-African phosphates, with the exception of those from Morocco, contain, in general, much less phosphoric acid than do the usual grades of commercial rock produced in the United States. In this respect they are comparable with the phosphate formerly mined in South Carolina. Morocco phosphate, on the other hand, usually contains about 34 to 35 percent phosphoric acid, and is comparable, in this respect, with Florida hard rock and the higher grades of Florida land pebble and Tennessee brown rock.

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[7] Bone phosphate of lime, an expression used in the phosphate-rock industry, to designate the phosphoric acid content of natural phosphates in terms of tricalcium phosphate, $Ca_3(PO_4)_2$.

The highest grade commercial phosphate rocks analyzed in this investigation were those from Angaur, Christmas, Curacao, Makatea, Nauru, and Ocean Islands, which contained 37.89 to 40.87 percent phosphoric acid, roughly equivalent to 82.5 to 89.0 percent B.P.L. (tables 6 and 14).

CALCIUM AND MAGNESIUM

Calcium is the predominating basic element in all the principal commercial types and grades of phosphate rock produced throughout the world. Although the calcium occurs principally in combination with the phosphate radical, it also occurs in combination with fluorine and the carbonate and sulphate radicals.

Excluding the Florida soft and waste-pond phosphates and the Tennessee phosphatic limestones, the results given in tables 3 to 5 indicate that the calcium oxide in the domestic types of phosphates ranges from about 42 to 52 percent in rock containing 27.0 to 37.5 percent phosphoric acid. Although the calcium content of a particular type of rock usually tends to increase with increase in the phosphoric acid content, the increase is not always in direct proportion to the increase in phosphoric acid, principally because of variations in the amounts of carbonate and sulphate. In proportion to the phosphoric acid, South Carolina land-rock phosphate contains more calcium than do the other domestic types of phosphate. The Wyoming rock and the lower grades of Florida land pebble come next in this respect, but the other domestic types and the higher grades of land pebble do not show consistent or marked differences.

As reported in the literature (*32, p. 533; 44; 58, p. 30; 90; 92; 99; 119, p. 210; 122; 126; 127; 134; 144; 158; 163; 168, p. 63; 179; 180*), the magnesium in domestic phosphate rock ranges from traces to about 2 percent magnesium oxide, the majority of the samples containing more than 0.3 percent. As a whole, the reported figures are much higher than those obtained in this investigation (tables 3–5). With the exception of one sample of Florida waste-pond phosphate (no. 727, table 3), none of the domestic materials showed more than 0.55 percent magnesium oxide, and the majority of the samples contained less than 0.20 percent. Although the results do not indicate any regularity in the magnesium content of a particular type of phosphate, with the possible exception of South Carolina land rock, the samples of Florida waste-pond and soft phosphates, Tennessee phosphatic limestone, and South Carolina rock average higher in magnesium than the other domestic types. Of the foreign and miscellaneous phosphates (table 6), Curacao Island rock and bone ash are the only samples containing more than 1 percent magnesium oxide. In general, the magnesium content of a particular type of rock tends to decrease as the phosphoric acid content increases.

ALUMINUM, IRON, AND TITANIUM

The results given in tables 3 to 5 show that, among the commercial domestic types of phosphate rock, the Tennessee brown and blue rocks, are generally characterized by comparatively high percentages of aluminum and iron, particularly the latter. In the blue-rock phosphates a large portion of the iron is usually present in the form of pyrite (FeS_2), whereas the brown-rock phosphates usually contain comparatively little or no pyrite. The other commercial domestic types of phosphate rock do not show striking differences in their percentages of aluminum and iron. The Florida soft and waste-pond phosphates, particularly the latter, contain, in general, very high percentages of aluminum. Although much of the aluminum in these phosphates is doubtless derived from extraneous materials such as soil clays, it is known that some samples contain significant quantities of aluminum phosphate (p. 75). As shown in table 6, the Morocco and the Christmas, Curacao, Nauru, and Ocean Islands phosphates are very low in aluminum and iron.

Titanium was found in all samples of domestic phosphates (tables 3–5), but, except in the Florida soft and waste-pond phosphates, the amount did not exceed 0.10 percent titanium dioxide (TiO_2). The results (0.03 to 0.06 percent TiO_2) on Florida hard-rock phosphate are considerably lower than those (0.13 to 0.86 percent TiO_2) previously reported (*32, p. 533; 122*) for this type of material. Gray (*58, p. 30*) reported a range of 0.02 to 0.30 percent titanium dioxide in five samples of Florida land pebble, whereas the results here given on 11 samples show a range of only 0.03 to 0.07 percent. Mansfield (*119, p. 210*) stated that titanium was not found in four samples of Idaho, Utah, and Wyoming phosphates. The figures given in table 5 indicate, however, that the western phosphates commonly contain small quantities of this element. The amount of titanium in a particular type of phosphate usually decreases with increase in the phosphoric acid.

SODIUM AND POTASSIUM

Data on the alkali content of domestic phosphate rock are reported by Clarke (*32, p. 533–534*), Gray (*58, p. 30*), Jenkins (*90*), Larison (*99*), Mansfield (*119, p. 210*), Matson (*122*), Pike (*144*), Ross and Merz (*168, p. 63*), and Shead (*179, 180*). The reported results range from traces in Florida hard-rock phosphate to about 2.5 percent sodium and potassium oxides in Utah rock and about 4 percent in rock from Johnson County, Tenn.

With the exception of the Idaho and South Carolina rocks, which contained 1.10 to 1.42 percent of Na_2O and K_2O, none of the domestic phosphates analyzed in this investigation contained more than 1 percent total alkali. The results indicate, in general, that the Florida waste-pond, Montana, and Tennessee phosphates, particularly Tennessee brown rock, contain higher percentages of potassium than of sodium, whereas the other types of phosphate, particularly Florida land pebble, South Carolina land rock, bone ash, and the foreign phosphates, usually contain more sodium than potassium. With a particular type of phosphate, the total alkali content tends, as a general rule, to decrease as the phosphoric acid content of the rock increases.

MANGANESE, CHROMIUM, AND VANADIUM

The possible occurrence of manganese in natural phosphates is of particular interest to the fertilizer industry because of the beneficial effect of this element on the growth of plants in certain soils (*171*).

Matson (*122*) reported 0.08 percent manganese oxide (MnO) in a sample of phosphatic limestone from Christina, Fla., and Gray (*58, p. 30*) reported 0.01 to 0.35 percent in six samples of the various commercial grades of Florida land pebble. Shead (*179, 180*) found 0.176 percent manganese oxide in a sample of low-grade phosphate from Cotton County, Okla. According to Jenkins (*90*), six samples of low-grade phosphate from deposits in Johnson County, Tenn., contained 0.46 to 17.53 percent manganese oxide. Murray and Renard (*128, p. 452–495*) have shown that fossil bones and phosphatic concretions from deep-sea deposits frequently contain comparatively large percentages of manganese.

With the exception of Tennessee brown-rock phosphate and phosphatic limestone, the materials analyzed during this investigation (tables 3–6) contained not more than 0.10 percent and usually less than 0.05 percent manganese oxide. Manganese was present, however, in all samples. The Tennessee brown rocks contained 0.066 to 0.27 percent and the phosphatic limestones 0.10 to 0.25 percent manganese oxide. The samples of African and island phosphates and bone ash were very low in manganese. The results indicate that the manganese in a particular type of phosphate tends to decrease with increase in the phosphoric acid content.

According to Mansfield (*119, p. 211*), F. K. Cameron was the first to suggest that the green color of solutions obtained by treating western phosphate rock with sulphuric acid might be due to the presence of chromium. This was confirmed in the United States Geological Survey by the analysis of several composite samples of rocks from Idaho, Utah, and Wyoming, which were found to contain 0.08 to 0.14 percent chromium trioxide (Cr_2O_3). The Geological Survey's chemists found 0.11 to 0.23 percent chromium trioxide in individual samples of high-grade phosphate from various deposits in Idaho. Larison (*99*) and Ross and Merz (*168, p. 63*) also reported 0.07 percent chromium trioxide in two samples of Idaho phosphate. Grammont (*56*) found 0.013 percent chromium trioxide in a sample of Florida pebble and 0.016 to 0.041 percent in six samples of north-African phosphate.

All samples of Tennessee phosphates analyzed in this investigation contained chromium in amounts ranging from <0.005 to 0.007 percent chromium trioxide (table 4). The chromium trioxide in the samples of western phosphates ranged from 0.05 to 0.13 percent (table 5), and in the Florida phosphates from 0.004 to 0.040 percent (table 3), excluding four samples of land pebble which contained no chromium.

According to Mansfield (*119, p. 212*), the presence of vanadium in western phosphates was recognized as early as 1911 by chemists in the Geological Survey. Analyses made later in the Survey laboratory showed 0.09 percent vanadium trioxide (V_2O_3)[8] in a composite sample of high-grade rocks from different parts of the Idaho field. The Survey's chemists found 0.33 to 0.43 percent vanadium trioxide in three samples of phosphate from Montpelier Canyon, Idaho, and 0.19 and 0.23 percent in two samples from the Paris Canyon district. The presence of vanadium in Idaho phosphate has been noted also by Larison (*99*) and by Ross and Merz (*168, p. 63*). Other instances of the occurrence of vanadium in phosphate rock have not come to the authors' attention.

Hess (*68, p. 580*) has pointed out the possibility of the commercial recovery of vanadium from Idaho phosphates in connection with the manufacture of phosphoric acid and phosphatic fertilizers.

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[8] Mansfield reported the vanadium content in terms of vanadium pentoxide (V_2O_5). Owing, however, to the lack of information on the nature of the vanadium compounds in phosphate rock, and in view of certain facts pointed out by Hillebrand (*79, p. 184*), it seems best to report the vanadium as the trioxide instead of the pentoxide.

As shown in table 5, all samples of western phosphates analyzed in this investigation contained vanadium in amounts ranging from 0.04 percent vanadium trioxide in Montana rock to 0.40 percent in Idaho rock, a sample from Cokeville, Wyo., containing 0.12 percent. Vanadium was not found in Tennessee brown-rock and South Carolina land-rock phosphates (tables 4 and 5). None of the samples of Tennessee blue and white rocks and phosphatic limestones contained more than 0.01 percent vanadium trioxide. With the exception of four samples of land-pebble and two of soft phosphate which contained no vanadium, the Florida phosphates contained vanadium trioxide in amounts ranging from 0.005 to 0.02 percent (table 3).

Comparing the occurrence of manganese, chromium, and vanadium in phosphate rock with their occurrence in other rocks, minerals, and soils is interesting. Clarke states that the weighted average content of manganese oxide in igneous rocks and limestones is 0.118 percent (*32, p. 34*) and that the chromium trioxide in 256 samples of igneous rocks averaged 0.05 percent (*32, p. 712*). Hillebrand (*75*) found as much as 0.03 to 0.05 percent of vanadium trioxide in some varieties of igneous rocks, particularly those poorest in silica, and he also reported that composites of a large number of samples of sandstones and building limestones contained 0.003 and 0.004 percent, respectively. Robinson and Holmes (*162*) reported 0.001 to 0.641 percent of manganese oxide in 34 samples of soil from various localities in the United States, the majority of the samples containing 0.05 to 0.15 percent. Robinson (*160*) found traces to 0.025 percent of chromium trioxide and 0.01 to 0.08 percent of vanadium, reported as the pentoxide, in 26 samples of soil from widely distributed localities in the United States.

On the basis of the data presented in this publication, it seems that, except possibly in the Tennessee phosphatic limestone and brown-rock phosphate, manganese has not concentrated in the domestic phosphate deposits. Mansfield (*119, p. 212*) has pointed out that the chromium content of the western phosphates is usually much greater than the average for igneous rocks, and that a concentration of this element has, therefore, occurred under special conditions. This is not the case, however, with the other domestic types of phosphate. Vanadium, like chromium, has concentrated in the western phosphates, particularly the Idaho rock, but not in the other domestic varieties.

COPPER, ZINC, AND ARSENIC

Grammont (*57*) reported 0.00036 to 0.0023 percent copper oxide (CuO) in six samples of phosphate rock from north Africa, and 0.00125 percent in one sample of Florida pebble. As shown in table 8, all the samples contained copper in amounts ranging from <0.0005 to 0.011 percent copper oxide. Only three samples (Counetable Islands, Idaho, and Wyoming phosphates) contained more than 0.005 percent copper oxide, whereas the majority contained 0.001 to 0.003 percent. In order to avoid possible contamination from bronze and brass sieves, cloth sieves were used in preparing the samples for the copper and zinc determinations.

TABLE 8.—*Occurrence of copper, zinc, and arsenic in natural phosphates*

Sample no.	Type or source of phosphate	P_2O_5	CuO	ZnO	As_2O_3
		Percent	*Percent*	*Percent*	*Percent*
910	Florida land pebble	31.09	0.003	<0.0005	0.0028
947	do	31.28	.002	<.0005	.0048
790	do	31.40	.001	<.0005	[1]
912	do	35.37	<.0005	<.0005	.0014
771	Florida hard rock	31.25	.001	<.0005	.0004
932	do	35.99	.002	<.0005	.0012
915	Florida waste pond	23.53	<.0005	.005	.0007
580	Florida soft	29.49	.001	.012	[1]
728	do	31.80	.003	.006	.0008
[2]56	Tennessee brown rock	31.28	.003	<.0005	.0022
762	do	33.73	.002	<.0005	[1]
906	do	34.39	.003	<.0005	.0032
908	do	34.44	.002	.001	.0038
772	Tennessee blue rock	30.45	.004	<.0005	.0023
930	do	30.97	.001	.0005	.0012
[3]1049	do	31.22	.003	.0005	[1]
1031	Tennessee white rock	35.80	.003	<.0005	[1]
917	Tennessee phosphatic limestone	11.68	.002	<.0005	[1]
973	Idaho	32.53	.011	.001	.0026
1011	Montana	27.63	[1]	[1]	.0088
1009	do	31.39	.003	.025	.0140
1010	do	37.47	[1]	[1]	.0024
948	Wyoming	30.19	.010	<.0005	.0012
1138	South Carolina land rock	27.85	.005	.0005	.0017
935	Curacao Island	38.59	.005	.045	[1]
904	Connetable Islands	54.51	.008	.031	[1]
971	Bone ash	40.36	.004	.017	≦.0001

[1] Not determined. [2] Bureau of Standards standard sample no. 56. [3] Kidney phosphate.

The only published figures on the occurrence of zinc in phosphate rock that have come to the attention of the authors are those of Grammont (*57*), who reported 0.015 to 0.034 percent zinc oxide (ZnO) in six samples of north-African phosphates, and 0.006 percent in one sample of Florida pebble.

As shown in table 8, all samples analyzed in this investigation contained zinc in quantities ranging from <0.0005 to 0.045 percent zinc oxide, the greatest amount being present in Curacao Island phosphate. With the exception of one sample each of Florida soft and Montana phosphates, none of the domestic materials contained more than 0.01 percent zinc oxide, and the majority contained less than 0.001 percent.

Mansfield (*119, p. 212*) states that no arsenic was found in a sample of phosphate from Driggs, Idaho. So far as known to the authors, the literature contains no other references to arsenic in domestic phosphates. The results given in table 8 indicate, however, that arsenic commonly occurs in these materials.[9] With the exception of bone ash which contained not more than 0.0001 percent, the samples showed 0.0004 to 0.0140 percent arsenic trioxide (As_2O_3), the largest amounts being found in two samples from Montana. With the exception of the Montana phosphates, none of the samples contained more than 0.005 percent arsenic trioxide and the majority contained less than 0.0025 percent.

Clarke (*32, p. 642*) reported that composites of numerous samples of igneous rocks, oceanic clays, river silts, and marine muds contained 0.01167, 0.0200, 0.0043, and 0.0160 percent copper oxide and 0.00638, 0.0052, 0.0010, and 0.0070 percent zinc oxide, respectively. These

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[9] The arsenic determinations were made by members of the Insecticide Division, Bureau of Chemistry and Soils.

materials also contained an average of 0.0005 percent arsenic trioxide. Robinson (*160*) reported the presence of copper in eight samples of soils from various parts of the United States, and McHargue (*108*) found 0.0090 percent copper oxide, 0.0034 percent zinc oxide, and 0.00142 percent arsenic trioxide in a sample of virgin Kentucky soil. Headden (*63*) found 0.00033 to 0.00066 percent arsenic trioxide in virgin Colorado soils, whereas the marls underlying these soils contained 0.00053 to 0.00198 percent. As determined by Zuccàri (*211*), 20 samples of soils, taken from different depths in different geological formations, contained 0.00025 to 0.0079 percent arsenic trioxide. A comparison of these results with those obtained on phosphate rock indicates that copper and zinc do not usually tend to concentrate in phosphate deposits. On the other hand, it seems that domestic phosphate rock usually contains somewhat more arsenic than is present in igneous rocks and virgin soils.

BARIUM, RARE EARTHS, AND OTHER METALLIC ELEMENTS

A few samples of phosphate rock were analyzed for barium by the method described by Hillebrand (*76, p. 170*). Barium was not found in a sample of Florida hard-rock phosphate (no. 932), whereas four samples of Florida land pebble (nos. 439, 617, 618, and 619) and two samples of South Carolina land rock (nos. 1138 and 1139) contained traces. The amounts of barium oxide found in other types of domestic phosphates were as follows: Tennessee brown rock (nos. 906 and 908), 0.03 and 0.01 percent, respectively; Tennessee blue rock (no. 930), 0.05 percent; Conda, Idaho, rock, 0.07 percent; and colloidal materials extracted from Florida soft and waste-pond phosphates (nos. 728 and 727), 0.02 and 0.03 percent, respectively.

Several samples were examined for molybdenum by treating their acid solutions with hydrogen sulphide in pressure bottles. The precipitates were ignited gently and tested for molybdenum colorimetrically with stannous chloride and potassium thiocyanate (*77, p. 256*). Negative results were obtained on samples of Florida land-pebble, Tennessee blue-rock, and Idaho phosphates. No tests were made on the other types of rock.

Samples of colloidal material extracted from Florida soft and waste-pond phosphates (nos. 728 and 727) and from Tennessee brown rock (no. 762) were analyzed for zirconium, by the method described by Hillebrand (*76, p. 170*), with negative results. On the other hand, these materials contained 0.01, 0.03, and 0.03 percent, respectively, of rare earths other than zirconium. The rare-earth metals are frequently present in apatites. Starynkevich-Borneman (*187*) reported that 23 samples of apatite from 14 localities in Asia, Europe, and North America contained up to 3.18 percent of rare-earth metal oxides, one sample from the Khibin Mountains, Russia, containing Ce_2O_3, 1.33; La_2O_3, 1.16; Yt_2O_3, 0.05; and Di_2O_3, 0.05 percent. Rare earths were also present in five samples of Russian phosphate rock in amounts ranging from traces to 0.3 percent. Tanakadate and Carobbi (*193*) found cerium, lanthanum, and yttrium in Chinese apatite.

Grammont (*57*) reported the presence of 0.00019 to 0.00076 percent of nickel in six samples of north-African phosphates, and 0.00060 percent in one sample of Florida pebble. Martini (*121*) found nickel in the leg bones of an ox and also in a specimen of human bone. He stated that nickel is apparently a normal constituent of bones. Tanakadate and Carobbi (*193*) found traces of strontium and 0.03 percent of lead oxide (PbO) in a sample of Chinese apatite. The occurrence of a very small quantity of tourmaline in Florida land-pebble phosphate no. 912 (p. 76) indicates the presence of boron. Determinations of these elements were not made in this investigation.

SILICA AND CARBON DIOXIDE

As shown in tables 3 to 5, the silica content of the commercial grades of the various types of phosphate rock produced in the United States ranges from about 4.5 to 10.0 percent, the higher grades of rock containing, in general, the smaller quantities of silica. Results on the commercial phosphate rocks indicate that the different types of rock are not characterized by their silica content. Florida hard-rock phosphate, however, contains, in general, somewhat less silica than do the same grades of Florida land pebble and Tennessee brown rock. As would be expected, the Florida soft and waste-pond phosphates usually contain comparatively large quantities of silica. This is particularly true of the waste-pond phosphates, three samples of which contained 16.80 to 23.27 percent silica (table 3). As shown in table 6, the Morocco and the island phosphates contain comparatively little silica, the figures ranging from 0.20 to 0.86 percent.

All samples of phosphate rock analyzed in this investigation contained carbon dioxide in amounts ranging from 0.37 percent in a sample of Florida soft phosphate (no. 580, table 3) to 5.96 percent in Tunisian phosphate (no. 552, table 6). The figures given in table 3 show, in general, that the carbon dioxide content of Florida land-pebble phosphate tends to decrease with increase in the phosphoric acid content. This tendency does not hold, however, with the other types of domestic phosphate. Of the principal types of domestic phosphate produced at present, Florida land pebble averages the highest in carbon dioxide, followed in order by Florida hard rock, Tennessee blue rock, Idaho rock, Tennessee brown rock, and Montana rock.

FLUORINE

In this investigation special attention has been given to the occurrence of fluorine not only in the domestic types and grades of phosphate rock but also in phosphates from all the important deposits throughout the world, some 200 samples having been analyzed.

Comparatively little information on the fluorine content of natural phosphates is recorded in the literature before the publication in 1928 of a paper by Jacob and Reynolds (*88*). About 25 years before the appearance of this paper, Carnot (*18, 19, 20, 21, 22, 23, 24, 25, 26*) published an important series of papers on the occurrence of fluorine in phosphate rock, phosphate minerals, and modern and fossil bones. Carnot's work on phosphate rock was, however, confined principally to the phosphates of Europe and north Africa. Although it has been recognized for many years that fluorine is present in all domestic phosphate rocks that have been used for commercial purposes, the few figures that have been published show very wide variations in the percentages of fluorine in the different types of rock and in the different grades of a particular type.

DOMESTIC PHOSPHATE ROCK

Excluding those on sample no. 442, which is run-of-mine material, the results given in table 9 show a range of 3.35 to 4.08 percent in the fluorine content of 37 samples of Florida land-pebble and hard-rock phosphates. These figures are, as a rule, much higher than those (1.86 to 3.68 percent fluorine) reported by Carnot (*26*), Eldridge (*44*), Gray (*58, p. 30*), and Parrish and Ogilvie (*136, p. 30*). The low figures on these and other types of domestic phosphate reported in the literature are due, no doubt, to the use of inaccurate analytical methods.

TABLE 9.—*Fluorine content of Florida phosphates*

LAND-PEBBLE PHOSPHATE

Sample no.	Location of deposit	P_2O_5	F[1]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
[2] 442	Mulberry	32.05	3.19	0.100
567	do	30.52	3.80	.126
618	Pierce	30.53	3.92	.128
[3] 617	Brewster	30.70	4.01	.131
619	Nichols	30.98	3.98	.128
910	Mulberry	31.09	3.94	.127
[3] 615	Brewster	31.25	3.96	.127
947	do	31.28	4.04	.129
[3] 616	do	31.35	4.08	.130
790	Not known	31.40	3.97	.126
[3] 436	Mulberry	31.42	3.91	.124
1040	Not known	32.05	3.82	.119
[3] 437	Mulberry	32.21	3.94	.122
[3] 628	Bartow	32.31	3.97	.123
620	Nichols	32.32	3.92	.121
568	Mulberry	32.63	3.97	.122
[3] 438	do	33.18	3.90	.118
[3] 439	do	33.22	3.87	.116
621	Nichols	33.27	3.96	.119
622	do	33.56	3.96	.118
627	Lakeland	33.70	3.90	.116
[3] 1243	Pierce	34.27	4.02	.117
[3] 440	Mulberry	34.64	3.88	.112
912	do	35.37	3.95	.112
570	do	35.50	3.95	.111
809	Lakeland	35.55	3.95	.111
[3] 441	Mulberry	35.63	3.93	.110
569	do	35.96	3.92	.109
	Average	32.78	3.91	.119

HARD-ROCK PHOSPHATE [4]

Sample no.	Location of deposit	P_2O_5	F[1]	$\frac{F}{P_2O_5}$
771	Not known	31.25	3.35	0.107
[3] 590	Benotis	33.52	3.48	.104
[3] 591	Inverness	33.52	3.77	.112
[3] 589	Floral City	34.68	3.79	.109
434	Dunnellon	35.33	3.70	.106
[3] 588	Floral City	35.70	3.86	.108
[3] 623	Hernando	35.74	3.93	.110
[3] 625	Dunnellon	35.75	3.95	.110
[3] 624	do	35.86	3.85	.107
632	do	35.90	3.91	.109
	Average	34.73	3.76	.108

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[1] Soft and waste-pond phosphates, except nos. 580, 723, and 443, were analyzed by the fusion-acid extraction method (*150*); other samples were analyzed by the volatilization method (*159*).

[2] Exceptionally high-grade run-of-mine material, other samples of land pebble are commercial washed and screened materials.

[3] Sample representing large shipment.

[4] All samples, except no. 771, the history of which is not known, are commercial washed and screened materials.

TABLE 9.—*Fluorine content of Florida phosphates*—Continued

SOFT PHOSPHATE

Sample no.	Location of deposit	P_2O_5	F	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
1091	Bartow	25.47	2.23	0.0876
580	Not known	29.49	1.23	.0417
728	Juliette	31.80	3.33	.1047
443	Gilchrist County	34.94	3.79	.1085
	Average	30.43	2.65	.0871

WASTE-POND PHOSPHATE

Sample no.	Location of deposit	P_2O_5	F	$\frac{F}{P_2O_5}$
826	Dunnellon	15.34	0.38	0.0248
581	Not known	18.18	1.53	.0842
828	Felicia	19.83	1.99	.1004
727	Dunnellon	21.63	1.94	.0897
827	do	22.29	2.26	.1014
726	Felicia	23.48	2.08	.0886
825	Dunnellon	23.48	1.81	.0771
[1] 915	do	23.63	1.84	.0779
824	do	24.24	1.93	.0796
725	Juliette	25.31	2.24	.0885
	Average	21.74	1.80	.0828

[1] Commercial material.

In comparison with the other domestic types of phosphate, the fluorine content of commercial land-pebble phosphate is very constant, and the fluorine-phosphoric acid ratios in this material tend, in general, to decrease inversely with phosphoric acid content. This is one of the distinguishing characteristics of Florida land pebble, since with the other domestic phosphate rocks the fluorine-phosphoric acid ratios in the different grades of a particular type usually show very slight variation.

There is considerable variation in the fluorine content of different samples of Florida soft and waste-pond phosphates (table 9). In proportion to their phosphoric acid content, these materials usually contain less fluorine than do the other types of domestic phosphate, and the fluorine-phosphoric acid ratios vary over a considerable range. The very low ratios in some samples, notably nos. 580 and 826, seem to be due to the presence of aluminum phosphate containing comparatively little or no fluorine (p. 75).

As shown in table 10, the fluorine content of Tennessee brown- and blue-rock phosphates and phosphatic limestone tends to vary directly with the phosphoric acid content. The different grades of the bedded variety of blue rock usually contain somewhat higher percentages of fluorine than do the same grades of brown rock. The results obtained on one sample (no. 1049) indicate that the kidney variety of blue rock runs lower in fluorine than does the bedded variety. Analyses of additional samples may show, however, that this is not generally true. The fluorine-phosphoric acid ratios in phosphatic limestone are approximately the same as those in brown-rock phosphate.

TABLE 10.—*Fluorine content of Tennessee phosphates*

BROWN-ROCK PHOSPHATE

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
[3] 585	Mountpleasant	25.74	2.80	0.109
[4] 573	do	29.40	3.22	.110
[4] 575	do	29.90	3.32	.111
587	Wales	30.17	3.24	.107
[5] 56	Not known	31.28	3.58	.114
[4] 577	Mountpleasant	31.57	3.48	.110
[4] 578	do	32.37	3.60	.111
[4] 574	do	32.80	3.49	.106
564	Wales	32.85	3.62	.110
506	Mountpleasant	33.30	3.72	.112
586	do	33.52	3.89	.116
762	do	33.73	3.87	.115
584	do	34.18	3.78	.111
906	Wales	34.39	3.77	.110
908	Mountpleasant	34.44	3.81	.111
565	do	34.80	3.94	.113
774	Wales	35.01	4.02	.115
[6] 583	Mountpleasant	37.51	4.08	.109
	Average	32.61	3.62	.111

BLUE-ROCK PHOSPHATE[1]

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
[4] 571	Gordonsburg	27.00	3.29	0.118
[4] 572	do	29.16	3.37	.116
772	Glover	30.45	3.49	.115
930	Gordonsburg	30.97	3.80	.123
[4] 576	do	31.22	3.71	.119
[7] 1049	Boma	31.22	3.09	.099
448	Gordousburg	32.03	3.67	.115
449	do	33.65	3.95	.117
	Average	30.83	3.55	.115

WHITE-ROCK PHOSPHATE

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
[8] 1048	Tomscreek	30.20	3.06	0.101
[8] 1031	Godwin	35.80	3.80	.106
	Average	33.00	3.43	.104

PHOSPHATIC LIMESTONE

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
775	Unknown	10.00	1.24	0.123
446	Gordonsburg	10.16	1.03	.101
579	Mountpleasant	10.53	1.20	.114
445	Wales	10.61	1.13	.107
918	Mountpleasant	11.22	1.12	.100
444	do	11.38	1.57	.138
917	Gordonsburg	11.08	1.05	.090
447	Mountpleasant	14.04	1.56	.111
791	Unknown	15.45	1.68	.109
770	do	19.13	2.28	.119
	Average	12.43	1.39	.111

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[1] Unless stated otherwise, all samples are from commercial materials.

[2] Determined by the volatilization method (*153*).

[3] Run-of-mine material.

[4] Sample representing large shipment.

[5] Bureau of Standards standard sample no. 56.

[6] Selected sample of exceptionally high-grade material.

[7] Selected sample of kidney phosphate; other blue-rock samples are bedded phosphates.

[8] Selected sample.

The figures for fluorine (2.91 to 6.98 percent) in western phosphates given in table 11 are very much higher than those (0.40 to 1.10 percent) reported by Gale and Richards (*51*) and Larison (*99*). It will be noted that two samples (nos. 1011 and 1012) of the Montana phosphates were exceptionally high in fluorine, containing 6.98 and 4.60 per cent, respectively. Of all the samples of domestic phosphates examined during this investigation, these were the only ones in which the presence of crystalline calcium fluoride (fluorite) was revealed by microscopical examination. The local occurrence of fluorite as coatings, seams, or specks in western phosphate rock had been noted previously by Mansfield and Girty (*119, p. 213*) and Gale and Richards (*51*).

TABLE 11.—*Fluorine content of phosphate rocks from Western United States*

IDAHO PHOSPHATE[1]

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
492	Montpelier	30.15	3.34	0.111
493	do	31.08	3.39	.109
469	Georgetown	31.97	3.49	.109
773	Conda	31.97	3.36	.105
1253	do	32.13	3.80	.118
550	Paris	32.21	3.43	.106
454	Conda	32.24	3.40	.105
973	do	32.53	3.33	.102
490	Paris	34.40	3.70	.109
494	Georgetown	34.96	3.70	.106
	Average	32.36	3.50	.108

MONTANA PHOSPHATE[3]

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
1011	Garrison	27.63	6.98	0.253
1013	do	28.85	2.91	.101
1018	do	29.81	2.99	.100
1016	do	30.27	3.05	.101
1009	do	31.39	3.19	.102
1019	do	31.47	3.66	.116
1020	do	32.24	3.39	.105
1007	do	32.54	3.54	.109
1017	do	34.92	3.80	.109
1014	do	35.12	3.80	.108
1012	do	36.07	4.60	.128
1252	do	36.38	4.03	.111
1008	do	36.90	4.05	.110
1010	do	37.47	3.83	.102
	Average[4]	33.12	3.52	.106

WYOMING PHOSPHATE[1]

Sample no.	Location of deposit	P_2O_5	F[2]	$\frac{F}{P_2O_5}$
[5]467	Cokeville	26.60	3.10	0.117
[5]491	do	28.84	3.39	.118
[5]469	do	29.75	3.51	.118
468	do	29.79	3.44	.116
948	do	30.19	3.54	.117
	Average	29.03	3.40	.117

[1] Samples of commercial materials.
[2] Determined by the volatilization method (*153*).
[3] Prospect samples, except no. 1252 which was from commercial material.
[4] Excluding nos. 1011 and 1012.
[5] Sample representing large shipment.

The results given in table 12 indicate that, in proportion to their phosphoric acid content, the Oklahoma and South Carolina phosphates generally contain significantly larger quantities of fluorine than do any of the other types of domestic phosphate rock analyzed in this investigation, except the two samples of Montana phosphate discussed in the preceding paragraph. The amounts of fluorine (2.21 to 3.16 percent) found by the authors in three samples of Kentucky brown-rock phosphate are very much higher than those (1.02 to 1.38 percent) reported by Phalen (*139*) in comparable grades of this material. On the other hand, Shead (*179, 180*) reported 4.31 percent fluorine in a sample of phosphate from Cotton County, Okla., whereas the authors found 3.32 percent fluorine in a sample from the same locality.

TABLE 12.—*Fluorine content of Arkansas, Kentucky, Oklahoma, and South Carolina phosphates*

Sample no.	Location of deposit	P_2O_5	F[1]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
[2]1267	Arkansas; Independence County	31.93	3.71	0.116
[5]1235	Kentucky; Wallace [4]	21.10	2.21	.104
[5]1245	____do	23.68	2.56	.108
[5]1234	____do	27.80	3.10	.114
[7]1242	Oklahoma; Cotton County	24.31	3.32	.137
[6]495	South Carolina land rock	16.07	2.20	.137
[7]1139	____do.[8]	26.02	3.58	.133
[7]1138	____do.[9]	27.85	3.77	.135
[6]950	____do	28.80	3.43	.119

[1] The Kentucky phosphates nos. 1235 and 1245 were analyzed by the fusion-acid extraction method (*160*); the other samples were analyzed by the volatilization method (*153*).
[2] Selected material.
[3] Sample from an abandoned mine.
[4] All Kentucky samples are brown-rock phosphate.
[5] Ground material formerly sold for direct application to the soil.
[6] Museum sample.
[7] Commercial material as formerly produced.
[8] Bulow mines, Johns Island.
[9] Lamb's mine, near Charleston.

The estimated reserves of domestic phosphate rock, containing phosphoric acid equivalent to approximately 55 percent or more of tricalcium phosphate, amount to more than 6,231,318,000 long tons (table 1). The data given in tables 9 to 12 indicate that the average fluorine content of this rock is approximately 3.25 percent. On this basis, the estimated reserves of phosphate contain at least 200,000,000 tons of fluorine which, as pointed out by Marshall, Jacob, and Reynolds (*120*), is more than 75 times the fluorine content of the known reserves of fluorspar, containing 85 percent or more of calcium fluoride, in the Illinois and Kentucky deposits.

FOREIGN PHOSPHATE ROCK

The figures given in table 13 show that the north-African phosphates, particularly those from Algeria, Morocco, and Tunis, are characterized by very high fluorine-phosphoric acid ratios. In this respect they are similar to South Carolina phosphate (table 12).

The results of analyses (3.35 to 4.28 percent fluorine) obtained by the authors on the samples from Algeria, Morocco, and Tunis are, as a general rule, much higher than those (0.99 to 3.78 percent fluorine) reported by Carnot (*26*), Dussert (*43*), Gray (*58, p. 26–29*), and Parrish and Ogilvie (*136, p. 33*) on comparable grades of rock from these deposits.

TABLE 13.—*Fluorine content of phosphates from foreign continental deposits*

Sample no.	Location of deposit	P_2O_5	F[1]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
560	Algeria, Dyr	23.39	3.35	0.143
551	Algeria, Tebessa	26.10	3.43	.131
558	Algeria, Rebiba	26.84	3.65	.136
562	Algeria, M'Zaita	28.59	3.68	.129
557	Algeria, Tocqueville	29.38	3.71	.126
559	Algeria, Bordj-Redir	32.34	4.16	.129
555	Egypt, Kosseir	30.60	3.65	.119
463	Morocco[2]	33.47	4.15	.124
563	do	34.30	4.28	.125
1162	do	35.11	4.24	.121
552	Tunis, Gafsa	27.55	3.46	.126
556	Tunis, Kalaa-Djerda	26.91	3.48	.129
561	Tunis, M'Dilla	28.66	3.72	.130
553	Tunis, Gafsa	29.13	3.77	.129
1227	Belgium, Mons	12.18	1.61	.132
1226	Belgium, Liege	18.13	1.83	.101
1154	Estonia, Tallinn	16.78	1.49	.089
1155	do	25.68	2.44	.095
1156	do	26.48	2.38	.090
1228	France, Somme	22.02	2.89	.131
1240	do	24.66	3.37	.137
1241	France, Pyrenees Mountains	26.87	2.69	.100
1239	France, Quercy	34.74	.74	.021
1161	Portugal, Marvão	27.14	2.49	.092
1144	Prussia, Staffel, Nassau	33.89	3.62	.107
1152	Russia, Volga River region	13.40	2.02	.151
1265	Russia, Aktyubinsk, Siberia	17.42	2.50	.144
1263	Russia, Saratov	18.40	2.73	.148
1266	Russia, Egoriev	19.50	2.43	.125
1264	do	22.37	3.42	.153
1262	Russia, Viatka	27.88	3.85	.138
582	British Columbia, Crow's Nest Pass	24.11	2.64	.109
1258	Palestine, Nebi Moussa	8.14	.99	.122
1255	do	16.60	1.67	.101
1256	do	17.50	1.97	.113
1257	do	20.40	2.58	.126
1157	South Australia, Kapunda	30.18	3.02	.120
1158	South Australia, Port Clinton	33.53	3.32	.099

[1] Determined by the volatilization method (*153*).
[2] Samples from either the Boujniba or the Kouriglia deposits, probably the latter.

In proportion to their phosphoric acid content, the samples of Russian phosphate rocks (table 13) contain even more fluorine than do the north-African phosphates. Next to those of the Russian phosphates, the highest fluorine-phosphoric acid ratios in samples from other European deposits were found in rocks from Mons, Belgium, and Somme, France. On the other hand, the sample (no. 1239) from Quercy, France, is comparatively low in fluorine (0.74 percent), although it contains 34.74 percent phosphoric acid. This analysis agrees closely with the one reported by Lacroix (*96*).

The fluorine-phosphoric acid ratios in the Estonian phosphates (table 13), which came from a deposit in the Obolus sandstone region near Tallinn (*130*), are somewhat lower than those usually found in continental phosphates.[9a] The material from this deposit is unusual in that the phosphatic portion consists of phosphatized shells. In their fluorine-phosphoric acid ratios (table 13), the samples of

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[9a] The terms "continental phosphates", "continental rocks", and "continental deposits", as used in this publication, refer to phosphates, rocks, and deposits occurring on the continents, regardless of whether they are of continental or marine origin.

phosphate rock from deposits in British Columbia, Palestine, and South Australia are similar to those from deposits in the United States.

The amounts of fluorine found in 17 samples of phosphate from deposits on eight widely distributed tropical islands (table 14) range from 0.06 percent in the hydrated aluminum phosphate (no. 904) from the Connetable Islands to 3.42 percent in one sample of Makatea Island phosphate. With the exception of the Connetable Islands phosphate, all the samples of insular rocks are calcium phosphates. As shown in tables 9 to 13, the fluorine-phosphoric acid ratios in phosphate rocks from continental deposits rarely fall below 0.09 and usually range from about 0.10 to 0.13. On the other hand, the ratios in phosphates from insular deposits are usually very much lower, rarely exceeding 0.09 and usually falling below 0.08. The ratios in phosphates from a particular island tend, however, to run quite uniformly, and in this respect the insular phosphates are similar to the individual varieties and types of continental phosphates. The ratios in the four samples of Curacao rock are unusually low, ranging from 0.0093 to 0.0240. In proportion to the phosphoric acid content, Curacao phosphate contains less fluorine than any of the other calcium phosphate rocks for which data are available.

TABLE 14.—*Fluorine content of phosphates from foreign insular deposits*

Sample no.	Location of deposit	P_2O_5	F[1]	$\frac{F}{P_2O_5}$
		Percent	*Percent*	
1223	Angaur Island[2]	40.00	2.96	0.0740
452	Christmas Island	39.40	1.32	.0335
1231	do	40.03	1.05	.0263
[3]904	Connetable Islands	54.51	.06	.0011
1022	Curacao Island	37.89	.91	.0240
985	do	38.59	.70	.0181
984	do	38.71	.75	.0194
943	do	40.60	.38	.0093
1222	Juan de Nova Island[4]	32.29	1.68	.0520
1230	Makatea Island[5]	37.94	3.42	.0901
1159	do	38.22	3.25	.0850
450	Nauru Island	38.92	2.62	.0673
1232	do	39.06	2.48	.0635
1160	do	39.21	2.10	.0536
451	Ocean Island	40.32	2.97	.0737
1229	do	40.33	2.97	.0736
1161	do	40.87	3.29	.0805

[1] Determined by the volatilization method (*155*).
[2] Pelew Group.
[3] Aluminum phosphate; other samples are calcium phosphates.
[4] Off the east coast of Madagascar.
[5] Society Group.

PHOSPHATE MINERALS

The theoretical fluorine-phosphoric acid ratio in fluorapatite, $Ca_{10}F_2(PO_4)_6$, is 0.0891. Analyses of nine samples from widely separated deposits gave, however, ratios ranging from 0.0769 to 0.110, the average being 0.0916 (table 15). The ratios in fluorapatite are, as a general rule, lower than those in phosphate rocks from continental deposits, but higher than those in rocks from insular deposits. Fluorapatite usually contains small percentages of chlorine (*39, p. 765; 78, p. 566–571*) and the deficiency of fluorine in many samples is generally ascribed to replacement of the fluorine by chlorine or by the hydroxyl group. Replacement of fluorine by chlorine in apatite occurs, however, only to a limited extent (*65*).

TABLE 15.—*Fluorine content of phosphate minerals, bones, and bird guano*

Sample no.	Material	Location of deposit	P_2O_5[1]	F[1]	$\frac{F}{P_2O_5}$
			Percent	*Percent*	
[2]1136	Fluorapatite	Virginia, Amherst County	38.12	2.93	0.0769
1261	do	Russia, Kola Peninsula	38.46	3.50	.0910
1260	do	do	39.08	3.49	.0893
640	do	Ontario, Renfrew County	39.63	3.84	.0969
647	do	do	39.77	3.89	.0978
633	do	do	39.88	3.88	.0973
648	do	New York, Hammond, St. Lawrence County.	38.58	4.24	.110
649	do	Mexico, Durango	40.88	3.44	.0842
905	do	Quebec Province	40.30	3.26	.0809
634	Chlorapatite	Norway, Kragerö	40.50	.17	
632	Amblygonite	California, Pala, San Diego County.	44.45	4.02	
631	Wavellite	Pennsylvania, Mount Holly Springs, South Mountain.	33.62	3.95	
971	Bone ash, commercial material		40.30	.054	.0013
	Bone meal, commercial material			[3].05	
	Modern bones and teeth[4]		40.17	.21	.0052
	Modern swine femurs[5]		40.30	.03	.0007
	do[6]		40.90	.86	.0210
	Fossil bones and teeth[7]		30.68	1.85	.0603
643	Fossil fish teeth	Florida land-pebble phosphate district.	37.10	3.48	.0938
644	Fossil animal teeth	do	38.91	1.76	.0452
645	Fossil animal bones	do	37.29	3.29	.0882
1106	Bird guano	Islands belonging to Peru	14.40	.06	.0042

[1] Figures not corrected to moisture-free basis.
[2] Material obtained by magnetic separation from ilmenite nelsonite.
[3] Average of four samples.
[4] Average composition of ash of 20 samples from humans, quadrupeds, reptiles, and fish (*23*).
[5] Average composition of ash of 2 samples from animals receiving feeds low in fluorine (7).
[6] Average composition of ash of 6 samples from animals receiving feeds high in fluorine (7).
[7] Average composition of ash of 52 samples from animals and reptiles (*22*).

Carnot (*23*) reported that four samples of wavellite (aluminum phosphate) from Ireland and the United States contained 1.81 to 2.79 percent fluorine. These figures, also those given by Dana (*39, p. 842*), are much lower than that of 3.95 percent fluorine obtained by the authors on a sample of wavellite from Mount Holly Springs, South Mountain, Pa. (table 15). This particular deposit is of interest because the mineral was used at one time as a raw material for the manufacture of phosphorus (*190*). Dana states that wavellite does not always carry fluorine. Besides wavellite only a few of the mineral aluminum phosphates, among which may be mentioned amblygonite, a fluorphosphate of aluminum and lithium, contain significant quantities of fluorine. Fluorine was not found in samples of the mineral iron phosphates, dufrenite and vivianite. Dana does not record the occurrence of fluorine in any iron phosphate minerals.

BONES AND BIRD GUANO

Inasmuch as the phosphatic constituent of bone has a crystal structure similar to that of fluorapatite and phosphate rock (*64, 65*), data on the fluorine content of bone are of interest. No comprehensive investigation of this subject seems to have been made in recent years. Owing largely, no doubt, to the use of inaccurate analytical methods and to certain other complications, the existence of which has been recognized only recently, the data reported in the literature are somewhat conflicting, and it is difficult to draw from them conclusions as to the fluorine content of normal bone.

Perhaps the most extensive investigation of the subject was made about 1892 by Carnot (*19, 20, 21, 22*), who reported an average of 0.21

percent fluorine in the ash of 20 samples of human, quadruped, reptile, and fish bones and teeth of the modern period. Bethke and coworkers (*7*) recently reported an average of 0.03 percent fluorine in the ash of two samples of femurs from swine fed on rations low in fluorine. However, when small quantities of fluorine compounds were added to the rations the fluorine content of the ash of the femurs increased considerably and roughly in proportion to the amount of fluorine in the feed, the results on six samples ranging from 0.53 to 1.10 percent, with an average of 0.86 percent fluorine. Likewise, Cristiani (*36*) found that the bones of cattle from districts where there were no factories discharging fluorine compounds into the atmosphere usually contained less than 0.05 percent fluorine, whereas the bones of cattle living in the neighborhood of aluminum works contained as much as 0.379 percent fluorine. This increase in the fluorine content of the bones resulted, no doubt, from the ingestion of herbage upon which fluorine compounds had been deposited from the atmosphere. Casares (*28*) reported that fluorine is not present in teeth, and that the bones of young animals contain less fluorine than those of old animals. On the other hand, Papish, Hoag, and Snee (*132*), using an indirect spectroscopic method, found fluorine in the bones and teeth of rats and pigs. The authors found an average of 0.05 percent fluorine in four samples of commercial bone meal and 0.054 percent in a sample of commercial bone ash (table 15). On the basis of these data, it would seem that fluorine is a normal constituent of the teeth and bones of animals, and that the normal fluorine content of bone is probably less than 0.1 percent. It is evident, furthermore, that the fluorine content of bone may be greatly increased by the ingestion of fluorine compounds.

The fluorine content of fossil bones and teeth is usually very much higher than that of modern bones and teeth. Samples of fossil fish teeth, animal teeth, and animal bones from the Florida land-pebble phosphate district contained 3.48, 1.76, and 3.29 percent fluorine, respectively (table 15). Carnot (*22*) analyzed 52 samples of ash from fossil animal and reptile bones and teeth of different geological ages and found that the fluorine content ranged from 0.44 to 3.62 percent, with an average of 1.85 percent. Carnot showed that the fluorine content of fossil bones increases with their age. Murray and Renard (*128, p. 488–495*) also observed that deep-sea fossil bones contain more fluorine than do modern marine bones.

The only published figures on the fluorine content of fresh bird guano that have come to the attention of the authors are those of Braun (*13*), who reported 0.05 to 0.34 percent fluorine in seven samples from deposits in various parts of the world. Three samples of fresh Peruvian guano, analyzed by Braun, contained 0.05 to 0.20 percent fluorine, whereas the authors found 0.06 percent fluorine in a sample of this material (table 15). It is evident from these figures that fresh bird guano contains in proportion to its phosphoric acid content very much less fluorine than is usually present in phosphate rock.

ORIGIN OF FLUORINE IN PHOSPHATE ROCK

Before considering the origin of the fluorine in phosphate rock, it is desirable to note briefly the possible sources of the phosphoric acid itself.

The phosphoric acid content of the majority of the tropical-island deposits was no doubt derived from the leaching of soluble phosphates from bird guano into underlying deposits of calcium carbonate. The phosphoric acid in the guano was in turn derived from the fish ingested by the birds formerly inhabiting the islands, and also from the bones of the birds themselves. The source of the phosphoric acid in the continental deposits is not so clearly defined, but it seems certain that in many deposits it was not derived from bird guano. There is abundant evidence that fish and animal remains have played a part in the formation of some continental deposits, whereas phosphate-bearing marine organisms, such as certain of the brachiopods, undoubtedly contributed to the formation of certain deposits, for example those in Estonia (*130*).

In order to arrive at a satisfactory explanation of the origin of the fluorine in phosphate rock it is necessary to decide whether the fluorine was present in the phosphate as laid down in the original deposits or whether it resulted from secondary changes during or after the formation of the deposits. Therefore bones, bird guano, marine invertebrates, fluorine minerals, and water as sources of fluorine will be considered.

It has been shown herein that, in proportion to their phosphoric acid content, bird guano and fresh teeth and bones from animals receiving feed of normal composition probably contain less than one twentieth as much fluorine as is present in phosphate rock from continental deposits. Although it is true that fossil teeth and bones usually contain very much larger quantities of fluorine than do fresh teeth and bones, there is satisfactory proof that this condition results from secondary chemical changes occurring over very long periods of time. It seems, therefore, that the fluorine content of phosphate rock cannot be attributed solely to the fluorine originally present in the bird guano and in the fish and animal remains that may have played a part in the formation of the deposits.

As shown by Clarke and Wheeler (*33*), the inorganic phosphoric acid content of marine invertebrates ranges from less than 1 percent in the majority of the species to about 21 percent in certain annelids and 34 to 42 percent in certain phosphatic brachiopods. Clarke and Wheeler state, however, that marine invertebrates contain, as a general rule, only traces of fluorine. Carles (*16, 17*)[10] reported 0.0054 percent fluorine in oyster and marine mussel shells, whereas shells of fresh-water mussels and snails contained only 0.0009 to 0.0018 percent. On the basis of these data, it seems that the high fluorine content of phosphate rock can hardly he attributed to the fluorine in the marine organisms that may have played a part in the formation of some of the phosphate deposits. Furthermore, it seems that the greater portion of the fluorine present in phosphate rock was derived from a source or sources other than those supplying the phosphoric acid.

The authors are not aware that any of the phosphate-rock deposits are closely associated with deposits of fluorite and other fluorine-bearing minerals, and with a few exceptions (pp. 36 and 73) fluorite and fluorine compounds, other than the fluorphosphates, have not been found in phosphate rock. In the few cases where fluorite has

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[10] In the original papers, Carles apparently expressed the results in terms of either sodium fluoride or calcium fluoride. On the assumption that his results are in terms of sodium fluoride, the corresponding fluorine equivalents have been calculated.

been found in phosphate rock there is evidence that it is of secondary origin. These observations indicate that the fluorine content of phosphate rock did not originate, to any significant extent, from the action of phosphoric acid and soluble phosphates on deposits of fluorine-bearing minerals. Some phosphate rocks contain as high as 150 times as much fluorine as the figure, 0.027 percent, given by Clarke (*32, p. 34*) for the weighted average fluorine content of the lithosphere.

Finally, water may be considered as the possible source of the fluorine in phosphate rock. Comparatively little information on the fluorine content of water is available, and, because of analytical difficulties, it is probably unsafe to place much confidence in the older figures reported in the literature.

Although fluorine is rarely determined in water analysis, Clarke (*32, p. 193*) states that it is almost invariably present in water. According to Gautier and Clausmann (*53*), the fluorine content of 18 samples of water from French rivers and lakes ranged from less than 0.010 to 0.60 mg per liter. The same authors (*54*) found 0.154 to 6.32 mg of fluorine per liter in 45 samples of mineral waters from various localities in Europe and north Africa, the average being 2.06 mg. Carles (*15*) reported 0.00 to 8.14 mg per liter in 92 samples of French natural mineral waters, the average being 3.17 mg (footnote 10.) Churchill (*30*) recently made a survey of the fluorine in potable waters from various parts of the United States. The fluorine content of five samples from Arkansas, Colorado, Idaho, and the Dakotas ranged from 2.0 to 13.7 mg per liter, the average being 8.94 mg. Waters from other localities west of the Appalachian Mountains contained less than 1 mg of fluorine per liter. No fluorine was found in waters east of the Appalachians. Clarke (*31, p. 114*) reported 5.2 mg of fluorine per liter in a sample of water from Ojo Caliente, near Taos, N.Mex. According to Gautier and Clausmann (*54*), the fluorine content of three samples of water from the Atlantic Ocean and Mediterranean Sea ranged from 0.240 to 0.334 mg, with an average of 0.291 mg. Carles (*15*) found 5.43 mg of fluorine per liter in a sample of water from the Bassin d'Arcachon, Bay of Biscay. In addition to the foregoing, two important papers (*185a, 193a*) on the occurrence of fluorine in water have recently been published.

In 1891 Murray and Renard (*128, p. 275*) advanced the theory that the high fluorine content of fossil bones and teeth from deep-sea deposits owes its origin to a continuous, though slowly progressing, double decomposition between the phosphate of the bones and teeth and the traces of dissolved fluorides in sea water. A similar theory was advanced by Carnot (*22*) two years later, who showed that when fragments of bone, originally containing 0.31 percent flourine, were kept in contact with a 2 percent solution of sodium flouride for five months the fluorine content increased to 4.74 percent. As pointed out by Carnot, this theory gives an adequate explanation of the high fluorine content of fossil bone as compared with that of modern bone. Carnot also found that the fluorine content of fossil bone shows, in general, a marked tendency to increase with increase in the geological age of the bone (*19, 20, 21, 22*), and he points out that this is consistent with the theory that the bones take up fluorine from the waters with which they come in contact.

It seems to be the general opinion that the fluorine in the fossil brachiopod shells, principally *Obolus apollinis*, which are the main source of the phosphoric acid in the phosphate deposits near Tallinn, Estonia, was an original constituent of the shells (*130*). Unfortunately, no information on the fluorine content of the fresh shells of *O. apollinis* seems to be available, but there is no reason to believe that the shells are radically different in this respect from other marine invertebrates which contain only minute quantities of fluorine. In the light of present knowledge, it is more logical to suppose that the fluorine in the fossil shells, like that in fossil bone, is of secondary origin, and that it results from long contact of the phosphatic shells with fluorine-bearing waters.

Although the relation between fluorine content and geological age is not so pronounced in phosphate rock as in fossil bone, it has been pointed out (*120, 152*) that the insular phosphate rocks which belong to recent geological periods contain, in general, much less fluorine than do the continental rocks which belong to older geological periods and, therefore, have been exposed for a much longer time to the action of fluorine-bearing waters. If we assume that the fluorine in phosphate rock is derived principally from sea water and that the average fluorine content of the water is 0.291 mg per liter,[11] it would require approximately 120,000 liters of water to supply the fluorine that is present in 1 kg of phosphate rock containing 3.5 percent fluorine.

It is beyond the scope of this publication to give an extended discussion of the chemical reactions involved in the formation of the phosphate-rock deposits as they exist today. It should be pointed out, however, that the reactions were undoubtedly quite complex and extended over very long periods of time. It is probable that during the intermediate stages of the process a considerable portion of the phosphate, if not all, was present as calcium hydroxyphosphate, $Ca_{10}(OH)_2(PO_4)_6$, and calcium carbonate-phosphate, $Ca_{10}(CO_3)(PO_4)_6$. Upon exposure to fluorine-bearing waters, these compounds were converted into the less-soluble calcium fluorphosphate, $Ca_{10}F_2(PO_4)_6$, through the replacement of the carbonate and hydroxyl groups by fluorine. In the old continental deposits, such as those in the United States, it appears that complete transformation into fluorphosphate has occurred, whereas in the comparatively young insular deposits the transformation is, as yet, incomplete.

There seems to be little doubt that water is the principal source of the fluorine in phosphate rock. In this connection the question of the source of the fluorine in water naturally arises. Although this subject has not been extensively investigated, Zies (*210*) expresses the opinion that volcanic activity is a very important factor in the distribution of fluorine. His investigations of the Valley of Ten Thousand Smokes, in the Katmai region of Alaska, indicate that in this area alone approximately 180,000 metric tons of fluorine in the form of hydrofluoric acid are discharged into the atmosphere annually, and that approximately 75 percent of this quantity, or 135,000 metric tons, finds its way into the sea. The investigations of Churchill (*30*), Carles (*15*), and Gautier and Clausmann (*53, 54*) have shown that spring and river waters from areas far from scenes of volcanic activity frequently carry appreciable quantities of fluorine. In such cases the fluorine is no doubt derived from contact of the waters with fluorine-bearing minerals.

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[11] This figure is the average of three results reported by Gautier and Clausmann (*54*).

CHLORINE, BROMINE, AND IODINE

Very little information on the chlorine content of domestic phosphate rock appears in the literature. Eldridge (*44*) reported 0.08 percent chlorine in a sample of Florida hard-rock phosphate containing 33.91 percent phosphoric acid. The presence of chlorine has also been observed in the phosphates of South Carolina (*163, 182*) and in those of Montana, Idaho, Utah, and Wyoming (*51, 134*).

The data given in tables 3 to 6 indicate that chlorine is a common constituent of phosphate rock. It occurs, however, only in small quantities, usually less than 0.02 percent of the sample. Occasional samples, such as Florida soft phosphate (no. 580, table 3) and the Curacao Island phosphates (table 6) contained 0.12 to 0.16 percent chlorine. Of the domestic types of phosphate, Florida hard rock generally contains the lowest percentages of chlorine and the western phosphates, particularly the Idaho and Wyoming rocks, the highest. According to Clarke (*32. p. 34*), the average chlorine content of igneous rocks is 0.048 percent and of limestones 0.02 percent, whereas the weighted average chlorine content of the lithosphere is 0.045 percent. Sandstones contain only traces of chlorine. It is evident, therefore, that chlorine, unlike fluorine, does not tend, in general, to concentrate in phosphate rock.

The results for bromine in three samples, the only analyses made, ranged from less than 20 parts per million in Florida land pebble (no. 910) to 30 parts per million in Florida hard rock (no. 932). A sample of Tennessee brown rock also contained 30 parts per million of bromine. Although it is believed that these results are reasonably accurate, it is not safe to draw from the limited data general conclusions on the bromine content of phosphate rocks.

Only a few figures on the bromine content of rocks in general are available. In five of nine samples of meteorites tested, Fellenberg (*46*) found bromine in amounts ranging from 2 to 56 parts per million, the quantities being much larger in stone than in iron meteorites. Fellenberg and Lunde (*47*) reported 2 and 8 parts per million of bromine, respectively, in one sample each of granite and basalt. Data on the bromine content of sedimentary rocks have not come to the attention of the authors. Our results, when compared with those of Fellenberg, indicate, however, that phosphate rock probably contains, as a general rule, more bromine than is usually present in igneous rocks.

During the last few years numerous data on the iodine content of various fertilizer materials have appeared in the literature. The results have been summarized in part by Orr and Leitch (*131*) and also by McHargue, Roy, and Pelphrey (*110*). All available data on phosphate rock have been summarized by Hill and Jacob (*70*). The majority of the analyses have been made on foreign phosphates, and the figures, as a rule, are not very consistent for rocks of a given type or from a given locality. On the foreign phosphates, the published results range from approximately 1 part per million of iodine in Podolia phosphate (*207*) and in certain samples of Egyptian and Nauru Island phosphates (*67*) to 280 parts per million in rock from Limburg, Germany (*207*). In the domestic phosphates, McHargue (*109*) reported 5.45 and 6.72 parts per million of iodine in samples of brown-rock phosphates from Tennessee and Kentucky, respectively. Wilke-Dörfurt, Beck, and Plepp (*207*) reported 3.8 parts per million of iodine in a sample of Florida pebble phosphate and 54.5 and 92.5 parts per million in two samples of Florida hard rock.

Analyses of 30 samples from all the present commercially important deposits in the United States (table 16) indicate that iodine is a common constituent of the domestic phosphates. The results range from 0.8 part per million in rocks from Garrison, Mont., and Cokeville, Wyo., to 130 parts per million in one sample of Florida hard rock. Although the iodine content of domestic phosphate does not run very constant for a particular type of rock, samples of a given type or from a given locality seem to be characterized, as a general rule, by certain more or less definite limits in iodine. The averages of the results obtained on the domestic materials indicate that the western phosphates contain the smallest quantities of iodine, and are followed in order by Tennessee blue rock, Florida land pebble, Tennessee brown rock, Florida soft and waste-pond phosphates, and Florida hard rock.

TABLE 16.—*Iodine content of natural phosphates*

UNITED STATES DEPOSITS

Sample no.	Type or source of phosphate	P_2O_5	Iodine
		Percent	*Parts per million*
619	Florida land pebble	30.98	10.3
910	do	31.09	10.9
947	do	31.28	13.1
439	do	33.22	15.4
912	do	35.37	8.2
771	Florida hard rock	31.25	72.0
589	do	34.68	93.2
434	do	35.33	87.0
932	do	35.99	130
728	Florida soft	31.80	88.3
720	Florida waste pond	23.48	50.8
915	do	23.63	63.5
[1] 56	Tennessee brown rock	31.28	9.8
762	do	33.73	18.1
1233	do	33.73	17.3
906	do	34.39	28.2
908	do	34.44	16.3
772	Tennessee blue rock	30.45	5.4
930	do	30.97	6.4
[2] 1049	do	31.22	3.0
1031	Tennessee white rock	35.80	20.0
454	Idaho	32.24	2.6
973	do	32.53	1.9
1009	Montana	31.39	.8
1010	do	37.47	.8
948	Wyoming	30.19	.8
1235	Kentucky brown rock	21.19	9.5
1234	do	27.80	6.1
1139	South Carolina land rock	26.92	3.7
1138	do	27.85	13.9

NORTH-AFRICAN DEPOSITS

Sample no.	Type or source of phosphate	P_2O_5	Iodine
562	Algeria	28.59	3.7
1102	Morocco	35.11	113
552	Tunis	27.55	4.7
561	do	28.66	8.0

ISLAND DEPOSITS

Sample no.	Type or source of phosphate	P_2O_5	Iodine
452	Christmas Island	39.46	75.4
904	Connetable Islands	54.51	<1.0
985	Curacao Island	38.59	122
943	do	40.66	37.0
450	Nauru Island	38.92	18.5
451	Ocean Island	40.32	18.3

[1] Bureau of Standards standard sample no. 56.

[2] Kidney phosphate; other blue-rock samples are bedded phosphates.

Three samples of Algerian and Tunisian phosphates contained 3.7 to 8.0 parts per million of iodine (table 16), the results being in good agreement with those previously reported (*207*). A sample of Moroccan phosphate contained 113 parts per million of iodine, a figure more than twice as high as that reported by Wilke-Dörfurt and coworkers (*207*). The results obtained on the samples of insular phosphates indicate that these materials are richer in iodine than are most continental phosphates. However, the aluminum phosphate from the Connetable Islands contained very little iodine (less than 1 part per million). This material also contained only very small quantities of fluorine and chlorine (table 6). A summary of all available data (*70*), including those obtained in this investigation, shows that the iodine content of 71 samples of phosphate rock from all parts of the world ranged from 0.8 to 280 parts per million, with an average of 31.3.

Hill and Jacob (*70*) have shown that, so far as increase in the iodine content with the age of the rock is concerned, there is no regular relation between the geological age and the iodine content of phosphate rock. They pointed out, however, that the phosphates from western United States, which are only sparingly fossiliferous, are very low in iodine, whereas certain other deposits which contain fossil remains in abundance are comparatively high in iodine. This observation is in line with the results obtained by Fellenberg (*45*) on rocks in general. One might infer from this that the iodine in phosphate rock is associated with organic matter, and that, consequently, a definite relation between the iodine and organic matter in phosphate rock might be expected. Such a relation is not indicated, however, by the data in tables 16 and 18. In fact, in a particular type of rock, samples containing the largest quantities of organic matter more often than not contain the smallest quantities of iodine. The comparison shows also that although the sparingly fossiliferous Idaho and Wyoming phosphates contain less than 4 percent as much iodine as does Florida hard rock they contain 4 to 15 times as much organic carbon. The source of the carbon in these materials is not known, but microscopical examination of Idaho phosphate no. 973 and Wyoming phosphate no. 948, by W. H. Fry, of the Bureau of Chemistry and Soils, showed the presence of plantlike fragments.

No trace of iodine was found in the organic matter separated from Florida land pebble (no. 912), Florida hard rock (no. 932), Tennessee brown rock (no. 906), and Idaho rock (no. 973) by heating 5-gram samples to boiling in about 10 minutes with 125 cubic centimeters of 1 to 1 hydrochloric acid, and washing the residues with 1 to 20 hydrochloric acid. However, these findings should be considered as only indicatory inasmuch as iodine-bearing organic matter, if present, may be hydrolyzed by acids, with the result that the iodine passes into solution.

It is not inconsistent with the chemistry of the complex calcium phosphate-halogen compounds to postulate that the iodine in phosphate rock is present in the form of a calcium iodophosphate similar, perhaps, to the chlor- and fluorphosphates. In fact, Ditte (*42*) claims to have prepared, by a high-temperature method, a complex calcium iodophosphate. Wilke-Dörfurt, Beck, and Plepp (*207*) were unable to duplicate Ditte's results, but the compounds they obtained always showed, nevertheless, small percentages of water-insoluble iodine. If a calcium iodophosphate is present in phosphate rock it would be easily soluble in mineral acids.

Although the source of the iodine in phosphate rocks is not so clearly defined as is that of the fluorine, it is possible that a portion of the iodine was derived from waters with which the phosphates have come in contact during and after their deposition. There is considerable variation in the published figures on the iodine content of ocean and sea water. The older results, which have been summarized by Clarke (*32, p. 122*), show a range of 0.02 to 2.83 parts per million of total iodine, whereas Reith (*149*) has recently reported that 13 samples of ocean and sea waters, taken from various localities and at different depths, contained an average of 0.0542 part per million.

Comparing the iodine content of phosphate rock with that of other rocks, and also of soils, is interesting. The average of Fellenberg's results (*45, p. 209*) on 30 samples of igneous rocks, pyromorphite, quartzite, anhydrite, gypsum, calcite, limestone, marble, and dolomite, is 0.91 part per million of iodine. Two samples of fluorapatite contained an average of 0.370 part per million of iodine. Hercus, Benson, and Carter (*66, p. 332*) reported that the iodine content of 473 samples of New Zealand soils ranged from 0.0 to 70.0 parts per million, the average being 2.7 parts per million. McHargue and others (*111*) found 0.103 to 8.250 parts per million of iodine in 16 samples of soil from Canada, Kentucky, New Jersey, and South Carolina, the average being 4.538 parts per million. It is evident, therefore, that phosphate rock contains, in general, much more iodine than is usually present in other rocks, both igneous and sedimentary, in soils, and in ocean and sea waters.

SULPHUR

Appreciable amounts of sulphur are present in all domestic phosphate rocks (tables 3, 4, 5, and 17). Of a given type of phosphate, the samples relatively high in phosphoric acid usually contain the smallest percentages of sulphur. Florida hard-rock, soft, and waste-pond phosphates, pyrite-free Tennessee brown rock, and Montana phosphate consistently show less than 1 percent of total sulphur (as SO_3), whereas Tennessee blue rock is much richer in this element than are any of the other types of phosphate for which data are available. The total sulphur content (0.56 percent SO_3) of Florida hard rock no. 932 (table 17) is unusually high for this type of phosphate. On three other samples the percentages ranged from 0.12 to 0.16, which is in good agreement with the results on four samples as reported by Clarke (*32, p. 533*).

TABLE 17.—*Sulphur content of phosphate rock*

Sample no.	Type or source of phosphate	P_2O_5	Total sulphur as SO_3	Fractional forms of sulphur as SO_3: Sulphate soluble in 1 to 4 hydrochloric acid	Sulphate insoluble in 1 to 4 hydrochloric acid	H_2S evolved with 1 to 4 hydrochloric acid	Sulphide insoluble in 1 to 4 hydrochloric acid	Total sulphur minus sum of fractional determinations
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
618	Florida land pebble	30.53	1.42	1.14	0.20	0.04	(1)	0.04
617	do	30.70	1.51	1.19	.13	.05	0.02	.12
619	do	30.98	1.29	1.06	.07	.04	(1)	.12
910	do	31.09	1.05	.98	.00	.05	(1)	.02
947	do	31.28	1.22	1.09	.05	.03	(1)	.05
790	do	31.40	1.36	1.19	.00	.03	.00	.14
627	do	33.70	1.08	.85	.01	.01	(1)	.21
912	do	35.37	.26	.20	.00	.05	(1)	.01
932	Florida hard rock	35.99	.56	.01	.00	.00	.00	.55
[2] 56	Tennessee brown rock	31.28	2.69	1.24	.00	Trace	1.19	.26
762	do	33.73	.81	.75	.00	.00	.00	.06
906	do	34.39	.71	.59	.02	.00	.00	.10
908	do	34.44	.76	.68	.02	.00	.00	.06
772	Tennessee blue rock	30.45	7.10	4.02	.06	Trace	2.71	.31
930	do	30.97	6.64	1.26	.01	Trace	5.21	.16
[3] 1049	do	31.22	4.07	2.00	(1)	Trace	2.02	.05
448	do	32.02	4.04	2.43	.02	Trace	1.37	.22
449	do	33.65	4.37	1.06	.00	Trace	3.19	.12
916	Tennessee phosphatic limestone	11.22	2.57	1.55	(1)	Trace	.97	.05
917	do	11.68	4.84	2.27	(1)	Trace	2.52	.05
550	Idaho	32.21	1.53	1.43	.00	.05	.00	.05
454	do	32.24	2.52	1.66	.00	.05	.00	.81
973	do	32.53	2.47	1.69	.05	.10	.00	.63
1009	Montana	31.39	.33	.12	.02	.00	.02	.17
1010	do	37.47	.38	.26	.02	.00	.02	.08
948	Wyoming	30.19	3.09	1.30	.05	.00	1.30	.35
1139	South Carolina land rock	26.92	2.51	1.74	.00	Trace	.48	.29
1138	do	27.85	2.65	1.97	.00	Trace	.46	.22
552	Tunis, Gafsa	27.55	3.53	2.87	.07	.00	.00	.59
1162	Morocco	35.11	1.46	1.40	(1)	.00	.00	.06

[1] Not determined.
[2] Bureau of Standards standard sample no. *56*.
[3] Kidney phosphate.

Previous data on the total sulphur content of Florida land-pebble and Tennessee brown-rock phosphates have not come to the authors' attention. A few results for sulphur, presumably total sulphur, in several other domestic types of phosphate have been reported in the literature. Thus, the range of the results (SO_3) on three samples from different localities in Idaho (*99; 119, p. 210; 143*) is 1.77 to 2.74 percent. Pardee (*134*) found 2.10 percent in one sample of Montana phosphate; Mansfield (*119, p. 210*) reported 2.34 and 2.98 percent in two samples of Utah rock; and the results on phosphate from South Carolina (*126, 127, 137*) ranged from 0.25 to 2 percent, expressed as SO_3. Small amounts of sulphur, 0.08 to 0.66 percent, have been reported in the phosphates from Johnson County, Tenn. (*90*), and traces have been found in North Carolina (*40*) and Oklahoma (*179, 180*) phosphates.

Relatively little information on the condition of the sulphur in phosphate rock is available. Published figures for sulphur trioxide in Florida land pebble (*58, p. 30*) range from 0.42 to 1.60 percent, with an average of 0.86 percent. The average of Memminger's results for sulphate sulphur (SO_3) on four samples of commercial Tennessee blue rock (black phosphate) is 2.70 percent, the range being 2.30 to 3.32 percent (*124*). The same author's results for pyritic sulphur in 14 samples of this material range from 0.40 to 3.71 percent in terms of SO_3, the average being 2.09 percent. In five samples of commercial blue rock, Hook (*81*) reported quantities of pyrite equivalent to 0.99 to 2.71 percent SO_3, with an average of 1.99 percent. Jones (*92*) found 2.24 percent sulphate and 1.72 percent iron sulphide in a sample of phosphate from Woodruff Creek, Rich County, Utah. Shepard (*182*) stated that the South Carolina phosphates rarely contain more than 1 percent of iron pyrites.

Table 17 shows that a considerable portion of the total sulphur is present as sulphate in all phosphates analyzed, except Florida hard rock. Furthermore, the sulphur is usually present in more than one inorganic form. Small quantities of acid-insoluble sulphate frequently occur, particularly in Florida land pebble. On treatment with acid, measurable quantities of hydrogen sulphide were evolved from Florida land pebble, and somewhat larger amounts from Idaho and Wyoming phosphates. This form of sulphur was not found in Florida hard rock, pyrite-free Tennessee brown rock, Montana, north-African, and the island phosphates. Relatively large amounts of pyritic sulphur are present in Tennessee blue rock and phosphatic limestone. The range of results on the former, 1.37 to 5.21 percent in terms of SO_3, is considerably higher than the range of previous figures for pyritic sulphur in blue rock. Somewhat smaller percentages of acid-insoluble sulphide were found in South Carolina and Wyoming phosphates and in one sample of Tennessee brown rock. Florida land pebble and hard rock, most samples of Tennessee brown rock, and the Montana, Idaho, and north-African phosphates do not contain significant quantities of acid-insoluble sulphide.

A comparison of the results for total sulphur with the sum of the results for the four inorganic forms of sulphur (table 17) shows that not all the sulphur is recovered in the fractional determinations. As indicated in the last column of this table, the differences range from 0.01 percent on Florida land pebble to 0.81 percent on phosphate from Conda, Idaho. Moreover, the greatest differences occur in material rich in organic carbon (table 18). In view of this and the fact that the organic material separated from several types of phosphate is relatively high in sulphur (table 20), it is concluded that the figures in the last column of table 17, aside from the relatively small analytical errors accumulated therein, give a good indication of the amounts of organic sulphur present in these materials. It has been shown in a recent paper (*74*) that the figures for organic sulphur arrived at in this manner are usually in good agreement with those obtained for acid-insoluble organic sulphur, as determined by Eschka's method on the rock residue insoluble in hydrochloric acid (1 to 4).

ORGANIC MATTER, NITROGEN, AND WATER

The presence of appreciable quantities of organic matter in domestic phosphate rock is well known, but very few quantitative figures on its occurrence are available. Clarke (*32, p. 553*) reported 0.12 to 0.22 percent of organic carbon in three samples of Florida hard rock. With the exception of these figures, the available data, so far as the authors are aware, are limited to qualitative results and figures for "organic matter and combined water," as determined from the ignition loss. The phosphates of Idaho, Utah, and Wyoming contain relatively large amounts of organic material, which in some instances is oil-bearing (*119, p. 211*). Nitrogen, in amounts ranging from a trace to 0.21 percent, has been reported in South Carolina phosphates (*127*).

Results for organic carbon in 29 samples of phosphate rock, as determined by the combustion method, are given in table 18. Except the burning of pyrite-bearing materials at 600° C., the combustions were made at 800° C., and the figures thus obtained were corrected for any carbon dioxide evolved from carbonates during the heating. Elemental carbon, if present, is included with the organic carbon.

TABLE 18.—*Organic carbon, nitrogen, and total water in phosphate rock*

Sample no.	Type or source of phosphate	P_2O_5	Organic carbon[1]	Nitrogen	Total water[2]
		Percent	*Percent*	*Percent*	*Percent*
619	Florida land pebble	30.98	0.33	0.018	2.27
[3] 910	do	31.09	.33	.006	2.57
947	do	31.28	.29	.008	2.49
439	do	33.22	.25	([4])	1.88
[3] 912	do	35.37	.38	.013	1.35
771	Florida hard rock	31.25	.52	.018	3.40
[3] 932	do	35.99	.18	.005	1.48
[3] 728	Florida soft	31.80	.16	.018	3.85
[3] 726	Florida waste pond	23.48	.22	.024	5.81
915	do	23.63	.47	.044	8.18
[5] 56	Tennessee brown rock	31.28	[6] .25	.023	[6] 1.66
762	do	33.73	.29	.015	1.30
[3] 906	do	34.39	.09	.006	1.29
[3] 908	do	34.44	.11	.004	1.31
772	Tennessee blue rock	30.45	[6] .36	.034	[6] 1.84
[3] 1030	do	30.97	[6] .20	.021	[6] 1.06
[3, 7] 1049	do	31.22	[6] 1.46	.26	[6] 2.42
[3] 1048	Tennessee white rock	30.20	.09	.016	1.55
[3] 1031	do	35.80	.26	.033	2.53
454	Idaho, Conda	32.24	2.29	.091	1.96
[8] 973	do	32.53	2.35	.10	1.90
[3] 1009	Montana, Garrison	31.39	.14	.008	1.10
[3] 1010	do	37.47	.09	.009	.60
[3] 948	Wyoming, Cokeville	30.19	[6] 2.69	.11	[6] 1.50
1138	South Carolina land rock	27.85	[6] .51	.051	[6] 3.31
552	Tunis, Gafsa	27.55	.86	.047	3.05
1162	Morocco	35.11	.17	.018	1.44
985	Curacao Island	38.59	.17	.013	2.29
[3, 9] 904	Connetable Islands	54.51	.28	.049	1.88

[1] Including elemental carbon.

[2] Unless indicated otherwise, these figures are for total water at 800° C. and do not include water driven off at 105° C.

[3] Air-dried material.

[4] Not determined.

[5] Bureau of Standards standard sample no. 56.

[6] Determination made at 600° C.

[7] Kidney phosphate.

[8] Crushed rock dried in a coal-fired rotary kiln.

[9] Hydrated aluminum phosphate. Sample lost 22.58 percent water when heated to constant weight at 105° C.

It will be noted that the phosphates from Conda, Idaho, and Cokeville, Wyo., are by far the richest in organic carbon. Whereas the carbon content of these samples ranges from 2.29 to 2.69 percent, the Tennessee kidney phosphate (no. 1049) is the only other sample that contains more than 1 percent. The results on the other samples of domestic phosphates range from 0.09 to 0.52 percent, and this range also includes the samples of Morocco and Curacao and Connetable Islands phosphates.

Before being used in the manufacture of phosphoric acid by the sulphuric acid process, the Conda, Idaho, rock is calcined at about 700° C. to remove the major portion of the organic matter, which would otherwise seriously foul the acid and apparatus (*99*). When Florida pebble phosphate is treated with dilute sulphuric acid for the manufacture of phosphoric acid, the foam formed by the evolution of carbon dioxide is stabilized to such an extent by the organic matter present in the rock that it sometimes seriously interferes with factory operation. Formation of a stable foam may be prevented by adding small quantities of crude mineral oil to the mixing vessel (*72*). Some of the pebble-phosphate mining companies calcine the rock to remove organic matter and other volatile constituents (*125*).

The materials richest in carbon also contain the largest percentages of nitrogen (table 18). Thus, the nitrogen figures for Idaho and Wyoming phosphates are approximately 0.1 percent, and that for the sample of Tennessee kidney phosphate (no. 1049) is 0.26 percent, in comparison with a range of 0.004 to 0.051 percent for all other samples analyzed. As indicated by its light color, phosphate from Paris, Idaho, carries much less organic matter than that from the Conda locality, and it may be noted in this connection that a sample of the Paris phosphate, not included in table 18, contained only 0.02 percent of nitrogen.

Figures for total water, exclusive of moisture driven off at 105° C., are given in the sixth column of table 18. The results were obtained in connection with the organic-carbon determinations and therefore include water derived from combustion of organic matter. Because of the uncertainty as to whether all the combined water is driven off at the temperatures employed in the carbon determinations, the figures may be somewhat low. Excluding results on the Florida soft and waste-pond phosphates, the results for total water range from 0.6 percent in high-grade Montana phosphate (no. 1010) to 3.4 percent in low-grade Florida hard rock (no. 771). Tennessee brown rock contains, in general, less water than the other types of phosphate, except Montana phosphate. As would be expected, the Florida soft and waste-pond phosphates show considerably higher percentages of water than do the rock phosphates.

Organic carbon in several samples was determined by isolation and combustion according to the method recommended by Fieldner, Selvig, and Taylor (*48*) for the analysis of carbonate rocks. As pointed out in a previous paper (*74*), any soluble organic material is lost in the filtrates, and losses may also occur as a result of hydrolytic and oxidation processes during the digestion with acid and the subsequent filtration and washing. In comparison with the figures obtained by direct combustion of the rocks, the results given in the fourth column of table 19 indicate considerable losses of carbon in Florida land pebble and hard rock as a result of the isolation treatment. The results by the two methods are in very good agreement, however, on Tennessee brown and blue rock and Idaho phosphate.

TABLE 19.—*Combined water in phosphate rock*

Sample no.	Type or source of phosphate	Organic carbon		H_2O		Total H_2O by combustion at 800° C.	Combined H_2O
		By direct combustion of rock	By isolation and combustion	From combustion of isolated organic matter	Equivalent to organic C found by direct combustion[1]		
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
[2] 910	Florida land pebble	0.33	0.18	0.14	0.26	2.57	2.31
[2] 912	do	.38	.11	.12	.41	1.35	.94
771	Florida hard rock	.52	.24	.16	.35	3.40	3.05
[2] 932	do	.18	.06	.04	.12	1.48	1.36
[2] 906	Tennessee brown rock	.09	.11	.04	.03	1.29	1.26
[2] 908	do	.11	.14	.07	.06	1.31	1.25
[2] 930	Tennessee blue rock	.20	.28	.16	.11	[3] 1.06	.95
454	Idaho	2.29	2.33	.85	.84	1.96	1.12
[4] 973	do	2.35	2.22	.77	.82	1.90	1.08

[1] Calculated on the assumption that the ratio of H_2O to C is the same in the isolated organic material as in that present in the original rock.
[2] Air-dried material.
[3] Combustion at 600° C.
[4] Crushed rock dried in a coal-fired rotary kiln.

Assuming that the ratio of water to organic carbon is the same in the isolated material as in the organic matter originally present in the rock, the water equivalent to the organic carbon found in the original rock by direct combustion may be calculated. If the figure thus obtained is subtracted from the total water found by direct combustion of the sample, a figure is obtained indicative of the amount of water associated with the inorganic constituents of that particular sample. The results for combined water given in the last column of table 19 were obtained in this way. Despite the accumulation of errors in these figures, as discussed elsewhere (*74*), it is the opinion of the authors that they give a good indication of the amounts of combined water which may be expected in the domestic phosphate rocks. Although these analyses indicate a range of about 1.0 to 1.5 percent in most types of phosphate, the lower grades of Florida land pebble and hard rock contain larger quantities of combined water.

Large-scale separations of the organic matter were made on five representative samples of commercial phosphates, using the procedure of Fieldner, Selvig, and Taylor (*48*). The greater portion of the quartz was removed by decantation during the early stages of the separations, and the isolated organic matter was dried at 105° C. The elementary analyses of the isolated materials (table 20) indicate that the composition of the organic matter present in different types of phosphate rock varies within rather wide limits. In particular, the material obtained from Florida hard rock is characterized by relatively low percentages of carbon and nitrogen, and by very high percentages of sulphur and ash. Furthermore, the results on the two samples of Florida land pebble indicate that the composition, especially the carbon content, of the material isolated from different samples of the same type of phosphate may also be subject to considerable variation. In all cases, iron oxide was the principal constituent of the ash of the isolated materials.

TABLE 20.—*Composition of organic material isolated from phosphate rock*

Sample no.	Type or source of phosphate	Weight of rock used in separation	Color of organic material	Elementary analysis				
				Ash[1]	C	H	N	S
		Grams		*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
910	Florida land pebble	200	Dark brown	2.50	68.3	5.26	3.41	7.32
912	do	200	do	12.6	53.1	4.39	1.68	10.2
932	Florida hard rock	400	Brownish black	50.2	22.6	2.08	.16	30.1
908	Tennessee brown rock	400	Dark brown	9.53	60.8	3.41	3.15	8.11
[2] 973	Idaho	30	Black	2.32	61.3	2.62	2.07	7.90

[1] Principally iron oxides.

[2] Crushed rock dried in a coal-fired rotary kiln; other samples were air-dried.

The data in tables 3 to 6 show that, on a number of samples, figures for ignition loss are given instead of those for total water plus organic carbon and nitrogen. When corrected for the carbon dioxide present as carbonates in the original sample, the figures for ignition loss are often considered to indicate the amounts of combined water and organic matter present. It has been shown (*74*), however, that in the case of phosphate rock the value of this determination is vitiated by the volatilization of fluorine and silicon, which becomes serious at temperatures as low as 1,000° C. and progressively increases at higher temperatures; by incomplete decomposition of the carbonates at 1,000° C., as much as 1 percent of carbon dioxide sometimes remaining in the residue after ignition to constant weight at this temperature; and by the erratic behavior of pyrite, which is a common constituent of some types of phosphate. The figures for ignition loss given in the tables have been corrected for the total carbonate carbon present in the original samples, but not for the volatilization of fluorine and silicon and for the carbon dioxide remaining after ignition. With samples containing pyrite, the figures for ignition loss have also been corrected for the oxidation of pyritic sulphur, as determined from analyses of the original samples and the ignition residues (*74*).

Data on the percentages of moisture lost from various types of phosphates upon drying to constant weight at 105° C. are given in table 21. Excluding the results on the Florida soft and waste-pond phosphates, the results indicate that the moisture content of phosphate rock usually ranges from about 0.30 to 1.25 percent. The range is higher in South Carolina land rock and lower in Montana rock. The samples include both air-dried and commercial kiln-dried materials. On the basis of their moisture content, however, no distinction can be made between the kiln-dried and air-dried samples of a particular type of rock. When rock that has been kiln dried by the customary commercial methods is allowed to remain in contact with the air until equilibrium with the atmospheric moisture is established it will contain approximately the same percentage of moisture as will an air-dried sample of the same rock.

TABLE 21.—*Moisture content of phosphate rock*

Type or source of phosphate	Samples analyzed	H_2O driven off at 105° C.	
		Range	Average
	Number	*Percent*	*Percent*
Florida land pebble	11	0.50–1.05	0.72
Florida hard rock	4	.50–1.27	.73
Florida soft	4	.44–2.80	1.32
Florida waste pond	3	2.51–3.48	3.07
Tennessee brown rock	6	.38–.82	.65
Tennessee blue rock	5	.46–2.34	1.07
Tennessee white rock	2	.30–.48	.39
Tennessee phosphatic limestone	2	.39–.52	.45
Idaho	3	.50–1.27	.89
Montana	3	.20–.42	.28
Wyoming	1	----------	.35
South Carolina land rock	2	.80–1.89	1.35
Island deposits [1]	5	.28–.88	.49
Tunis, Gafsa	1	----------	2.20
Morocco	1	----------	.95

[1] Including samples from Christmas, Curacao, Nauru, and Ocean Islands.

ACID-INSOLUBLE PHOSPHORIC ACID, ALUMINUM, IRON, TITANIUM, CALCIUM, AND MAGNESIUM

Determinations of hydrochloric acid-insoluble phosphoric acid, aluminum, iron, titanium, calcium, and magnesium were made on several samples of the various types of phosphate rock. The insoluble residues were prepared by the procedure of Lundell and Hoffman (*104*), which involves treating 2.5 grams of the rock powder in a platinum dish with 50 cubic centimeters of 1 to 1 hydrochloric acid and digesting on the simmering steam bath for exactly 1 hour. The residue was filtered off, washed with 1 to 20 hydrochloric acid, fused with sodium carbonate and potassium nitrate, and the solution of the melt was analyzed by the methods mentioned previously (p. 17).

The results given in table 22 show that, with a single exception (Florida waste-pond phosphate no. 726), all the samples of domestic phosphate contained insoluble phosphoric acid in amounts ranging from 0.01 percent in Tennessee brown rock no. 587 to 0.13 percent in Idaho rock no. 973. The majority of the samples, however, did not contain more than 0.02 percent, and the average for all samples is 0.03 per cent of insoluble phosphoric acid. Lundell and Hoffman (*104*) state that Bureau of Standards standard sample no. 56 (Tennessee brown-rock phosphate) contains 0.02 to 0.03 percent of phosphoric acid that is insoluble in aqua regia when the sample is digested according to the method of the Association of Official Agricultural Chemists (*6, p. 15*). Determinations on this sample by the authors gave an average of 0.02 percent of phosphoric acid insoluble in aqua regia, which is in exact agreement with the figure obtained for phosphoric acid insoluble in 1 to 1 hydrochloric acid. Similar determinations were not made on the other samples. The state of combination of the acid-insoluble phosphoric acid is not known.

TABLE 22.—*Hydrochloric acid-insoluble phosphoric acid, aluminum, iron, and titanium in natural phosphates*

Sample no.	Type or source of phosphate	P_2O_5		Al_2O_3		Fe_2O_3		TiO_2	
		Total	Insoluble	Total	Insoluble	Total	Insoluble	Total	Insoluble
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
910	Florida land pebble	31.09	0.02	1.11	0.07	2.59	0.03	0.072	0.035
947	do	31.28	.05	.97	.08	1.69	.00	.064	.026
790	do	31.40	.02	.99	.25	1.62	.00	.06	(1)
439	do	33.22	.02	1.01	.00	1.90	.24	.05	.027
622	do	33.56	.04	.99	.00	.86	.11	.03	.010
912	do	35.37	.05	1.05	.02	.70	.16	.060	.020
771	Florida hard rock	31.25	.02	2.61	.00	1.83	.24	.06	(1)
932	do	35.99	.02	.52	.00	.69	.24	.039	.019
727	Florida waste pond	21.63	.03	13.73	3.73	2.57	.65	.22	(1)
726	do	23.48	.00	11.49	2.03	3.91	.55	.36	(1)
915	do	23.63	.06	16.07	3.48	4.25	.33	.30	.054
1091	Florida soft	25.47	.03	10.49	.93	3.26	.21	.17	.060
580	do	29.49	.03	23.05	.00	3.28	.20	.19	.050
728	do	31.80	.02	5.82	.02	1.54	.05	.11	(1)
443	do	34.04	.02	2.08	.00	.86	.04	.05	.013
587	Tennessee brown rock	30.17	.01	2.72	.59	3.43	.50	.16	.029
[2] 56	do	31.28	.02	3.06	.86	3.30	.85	.08	.035
762	do	33.73	.02	1.78	.05	2.25	.18	.05	(1)
906	do	34.39	.02	1.17	.19	3.42	.53	.05	.024
908	do	34.44	.02	1.16	.40	2.52	.07	.07	.024
772	Tennessee blue rock	30.45	.03	.72	.08	3.54	1.33	.05	(1)
930	do	30.97	.03	1.22	.53	3.42	2.83	.086	.019
[3] 1049	do	31.22	.04	1.19	.30	1.79	1.28	.081	.010
448	do	32.03	.03	.61	.05	3.30	.89	.05	.025
449	do	33.65	.03	.89	.14	2.35	1.78	.06	.016
1048	Tennessee white rock	30.20	.02	1.39	.00	1.75	.23	.075	.02
917	Tennessee phosphatic limestone	11.08	.02	.27	.07	1.95	1.11	.038	.01
550	Idaho, Paris	32.21	.02	1.90	.41	.97	.27	.09	.010
973	Idaho, Conda	32.53	.13	1.16	.27	.87	(1)	.06	(1)
948	Wyoming	30.19	.08	1.19	.42	.87	.57	.10	.008
[4] 904	Connetable Islands	54.51	.69	36.92	2.54	4.43	.09	.16	.10

[1] Not determined.
[2] Bureau of Standards standard sample no. 56.
[3] Kidney phosphate.
[4] Hydrated aluminum phosphate.

In the Florida waste-pond phosphates, Idaho and Wyoming rocks, and some samples of Tennessee brown and blue rocks, a comparatively large portion of the aluminum is insoluble in 1 to 1 hydrochloric acid. On the other hand, Florida land pebble usually contains very little acid-insoluble aluminum, and none was found in two samples of Florida hard rock. The insoluble aluminum is probably present in the form of complex silicates.

Except in two samples of Florida land pebble, acid-insoluble iron was found in all samples analyzed, the amounts ranging from 0.03 to 2.83 percent Fe_2O_3. The presence of pyrite accounts for a large portion of the insoluble iron in Tennessee blue rock and phosphatic limestone and Wyoming rock.

All the samples contained small quantities of acid-insoluble titanium (not more than 0.06 percent TiO_2 in the domestic phosphates).

Analyses of five samples showed the presence of not more than 0.05 percent of insoluble calcium oxide (table 23). The insoluble magnesium content of these samples ranged from 0.06 to 0.13 percent MgO, or approximately 30 to 100 percent of the total magnesium present.

TABLE 23.—*Hydrochloric acid-insoluble calcium and magnesium in phosphate rock*

Sample no.	Type or source of phosphate	CaO		MgO	
		Total	Insoluble	Total	Insoluble
		Percent	*Percent*	*Percent*	*Percent*
790	Florida land pebble	47.37	0.05	0.14	0.09
771	Florida hard rock	42.52	.05	.21	.06
762	Tennessee brown rock	47.62	.04	.06	.06
772	Tennessee blue rock	44.51	.01	.30	.10
973	Idaho	45.99	.08	.31	.13

COMPOSITION OF BONE ASH

The elements that occur in domestic phosphate rock usually occur also in bone ash. A comparison of the results of analyses (tables 3–6, and 8) indicates that bone ash usually contains higher percentages of magnesium, sodium, copper, zinc, and chlorine, and lower percentages of iron, potassium, titanium, manganese, chromium, vanadium, arsenic, silicon, sulphur, and fluorine than are present in phosphate rock. Aluminum was not found in the particular sample of bone ash analyzed. It should be borne in mind that this sample was a commercial product, and some of the elements found may owe their presence to contamination with foreign materials.

It will be noted that the analysis on bone ash totals only about 99 percent (table 6). This deficiency is attributed to incomplete expulsion of the water at 800° C. The total recovery was not improved by using, instead of the figure for total water and organic carbon, the figure for ignition loss (corrected for carbon dioxide) obtained by heating a sample to constant weight in a muffle furnace at 1,000° C. When, however, a sample was heated to constant weight at 1,250° C. in a tube furnace in a current of air dried by sulphuric acid there was a considerable increase in the ignition loss. Analysis of the ignition residue showed no significant loss of sulphur and alkalies. By using the figure for ignition loss at 1,250° C. the total analysis of the bone ash was increased to 99.89 percent. These results show that a considerable portion of the water in bone ash cannot be driven off at temperatures below about 1,250° C.

COMPOSITION OF MECHANICAL SEPARATES FROM NATURAL PHOSPHATES

With the exception of some of the furnace processes, practically all methods of converting phosphate rock into fertilizer materials and other products involve grinding the rock at some stage of the operation. During recent years, considerable stress has been placed on the importance of the fine grinding of rock that is to be applied directly to the soil as a fertilizer. Inasmuch as phosphate rock is not a homogeneous material it is to be expected that the chemical composition of the ground material will not be the same in particles of different sizes, because of the differences in the hardness and the degree of resistance to grinding exhibited by the various individual components of the rock. Information on the composition of the mechanical fractions, not only of ground phosphate rock but also of the Florida soft and waste-pond phosphates in their natural finely divided condition, is therefore important.

MECHANICAL COMPOSITION OF NATURAL PHOSPHATES

The samples of hard phosphates, except certain samples of Tennessee brown rock which were ground on a commercial scale, were first crushed to about 10-mesh size and then ground to pass a 100-mesh sieve having openings 0.147 millimeter square. The grinding was done in a small rotary-disk power mill; the entire sample was run through the mill and the 100-mesh material sieved out, the operation being repeated until the sample was completely reduced to the desired fineness.

The Florida soft and waste-pond phosphates were obtained in the form of comparatively soft lumps, which were crushed to pass a 10-mesh sieve. Grinding during the crushing operation was avoided as much as possible, in order not to break up hard particles that might otherwise fail to disintegrate under the action of water and dispersing agents alone.

The mechanical composition of the samples was determined by the pipette method as modified by Alexander and Jacob (*4*) for the mechanical analysis of finely divided natural phosphates. The ranges of particle size were the same as those customarily used in the mechanical analysis of soils in the United States; namely, (1) particles greater than 50μ in diameter; (2) particles from 50μ to 5μ; and (3) less than 5μ. Following the terminology used in soil analysis, the material comprising these classes will be designated as (1) "sand", (2) "silt", and (3) "clay". It should be noted, however, that these terms are used in this bulletin only for the sake of convenience, and in order to avoid any implication that the chemical composition of the material is similar to that of soil they will always be inclosed in quotation marks.

The results of the mechanical analyses (table 24) show that none of the waste-pond phosphates contained significant quantities of particles coarser than 50μ in diameter. The "sand" fractions, which were separated from the fine material by wet sieving, usually contained considerable organic matter in the form of rootlets and other fibrous vegetative residues. The soft phosphates contained much higher percentages of material coarser than 50μ than were present in the waste-pond phosphates and, as would be expected, the samples showed, in general, considerable differences in their mechanical composition.

TABLE 24.—*Mechanical composition of finely divided natural phosphates as determined by the pipette method of analysis*

Sample no.	Type or source of phosphate[1]	"Sand" >50μ	"Silt" 50μ to 5μ	"Clay" <5μ	<2μ
		Percent	*Percent*	*Percent*	*Percent*
725	Florida waste pond	0.3	15.9	83.3	72.3
726	do	.4	11.7	88.1	72.3
727	do	.5	10.1	89.1	78.9
824	do	2.2	15.9	82.6	70.8
825	do	2.2	15.9	81.8	70.6
826	do	1.0	19.5	80.7	69.5
827	do	.2	9.0	91.2	83.0
828	do	.1	12.8	87.0	75.4
915	do	1.7	13.9	84.0	71.9
443	Florida soft	52.1	18.7	29.1	21.4
580	do	40.0	5.2	54.8	54.5
728	do	32.5	15.7	51.3	40.3
910	Florida land pebble	42.1	45.5	12.4	8.2
912	do	35.4	45.5	19.0	13.6
947	do	47.7	42.8	9.4	6.2
932	Florida hard rock	33.2	43.9	22.8	17.7
906	Tennessee brown rock	47.0	37.2	15.7	11.4
908	do	36.7	46.4	16.4	11.4
930	Tennessee blue rock	35.7	54.1	9.2	1.6
973	Idaho	25.6	49.8	24.4	17.7
948	Wyoming	50.1	40.6	8.9	5.3

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[1] The soft and waste-pond phosphates were crushed to pass a 10-mesh sieve. The other samples were ground to pass a 100-mesh sieve having openings 0.147 millimeter (147μ) square.

The mechanical analyses of the ground phosphates show a considerable variation in the distribution of particle size with the different samples, particularly between the "sand" and "clay" fractions. This is owing not only to variations in the physical character of the phosphates themselves but also to the presence of variable quantities of admixed materials, such as quartz and silicates.

Mechanical analyses were also made on four samples of Tennessee brown-rock phosphate, which had been ground to different degrees of fineness as determined by screen analysis. These samples, which were prepared from a regular commercial grade of washed and kiln-dried rock taken from one deposit, were ground experimentally by one of the large phosphate-rock mining companies in a commercial ring-roll type mill equipped with an air-separator. The results of the mechanical analyses by sieving and by the pipette method, which are given in table 25, show that increasing the fineness of phosphate rock from 74.0 percent to 91.5 percent through a 400-mesh sieve does not result in an important increase in the amount of material finer than 5μ in diameter. The principal effect of the finer grinding is to decrease the amount of material coarser than 50μ in diameter.

TABLE 25.—*Mechanical composition of Tennessee brown-rock phosphate ground to different degrees of fineness*

Sieve analysis,[1] material through—				Mechanical analysis by pipette method				
100 mesh	200 mesh	300 mesh	400 mesh	"Sand"		"Silt" 50μ to 5μ	"Clay"	
				>100μ	100μ to 50μ		<5μ	<2μ
Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
99.0	91.0	79.3	74.0	2.2	15.3	62.5	19.6	13.2
98.7	94.0	83.5	77.5	1.0	9.9	68.0	20.7	14.2
99.7	98.0	92.1	86.3	.7	6.2	72.2	20.6	14.9
99.8	99.0	95.7	91.5	.3	2.7	71.8	24.8	17.2

[1] Analyses supplied by company furnishing the samples.

PREPARATION OF MECHANICAL SEPARATES

In order to obtain sufficient material for chemical analysis, mechanical separations into "sand," "silt," and "clay" sizes were made on 800-gram samples of the phosphates, prepared as described on pages 57 and 58. The method used for the separations has been described in detail by Alexander and Jacob (*4*), who have also discussed the preparation of the separates used in the present study.

A comparison of the results obtained by the large-scale separations with those obtained by the pipette method of mechanical analysis is given in table 26. In general, the results obtained by the two methods agree very closely. Duplicate determinations by the pipette method do not give results that will check more closely than those obtained on the Florida land-pebble and hard-rock phosphates by the large-scale separations and by the pipette method, respectively. The large-scale separation on waste-pond phosphate no. 726 was not performed so carefully as with the other samples, and quantitative figures were not obtained.

TABLE 26.—*Comparison of results of large-scale separations with analyses made by the pipette method*

Sample no.	Type or source of phosphate	"Sand", >50μ by —		"Silt", 50μ to 5μ by —		"Clay", <5μ by —		Solution and mechanical losses by —		"Clay" <2μ by pipette method
		Large-scale separation	Pipette method	Large-scale separation	Pipette method	Large-scale separation	Pipette method	Large-scale separation	Pipette method	
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
727	Florida waste pond	0.2	0.5	12.9	10.1	85.3	89.1	1.6	0.3	78.9
915	do	5.1	1.7	19.5	13.9	75.1	84.0	.2	.4	71.9
728	Florida soft	30.4	32.5	20.9	15.7	48.7	51.3	.0	.5	40.3
910	Florida land pebble	41.7	42.1	43.3	45.5	11.8	12.4	[1] 3.2	.0	8.2
912	do	35.1	35.4	45.4	45.5	19.2	19.0	.3	.1	13.6
947	do	48.2	47.7	42.0	42.8	9.6	9.4	.2	.1	6.2
932	Florida hard rock	33.7	33.2	43.8	43.9	22.3	22.8	.2	.1	17.7
906	Tennessee brown rock	46.2	47.0	38.8	37.2	14.0	15.7	1.0	.1	11.4
[2] 908	do	37.6	36.7	40.8	40.4	13.9	16.4	1.7	.5	11.4
[2] 948	Wyoming	49.8	50.1	43.6	40.6	6.6	8.9	.0	.4	5.3
973	Idaho	26.0	25.6	45.5	49.8	27.9	24.4	.6	.2	17.7

[1] A small portion of the "silt" and "clay" was accidentally spilled in this separation.
[2] Lithium oxalate used as a dispersing agent in the large-scale separation.

In addition to the large-scale separations into "sand," "silt," and "clay" fractions, quantities of colloidal material were also extracted from Florida soft and waste-pond phosphates and ground Tennessee brown-rock phosphate by means of the supercentrifuge. For this purpose, the soft and waste-pond phosphates were crushed to pass a 10-mesh sieve. The Tennessee brown rock was a commercially ground material prepared from washed and kiln-dried rock, and had a fineness of approximately 100 percent through a 100-mesh sieve. The method of separating the colloidal material, which has been described by Jacob, Hill, and Holmes (*85*), was the same as that outlined by Gile and coworkers (*55*) for the separation of colloid from soils, except that in no case was it necessary to use a dispersing agent.

As shown in table 27, the amounts of colloidal material obtained from the Tennessee brown rock and the Florida soft and waste-pond phosphates were 11.5, 38.6, and 60.1 percent, respectively. These figures are in fair agreement with the percentages of colloid indicated by the results of mechanical analyses and of water-absorption experiments. The mechanical-analysis figures are those obtained for "clay" finer than 2μ, and may be expected to be somewhat high, since it is hardly probable that all the particles finer than 2μ are colloidal. The size of the colloidal particles extracted from the phosphates was not determined, but, with the method of separation used, it is unlikely that very many, if any, exceeded 1μ in diameter, and the majority were probably 0.3μ and less in diameter. In estimating the percentages of colloid from the results of water-absorption experiments, the equation worked out by Robinson (*161*) for estimating the colloid content of soils has been used. In considering these results it is necessary to assume that the physical properties of the colloidal material in finely divided natural phosphates are similar to those of soil colloids. Unpublished data obtained in this bureau indicate that such an assumption is not far-fetched.

TABLE 27.—*Colloidal material in finely divided natural phosphates*

Sample no.	Type of phosphate	Colloid content		
		Extracted by means of supercentrifuge	As indicated by—	
			Mechanical analysis	Water absorption
		Percent	*Percent*	*Percent*
[1] 726	Florida waste pond	60.1	72.3	58.4
[2] 728	Florida soft	38.6	40.3	41.3
[3] 762	Tennessee brown rock	11.5	13.4	14.4

[1] 200 grams used for extraction of colloid.

[2] 300 grams used for extraction of colloid.

[3] 1,000 grams used for extraction of colloid.

CHEMICAL COMPOSITION OF SEPARATES

Data on the chemical composition of the mechanical separates are given in tables 28 to 30. In the case of the Florida soft and waste-pond phosphates, the results show that the "silt" fractions contain, as a general rule, higher percentages of calcium, phosphoric acid, and fluorine, and lower percentages of silica, total iron, and aluminum than do either the original materials or the other fractions. The silica tends to concentrate, either in the "sand" fractions as relatively coarse quartz grains, or in the "clay" and colloid fractions as amorphous silica and silicates. The aluminum in the waste-pond phosphates tends to concentrate in the "clay" and colloid fractions, whereas in the soft phosphate it is concentrated to a considerable extent in the "sand" fraction. In general, iron tends to concentrate to a slight extent in the "clay" fractions.

TABLE 28.—*Chemical composition of "sand", "silt", and "clay" fractions of Florida phosphates*

LAND-PEBBLE PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3 [1]	TiO_2	CO_2	F	SiO_2 [2]	Insoluble in 1:1 HCl	Ignition loss [3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*		
910	Original material	31.09	46.57	0.25	1.11	2.59	0.072	3.76	3.94	6.04	6.56	6.10	0.127	0.121
	"Sand", 147μ to 50μ	30.28	45.19	.23	.76	2.51	.064	3.52	3.70	9.05	9.57	5.74	.122	.116
	"Silt", 50μ to 5μ	32.02	47.64	.20	1.01	2.50	.068	3.65	3.89	4.47	4.90	6.12	.121	.114
	"Clay", <5μ	32.06	46.36	.32	2.23	3.72	.085	3.26	3.91	2.29	2.78	6.80	.122	.102
912	Original material	35.37	49.05	.08	1.05	.70	.060	1.48	3.95	6.34	6.70	2.79	.112	.042
	"Sand", 147μ to 50μ	33.85	47.38	.06	.85	.50	.054	1.45	3.70	11.13	11.52	2.45	.109	.043
	"Silt", 50μ to 5μ	36.01	49.30	.06	.94	.65	.056	1.38	3.82	4.88	5.19	3.02	.106	.038
	"Clay", <5μ	36.10	50.40	.15	1.97	1.00	.062	1.51	3.92	1.84	2.10	3.92	.109	.042
947	Original material	31.28	47.20	.20	.97	1.69	.064	3.70	4.04	6.52	6.74	5.99	.129	.118
	"Sand", 147μ to 50μ	30.97	45.96	.26	.87	1.57	.064	3.57	3.84	9.45	9.72	5.71	.124	.115
	"Silt", 50μ to 5μ	31.93	48.07	.26	.88	1.68	.072	3.74	4.08	4.77	5.03	6.52	.128	.117
	"Clay", <5μ	31.98	47.69	.30	1.60	2.34	.062	3.37	3.84	2.55	2.48	7.08	.120	.105

HARD-ROCK PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3 [1]	TiO_2	CO_2	F	SiO_2 [2]	Insoluble in 1:1 HCl	Ignition loss [3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
932	Original material	35.99	51.08	0.05	0.52	0.69	0.039	2.19	3.91	4.11	4.56	3.07	0.109	0.061
	"Sand", 147μ to 50μ	35.57	50.09	.06	.41	.51	.033	1.93	3.81	7.20	7.74	2.94	.107	.054
	"Silt", 50μ to 5μ	37.09	51.59	.06	.51	.69	.035	2.02	3.88	3.48	3.80	3.35	.105	.054
	"Clay", <5μ	37.13	51.14	.09	1.15	.69	.043	1.92	3.99	.63	1.12	3.88	.107	.052

SOFT PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3 [1]	TiO_2	CO_2	F	SiO_2 [2]	Insoluble in 1:1 HCl	Ignition loss [3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
728	Original material	31.80	41.61	0.22	5.82	1.54	0.11	1.87	3.33	9.80	9.67	5.75	0.105	0.059
	"Sand", >50μ	29.54	31.51	(4)	9.74	1.36	.08	(5)	2.62	18.76	19.23	7.01	.089	----------
	"Silt", 50μ to 5μ	36.33	48.65	(4)	3.40	.83	.09	----------	3.75	2.50	2.71	4.94	.103	----------
	"Clay", <5μ	32.90	44.58	(4)	5.17	1.18	.16	----------	3.18	6.77	7.00	5.44	.097	----------

WASTE-POND PHOSPHATE

726	Original material	23.48	30.89	0.55	11.49	3.01	0.36	1.70	[6] 2.08	18.10	20.02	7.34	0.089	0.072
	"Sand", >50μ	14.20	(4)	(4)	(4)	(4)	(4)	--------	.51	(4)	(4)	(4)	.036	--------
	"Silt", 50μ to 5μ	29.00	38.76	(4)	7.45	3.04	(4)	--------	[6] 2.76	10.51	(4)	(4)	.095	--------
	"Clay", <5μ	22.01	29.55	(4)	12.85	4.23	(4)	--------	[6] 2.10	19.47	(4)	(4)	.095	--------
727	Original material	21.63	28.70	.84	13.73	2.57	.22	1.00	[6] 1.94	22.94	27.47	6.86	.090	.046
	"Sand", >50μ	16.40	5.72	(4)	10.88	7.42	.17	--------	(4)	16.60	22.39	26.37	--------	--------
	"Silt", 50μ to 5μ	27.05	34.07	(4)	9.05	2.16	.24	--------	[6] 2.40	16.10	18.21	6.01	.089	--------
	"Clay", <5μ	21.09	27.65	(4)	13.56	2.71	.20	--------	[6] 1.97	24.36	20.32	7.13	.093	--------
915	Original material	23.63	25.20	.21	16.67	4.25	.36	1.26	[6] 1.84	16.34	19.40	10.60	.078	.053
	"Sand", >50μ	19.47	21.31	.07	12.22	3.78	.23	--------	[6] 1.53	29.32	39.01	10.73	.079	--------
	"Silt", 50μ to 5μ	27.60	31.10	.01	12.29	3.58	.29	--------	[6] 2.37	12.68	13.82	9.79	.086	--------
	"Clay", <5μ	23.36	24.10	.20	17.12	4.76	.33	--------	[6] 1.73	16.37	19.05	10.81	.074	--------

[1] Total Fe.

[2] Without regard for F.

[3] Constant weight at 1,000° C. after drying at 105°.

[4] Not determined.

[5] Not determined on mechanical fractions of soft and waste-pond phosphates.

[6] Determined by the fusion-acid extraction method (*150*).

TABLE 29.—*Chemical composition of "sand", "silt", and "clay" fractions of Tennessee, Idaho, and Wyoming phosphates*

TENNESSEE BROWN-ROCK PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	CO_2	F	SiO_2[2]	Insoluble in 1:1 HCl	Ignition loss[3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*		
906	Original material	34.39	47.61	0.10	1.17	3.42	0.05	1.31	3.77	4.86	5.71	3.64	0.110	0.038
	"Sand", 147μ to 50μ	34.77	48.30	(4)	.71	3.11	(4)	.88	3.78	5.56	5.92	2.28	.109	.025
	"Silt", 50μ to 5μ	35.06	48.39	(4)	1.06	3.24	(4)	1.23	3.84	4.20	4.54	2.46	.110	.035
	"Clay", $< 5\mu$	31.69	43.86	(4)	3.79	4.74	(4)	1.13	3.36	6.83	7.65	3.86	.106	.036
908	Original material	34.44	49.19	.02	1.16	2.52	.07	1.96	3.81	4.75	5.46	2.90	.111	.057
	"Sand", 147μ to 50μ	34.49	49.68	.01	.70	2.16	.05	1.39	3.77	5.58	6.02	2.62	.109	.040
	"Silt", 50μ to 5μ	34.85	50.23	.01	.77	2.36	.07	1.50	3.77	4.51	5.04	3.15	.108	.043
	"Clay", $< 5\mu$	32.35	46.27	.06	3.02	3.67	.12	1.27	3.50	5.60	6.96	4.36	.108	.039

IDAHO PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	CO_2	F	SiO_2[2]	Insoluble in 1:1 HCl	Ignition loss[3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
973	Original material	32.53	45.99	0.31	1.16	0.87	0.06	1.72	3.33	6.02	6.86	5.89	0.102	0.053
	"Sand", 147μ to 50μ	35.69	51.25	.01	.17	.16	.03	1.62	3.55	1.65	2.38	5.25	.099	.045
	"Silt", 50μ to 5μ	32.96	45.13	.02	.63	.40	.08	1.59	3.49	7.67	8.48	5.36	.106	.048
	"Clay", $< 5\mu$	28.60	39.20	.17	3.09	2.04	.15	.86	3.01	9.09	12.40	8.55	.105	.030

WYOMING PHOSPHATE

Sample no.	Mechanical fraction	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	CO_2	F	SiO_2[2]	Insoluble in 1:1 HCl	Ignition loss[3]	$\frac{F}{P_2O_5}$	$\frac{CO_2}{P_2O_5}$
948	Original material	30.19	46.22	0.08	1.19	0.87	0.10	4.13	3.51	5.69	7.54	6.78	0.117	0.137
	"Sand", 147μ to 50μ	33.41	49.41	.09	.46	.46	.06	3.35	3.62	3.11	3.96	5.81	.108	.100
	"Silt", 50μ to 5μ	26.73	42.81	.08	1.59	1.11	.14	3.41	3.29	9.56	11.77	5.83	.123	.128
	"Clay", $< 5\mu$	23.67	37.28	.15	4.47	2.22	.15	1.05	2.93	9.76	14.08	15.22	.124	.044

[1] Total Fe.

[2] Without regard for F.

[3] Constant weight at 1,000° C. after drying at 105° C.

[4] Not determined.

TABLE 30.—*Chemical composition of colloidal material extracted from natural phosphates*

Sample analyzed	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3[1]	TiO_2	Na_2O	K_2O	MnO	Cr_2O_3	V_2O_3	SiO_2[2]	CO_2	F	Cl	SO_3[3]	Ignition loss[4]	Total	
																		Uncorrected	Corrected[5]
FLORIDA SOFT PHOSPHATE NO. 728																			
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
Original material	31.80	41.61	0.22	5.82	1.54	0.11	0.26	0.14	0.014	0.018	0.00	10.67	1.87	3.33	Trace.	0.17	5.75	103.32	100.05
Colloid	31.43	41.76	.30	6.37	1.60	.23	.13	.30	.023	.016	(6)	10.60	1.74	[7] 2.09	(6)	.01	5.81	103.31	100.31
FLORIDA WASTE-POND PHOSPHATE NO. 726																			
Original material	23.48	30.89	0.55	11.49	3.91	0.36	0.20	0.47	0.022	0.028	0.02	10.78	1.70	[7] 2.08	0.005	0.14	7.34	102.47	99.89
Colloid	18.12	23.73	.70	15.87	5.12	.53	.12	.65	.048	.038	(6)	26.20	.97	[7] 1.61	(6)	.01	8.35	102.07	100.42
TENNESSEE BROWN-ROCK PHOSPHATE NO. 702																			
Original material	33.73	47.62	0.06	1.78	2.25	0.05	0.14	0.31	0.27	0.007	0.00	7.49	1.71	3.87	0.005	0.81	3.03	103.13	99.79
Colloid	25.02	33.68	.05	9.97	4.57	.23	.31	1.19	.57	.010	.00	16.48	1.17	[7] 2.64	(6)	.10	6.96	102.95	100.67

[1] Total Fe.
[2] Total Si.
[3] Total sulphur.
[4] Constant weight at 1,000° C. after drying at 105° C.
[5] Corrected for CO_2 and O equivalent of F and Cl.
[6] Not determined.
[7] Determined by fusion-acid extraction method (*150*).

The data given in table 28 show that the silica in the ground Florida land-pebble and hard-rock phosphates concentrates to a marked extent in the "sand" fractions, and that there is a progressive and significant decrease in the percentage of silica as the particle size decreases. This is undoubtedly because of the presence of considerable quantities of quartz, which, in comparison with the phosphate, is relatively difficult to grind. In general, iron and aluminum tend to concentrate in the "clay" fractions, whereas calcium and phosphoric acid concentrate to a small extent in the "silt" and "clay" fractions.

Contrary to the results obtained on the Florida phosphates, there is no very considerable variation in the silica content of the "sand," "silt," and "clay" fractions separated from the Tennessee brown-rock phosphates (table 29), although the silica tends to concentrate somewhat in the "sand" and "clay" fractions. On the other hand, silica concentrated to a very marked extent in the colloid fraction of no. 762 (table 30). The percentages of iron and aluminum in the fractions increase with decrease in particle size, the aluminum, in particular, concentrating to a marked extent in the "clay" and colloid fractions. Calcium and phosphoric acid tend to concentrate to a slight extent in the "silt" fractions, whereas the "clay" fractions contain decidedly smaller percentages. There was a very marked decrease in the percentages of calcium and phosphoric acid in the colloid fraction as compared with those in the original material.

In the Idaho and Wyoming phosphates (table 29) the percentages of silica, iron, and aluminum increase considerably as the particle size decreases, the iron and aluminum concentrating particularly in the "clay" fractions. The percentages of calcium and phosphoric acid decrease to a significant extent with decrease in particle size.

As a general rule, the fluorine-phosphoric acid ratios are approximately constant in the mechanical fractions of a particular sample and are close to the ratio in the original phosphate. There is some variation from this rule in certain of the soft and waste-pond phosphates. This is probably because of the presence of aluminum phosphate in these samples (p. 75).

There is, in general, a fair degree of constancy in the carbon dioxide-phosphoric acid ratios in the mechanical fractions of a particular sample. It will be noted, however, that the ratios in the fractions are almost invariably lower than the ratio in the original phosphate. Inasmuch as large volumes of water were used in making the mechanical separations, it is probable that the lower ratios in the mechanical fractions are caused, at least in part, by the dissolution of calcium carbonate during the process of separation.

AMMONIUM CITRATE- AND CITRIC ACID-SOLUBLE PHOSPHORIC ACID IN NATURAL PHOSPHATES

In fertilizer-control work in the United States, the neutral ammonium citrate method is used for the laboratory determination of available phosphoric acid in all phosphates and phosphatic fertilizers except basic slag, which is evaluated by the 2 percent citric acid method. Although the direct use of ground phosphate rock as a fertilizer is limited, in the United States, to about 30,000 to 40,000 tons annually, principally Tennessee brown rock, comparative data on the solubilities of the different types of domestic phosphates in neutral ammonium citrate and 2 percent citric acid solutions are, nevertheless, of general interest.

Citric acid-soluble phosphoric acid was determined by the method of the Association of Official Agricultural Chemists (*6, p. 27*), as devised for the evaluation of basic slag. Ammonium citrate-soluble phosphoric acid was determined by the former official method (*6, p. 17*), using 2-gram samples and digesting with 100 cubic centimeters of neutral ammonium citrate solution for 0.5 hour at 65° C. Shortly after this study was completed the official method for citrate-soluble phosphoric acid was changed to specify the use of 1-gram samples and the time of digestion was increased from 0.5 to 1 hour (*89; 98, p. 66; 166; 167*). The modified method when applied to such materials as dicalcium and tricalcium phosphates and raw, steamed, and naphtha-extracted bones (*84, 86, 87, 167*) gives significantly higher percentages of citrate-soluble phosphoric acid than does the old procedure, but with mineral phosphates and bone ash the results by the two procedures do not differ greatly. For example, with several samples of phosphate rock, apatite, and bone ash, the average increase in citrate-soluble phosphoric acid obtained by the modified method amounted to only 0.97 percent on the sample, or 2.3 percent on the total phosphoric acid. Although this increase is insignificant, the effect of the change in the method should be borne in mind in connection with the results for citrate-soluble phosphoric acid given in this publication.

All samples used in the ammonium citrate- and citric acid-solubility determinations were ground to pass a 100-mesh sieve. The ammonium citrate extracts were filtered by means of short Pasteur-Chamberland tubes (grade F), in order to obtain clear filtrates, since cloudy filtrates were usually obtained when the extracts were filtered through papers, even those of the closest texture. Neutral ammonium citrate solution was prepared by the official method (*6, p. 17*), using phenol red as an indicator, the pH values of the several solutions used during the course of this work ranging from 6.9 to 7 as determined potentiometrically by means of the hydrogen electrode.

The results of analyses (tables 31 and 32) indicate that the citrate-soluble phosphoric acid content of the domestic commercial types of phosphate rock ranges from about 0.3 to 2.5 percent on the sample or about 1 to 8 percent on the total phosphoric acid. Despite the fineness of the individual particles, Florida waste-pond phosphates contain, in general, smaller percentages of citrate-soluble phosphoric acid than do any of the domestic phosphate rocks, except the rock from Cokeville, Wyo. The Florida land-pebble and hard-rock and the South Carolina phosphates average highest in citrate-soluble phosphoric acid, followed in descending order by the Tennessee white-rock, Florida soft, Idaho, Montana, Tennessee blue-rock and brown-rock, Florida waste-pond, and Wyoming phosphates. The lower grades of Florida land pebble contain, in general, somewhat larger quantities of citrate-soluble phosphoric acid than do the higher grades, whereas the reverse is true with the Tennessee brown rock. In the other types of phosphate, there seems to be no definite relation between the grade of the rock and its citrate-soluble phosphoric acid content. As compared with the phosphate rocks in general, fluorapatite is very low in citrate-soluble phosphoric acid.

TABLE 31.—*Ammonium citrate- and citric acid-soluble phosphoric acid in Florida phosphates*

LAND-PEBBLE PHOSPHATE

Sample no.	Total P_2O_5	Citrate-soluble P_2O_5[1]	Citric acid-soluble P_2O_5[2]
	Percent	*Percent*	*Percent*
618	30.53	2.63	6.53
617	30.70	2.58	6.14
619	30.98	2.45	6.55
910	31.09	1.55	7.17
947	31.28	1.71	6.59
790	31.40	2.25	6.77
439	33.22	2.42	6.68
622	33.66	1.60	6.38
627	33.70	1.02	6.08
912	35.37	.77	6.67
898	35.55	1.18	6.25
Average	32.49	1.88	6.53

HARD-ROCK PHOSPHATE

Sample no.	Total P_2O_5	Citrate-soluble P_2O_5[1]	Citric acid-soluble P_2O_5[2]
771	31.25	2.13	6.87
589	34.68	.90	6.40
434	35.33	2.00	6.50
932	35.99	1.89	7.23
Average	34.31	1.73	6.76

SOFT PHOSPHATE

Sample no.	Total P_2O_5	Citrate-soluble P_2O_5[1]	Citric acid-soluble P_2O_5[2]
1091	25.47	2.11	8.02
580	29.40	.79	5.82
728	31.80	1.50	7.12
443	34.94	1.94	7.26
Average	30.43	1.50	7.06

WASTE-POND PHOSPHATE

Sample no.	Total P_2O_5	Citrate-soluble P_2O_5[1]	Citric acid-soluble P_2O_5[2]
826	15.34	0.09	1.21
828	10.83	.84	7.90
727	21.63	.75	6.35
827	22.20	.37	7.28
726	23.48	.97	7.12
825	23.48	.18	7.16
915	23.03	.34	7.50
824	24.24	.66	7.24
725	25.31	1.34	6.88
Average	22.14	.58	6.53

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[1] 2-gram samples digested for 30 minutes at 65° C. with 100 cubic centimeters of neutral ammonium citrate solution.

[2] 2-gram samples shaken for 30 minutes with 200 cubic centimeters of 2 percent citric acid solution.

TABLE 32.—*Ammonium citrate- and citric acid-soluble phosphoric acid in Tennessee and other phosphates*

Sample no.	Type or source of phosphate	Total P_2O_5	Citrate-soluble P_2O_5[1]	Citric acid-soluble P_2O_5[2]
		Percent	*Percent*	*Percent*
587	Tennessee brown rock	30.17	0.80	5.84
[3] 56	do	31.28	.77	5.74
504	do	32.85	.84	5.90
702	do	33.73	1.19	5.88
906	do	34.39	1.20	5.87
903	do	34.44	1.14	6.25
Average		32.81	.99	5.88
772	Tennessee blue rock	30.45	1.83	4.75
930	do	30.97	1.28	6.90
1040	do	31.22	.54	5.42
448	do	32.03	1.00	6.43
449	do	33.65	1.15	6.98
Average		31.66	1.16	6.10
1048	Tennessee white rock	30.20	1.64	5.94
1031	do	35.80	1.79	7.35
Average		33.00	1.71	6.64
1139	South Carolina land rock	26.92	2.51	7.83
1138	do	27.85	2.43	8.05
Average		27.38	2.47	7.94
550	Idaho	32.21	1.21	8.16
454	do	32.24	.87	5.95
973	do	32.53	1.56	6.05
Average		32.33	1.21	6.72
1009	Montana	31.39	1.02	4.87
1010	do	37.47	1.35	5.54
Average		34.43	1.18	5.20
948	Wyoming	30.19	.33	4.15
1162	Morocco	35.11	2.75	11.25
552	Tunis, Gafsa	27.55	2.21	10.08
985	Curacao Island	38.59	2.92	13.74
905	Fluorapatite	40.39	.67	2.18
971	Bone ash	40.36	3.31	11.29
[4] 904	Connetable Islands	54.51	3.30	.32

[1] 2-gram samples digested for 30 minutes at 65° C. with 100 cubic centimeters of neutral ammonium citrate solution.

[2] 2-gram samples shaken for 30 minutes with 200 cubic centimeters of 2 percent citric acid solution.

[3] Bureau of Standards standard sample no. 56.

[4] Hydrated aluminum phosphate.

The percentages of citric acid-soluble phosphoric acid in the various types of phosphate rock tend, as a general rule, to run parallel to the percentages of citrate-soluble phosphoric acid. The results (tables 31 and 32) indicate that the citric acid-soluble phosphoric acid content of the domestic rocks ranges from about 4 to 8 percent on the sample, or 14 to 29 percent on the total phosphoric acid. The Florida soft and waste-pond phosphates contain, in general, somewhat higher percentages of citric acid-soluble phosphoric acid than are found in the majority of samples of hard phosphates. It will be noted that the Curacao Island, Morocco, and Tunis phosphates are more soluble and fluorapatite is less soluble in 2 percent citric acid than are any of the domestic rocks. The aluminum phosphate from the Connetable Islands is practically insoluble in citric acid. Unlike the calcium phosphates, the phosphates of iron and aluminum are more soluble in neutral ammonium citrate solution than in 2 percent citric acid (*87*). Numerous results on the solubility of phosphates in citric acid solutions have appeared in the literature during the past 17 years (*2*, *3*, *87*, *157*, *159*).

The data in table 33 show that the percentages of ammonium citrate- and of citric acid-soluble phosphoric acid in the mechanical fractions of the ground phosphate rocks increase with decrease in particle size. In ammonium citrate-soluble phosphoric acid, the average increase in going from the "sand" to the "clay" fractions amounted to 1.58 percent on the sample, or 4.9 percent on the total phosphoric acid. In citric acid-soluble phosphoric acid, the average increase amounted to 1.91 percent on the sample, or 7.2 percent on the total phosphoric acid. The low ammonium citrate solubility of the phosphoric acid in the original sample of Wyoming phosphate follows through into the mechanical fractions. The percentages of ammonium citrate- and citric acid-soluble phosphoric acid in the Florida soft and waste-pond phosphates show no regular changes with decrease in particle size. The phosphoric acid in the "clay" fractions of these materials is, in general, less soluble in citrate solution than is the phosphoric acid in the "clay" fractions of the ground phosphate rocks.

TABLE 33.—*Effect of particle size on the solubility of natural phosphates in ammonium citrate and citric acid solutions*

FLORIDA LAND-PEBBLE PHOSPHATE

Sample no.	Mechanical fraction	Total P_2O_5	Citrate-soluble P_2O_5 [1]	Citric acid-soluble P_2O_5 [2]
		Percent	*Percent*	*Percent*
910	Original material	31.09	1.55	7.17
	"Sand"	30.28	.35	6.56
	"Silt"	32.02	1.71	7.27
	"Clay"	32.06	2.60	8.80
912	Original material	35.37	.77	6.67
	"Sand"	33.85	.51	6.21
	"Silt"	36.01	.60	6.71
	"Clay"	36.10	1.14	7.46
947	Original material	31.28	1.71	6.59
	"Sand"	30.97	.50	5.81
	"Silt"	31.93	1.51	6.87
	"Clay"	31.98	2.57	8.59
	FLORIDA HARD-ROCK PHOSPHATE			
932	Original material	35.99	1.89	7.23
	"Sand"	35.57	.98	6.12
	"Silt"	37.09	1.87	6.93
	"Clay"	37.13	2.41	8.20
	FLORIDA SOFT PHOSPHATE			
728	Original material	31.80	1.60	7.12
	"Sand"	29.54	1.13	6.36
	"Silt"	30.33	.72	7.84
	"Clay"	32.90	.96	7.84
	Colloid	31.43	.68	7.60

[1] 2-gram samples digested for 30 minutes at 65° C. with 100 cubic centimeters of neutral ammonium citrate solution.

[2] 2-gram samples shaken for 30 minutes with 200 cubic centimeters of 2 percent citric acid solution.

TABLE 33.—*Effect of particle size on the solubility of natural phosphates in ammonium citrate and citric acid solutions*—Continued

FLORIDA WASTE-POND PHOSPHATE

Sample no.	Mechanical fraction	Total P_2O_5	Citrate-soluble P_2O_5	Citric acid-soluble P_2O_5
		Percent	*Percent*	*Percent*
726	Original material	23.48	0.97	7.12
	"Sand"	14.20	1.57	(2)
	"Silt"	29.00	1.81	6.74
	"Clay"	22.01	1.65	7.30
	Colloid	18.12	.87	7.20
[4] 727	Original material	21.63	.75	6.35
	"Silt"	27.05	.45	8.80
	"Clay"	21.09	.86	7.45
915	Original material	23.63	.34	7.60
	"Sand"	19.47	.48	7.25
	"Silt"	27.60	.11	7.08
	"Clay"	23.38	.88	7.52

TENNESSEE BROWN-ROCK PHOSPHATE

Sample no.	Mechanical fraction	Total P_2O_5	Citrate-soluble P_2O_5	Citric acid-soluble P_2O_5
762	Original material	33.73	1.19	5.88
	Colloid	25.02	2.06	7.70
906	Original material	34.39	1.20	5.67
	"Sand"	34.77	.69	5.57
	"Silt"	35.06	1.28	6.07
	"Clay"	31.69	2.04	6.97
908	Original material	34.44	1.14	6.25
	"Sand"	34.49	.26	5.95
	"Silt"	34.85	.97	6.64
	"Clay"	32.35	1.62	7.70

IDAHO PHOSPHATE

Sample no.	Mechanical fraction	Total P_2O_5	Citrate-soluble P_2O_5	Citric acid-soluble P_2O_5
973	Original material	32.53	1.56	6.05
	"Sand"	35.69	.13	5.87
	"Silt"	32.96	1.09	6.45
	"Clay"	26.00	2.63	7.31

WYOMING PHOSPHATE

Sample no.	Mechanical fraction	Total P_2O_5	Citrate-soluble P_2O_5	Citric acid-soluble P_2O_5
948	Original material	30.19	0.33	4.15
	"Sand"	33.41	.16	4.14
	"Silt"	26.73	.66	4.82
	"Clay"	23.67	.91	6.42

[2] Not determined.

[4] Insufficient quantity of "sand" fraction for analysis.

COMPOUNDS PRESENT IN PHOSPHATE ROCK

The compounds present in phosphate rock may be divided into two classes, phosphatic and nonphosphatic or admixed materials. Identification of all the compounds comprised in these classes remains to be accomplished, but progress in this direction has been made by means of careful studies of the combined results of microscopical, X-ray diffraction, and chemical examinations.

Numerous difficulties arise when these methods of attack are applied individually to such a material as phosphate rock. Microscopical examination is of great value in the identification of minute quantities of crystalline substances, but the very fine particle size of most of the compounds in phosphate rock limits the applicability of this method. X-ray diffraction photographs are of some value in the identification of impurities present in amounts greater than about 2 percent, but they are of far greater value in characterizing the principal constituent in the material under examination. However, several phosphate compounds that may be present in phosphate rock have very similar structures and give almost identical diffraction photographs. Furthermore, these compounds seem to be able to form a rather extensive series of solid solutions. Therefore, extreme care must be exercised in interpreting the photographs. Chemical analysis is of value in determining the amounts of the various elements and certain of the radicals in phosphate rock, but it is not possible from such results alone to distribute correctly these elements and radicals among the compounds that may be present, for example, to distribute fluorine and carbon dioxide among the phosphate minerals and possible fluoride and carbonate impurities.

PHOSPHATIC COMPOUNDS

Except in rare instances, the calcium phosphates present in phosphate rock have complicated structures, which, in general, may be represented by the type formula $3Ca_3(PO_4)_2.CaX$, or $Ca_{10}X(PO_4)_6$, where X may be one or more negative radicals such as halogens, carbonate, hydroxyl, etc. Fluorapatite, $Ca_{10}F_2(PO_4)_6$, is the best-known crystalline representative of such compounds. Other compounds of this type, which are known to exist in nature or have been prepared in the laboratory, are hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$; chlorapatite, $Ca_{10}Cl_2(PO_4)_6$; and carbonate apatite, $Ca_{10}(CO_3)(PO_4)_6$, which probably carries one molecule of water. Owing to the similarity in their crystal structures as shown by X-ray diffraction studies (*64*, *65*), the formation of solid solutions among these compounds is to be expected. The presence of solid solutions would explain, in a large measure, the variable compositions of many of the poorly defined minerals described as occurring in phosphate rock (*39*, *p. 768*; *78*).

The possibility of the presence of significant quantities of chlorapatite in the domestic phosphate rocks is eliminated by the fact that these materials usually contain less than 0.02 percent of chlorine.

The universal presence of comparatively large percentages of fluorine in phosphate rocks, particularly those from the continental deposits, led more than 40 years ago to the conclusion that phosphate rock is essentially fluorapatite (*101*). This conclusion is supported by the recent X-ray diffraction studies of Hendricks and coworkers (*64*). The results of these studies show that fluorapatite is the predominating constituent of all the commercial varieties and grades of phosphate rock produced in the United States. On the other hand, X-ray analysis indicates that hydroxyfluorapatite, $Ca_{10}(OH, F)_2 (PO_4)_6$, is an important constituent of the Nauru, Christmas, and Ocean Island phosphates. So far as is known to the authors, fluorapatite is the only coarsely crystalline calcium phosphate mineral that has been identified with certainty in the commercial types of domestic phosphate rock by means of the microscope, and this only in rare instances. In the present investigation, macrocrystalline fluorapatite was found in only two samples, namely, no. 1011 (table 5) from Garrison, Mont., and no. 910 (table 3) from Mulberry, Fla.

Chemical analyses (tables 9–12) show that the domestic types of phosphate rock, excluding the Florida soft and waste-pond phosphates, usually contain about 20 to 35 percent more fluorine than is theoretically required to combine with the phosphate for the formation of fluorapatite, the excess running as high as about 55 percent in Oklahoma phosphate and in certain samples of Florida land pebble and South Carolina land rock. Satisfactory proof of the exact state of combination of this excess fluorine has not been obtained. Microscopical examination showed the presence of coarsely crystalline calcium fluoride (fluorite) in only two samples (nos. 1011 and 1012, table 11), which were exceptionally high in fluorine. The X-ray diffraction photographs also showed the presence of calcium fluoride in these samples, whereas they gave no indication of its presence in other samples. Fluorite has previously been identified in phosphate rock from western United States (*51; 119, p. 213*) and Palestine (*5*).

According to Bredig and coworkers (*14*), fluorapatite can take into its lattice excess calcium fluoride to the extent of approximately 70 percent of that theoretically required by the formula $Ca_{10}F_2(PO_4)_6$ without causing more than a very slight broadening of the lattice. The same authors offer this as an explanation of the presence of the excess fluorine usually found in continental phosphate rocks and frequently in coarsely crystalline fluorapatite. Although further work in this direction is needed, it should be pointed out that, with the exception of the samples in which the presence of fluorite was detected, none of the domestic phosphates analyzed in this investigation contained more fluorine than corresponds to an excess of 70 percent over that required to form fluorapatite with all the phosphoric acid present. The excess fluorine in several samples of Russian phosphate (table 13), which were not examined microscopically for the presence of fluorite, slightly exceeded this figure.

Conclusive evidence of the presence of carbonate apatite, $Ca_{10}(CO_3)(H_2O)(PO_4)_6$, in domestic phosphate rock has not been obtained. This compound, which seems to be the essential phosphatic component of fresh bone (*64, 65, 164*), is probably a constituent of certain insular phosphate rocks, but X-ray data indicate that there is no great displacement of fluorine by either carbonate or hydroxyl groups in the apatite mineral that is predominant in domestic rock (*64*). Microscopical examination of phosphate rock usually shows the presence of calcite, often in sufficient quantity to account for all the carbon dioxide. Hendricks and coworkers (*64*) have pointed out, however, that in some samples, particularly certain of the Florida land-pebble phosphates, the amount of calcite is markedly lower than is indicated by the carbon dioxide content. In such samples, the X-ray data also indicate that crystalline calcium carbonate is not present in amounts greater than about 2 percent. These samples do not contain sufficient magnesium carbonate to account for the discrepancy. It is possible that the excess carbon dioxide is present as very finely divided calcium carbonate in quantities too small to be determined by microscopical and X-ray analyses. It is also possible that at least a part of this carbon dioxide is present in the form of carbonate apatite or of solid solutions of carbonate apatite and other apatites. Finally, there is the possibility that carbon dioxide has gone into the fluorapatite lattice as calcium carbonate in the manner postulated by Bredig and coworkers (*14*) to explain the presence of excess fluorine in phosphate rock. In this connection, it should be noted that coarsely crystalline fluorapatite very frequently contains significant quantities of carbon dioxide (*39, p. 765*).

The properties of the submicrocrystalline carbonate present in phosphate rock are somewhat different from those of coarsely crystalline calcite. For example, it has recently been pointed out (*74*) that complete removal of the carbon dioxide by heating at high temperatures is more difficult with phosphate rock than with either dolomite or high-calcium limestone. Schucht (*172, p. 311*) and Gale and Richards (*61*) state that certain samples of Florida and Utah phosphates contain carbon dioxide which is not liberated on treatment of the rock powder with cold dilute acetic, phosphoric, or hydrochloric acid, but comes off when the sample is treated with hot dilute phosphoric or hydrochloric acid. Since calcite is completely decomposed by dilute acetic acid, these authors suggest that the difficultly soluble carbonate may be present as a carbonate phosphate.

The results of experimental work on the purification of phosphate rock by the flotation process indicate that coarsely crystalline calcite may be readily removed by this method, whereas the remainder of the carbonate is removed only in part, if at all, even though the rock be ground to a fineness of 200 mesh.[12] This behavior may be due either to carbonate apatite or to calcium carbonate in the fluorapatite lattice, or to the presence of free calcium carbonate so thoroughly disseminated throughout the phosphate particles that separation by flotation is impossible unless the rock be ground extremely fine. While these observations do not prove the presence of carbonate apatite, they show that at least a part of the carbonate manifests properties unlike those of calcite.

As further evidence of the presence of carbonate phosphates in phosphate rock, Matson (*122, p. 86*) has reported that Florida phosphates contain a mineral having optical properties corresponding to those of francolite or staffelite, $3Ca_3(PO_4)_2.CaCO_3.CaF_2.H_2O$ (*95; 96; 169, p. 89–100*). Correlating the results of his microscopical examination with the chemical analyses reported by other investigators, Matson suggests that the Florida phosphates are mixtures of francolite and fluocollophanite, $3Ca_3(PO_4)_2.Ca(F_2,CO_3).H_2O+nH_2O$. Aside from the optical data, this suggestion is based largely upon the molecular ratios of total calcium oxide, phosphoric acid, carbon dioxide, and fluorine calculated from the chemical analyses. It should be pointed out, however, that the fluorine figures on the majority of the samples were unquestionably much too low, and that Matson failed to take into consideration the fact that in most samples a portion of the carbon dioxide is undoubtedly present in the form of calcite (*64*).

As in the case of carbonate apatite, there is no direct evidence of the presence in domestic phosphate rock of hydroxyapatite, either as the individual compound or as solid solutions with other apatites. The microscopical and X-ray diffraction examinations do not throw any light on this subject, but the chemical analyses (tables 3–6 and 17) indicate that many samples may contain small quantities of calcium in combination with the hydroxyl group.

Thus, most phosphate rocks contain appreciable amounts of calcium in excess of that required to combine with the fluorine, carbon dioxide, and the acid-soluble sulphate radical, and with the phosphoric acid in the ratio required by the calcium phosphate portion of the apatite formula. For example, the excess calcium in the samples of Christmas Island, Nauru, and Ocean Island phosphates (table 6) ranges from 2.53 to 3.73 percent CaO. The X-ray data indicate that

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[12] Private communication from Charles E. Heinrichs, of the Phosphate Recovery Corporation.

these phosphates contain hydroxyfluorapatite (*64*). Likewise, in 15 samples of various types of domestic phosphates the excess calcium ranged from 0.22 to 2.11 percent CaO, the average being 0.95 percent. It is hardly possible that analytical errors, which accumulate in the results for excess calcium, can account for the rather large values obtained in many cases. The presence of dicalcium phosphate and of phosphoric acid, fluorine, carbon dioxide, or sulphuric acid in combination with elements other than calcium would only serve to increase the excess of calcium. Except for the presence of insignificant quantities of acid-insoluble calcium (table 23), there is no direct evidence that calcium occurs in domestic phosphate rock in combination with acid radicals other than those mentioned, although Schucht (*172, p. 74*) states that calcium silicate occurs in Algerian and Belgian phosphates. On the basis of the information available at present, it does not seem unreasonable to postulate the existence of at least a portion of the excess calcium in the form of hydroxyapatite, or solid solutions of this compound with other apatites, or as calcium hydroxide within the lattice of fluorapatite.

There is no evidence that dicalcium and tricalcium phosphates occur in any of the varieties of domestic phosphates. Hendricks and coworkers (*64*) have shown, however, that Curacao Island phosphate contains a compound which gives the same X-ray diffraction pattern as does anhydrous tricalcium phosphate. Dicalcium phosphate has been reported to occur in isolated masses on the islands of Moneta and Mona, West Indies (*39, p. 784*).

Microscopical examination has not revealed the presence of iron or aluminum phosphates in the samples used in this investigation. The occurrence of vivianite, $Fe_3(PO_4)_2.8H_2O$, has been noted in several localities in the Florida land-pebble district (*122, p. 85*), particularly in a phosphate rock deposit near Plant City (*203*). Larsen and Shannon (*100*) reported the presence of complex phosphate minerals containing calcium, aluminum, and, in some cases, sodium in a deposit near Fairfield, Utah. Mineralogical evidence of the presence of these or of any other iron and aluminum phosphates in the commercial grades of domestic rock has not come to the attention of the authors. The results of chemical analyses, however, give evidence of the presence of iron or aluminum, probably the latter, combined with phosphoric acid in certain samples of the Florida soft and waste-pond phosphates.

Thus, the soft phosphates nos. 580 and 1091, and the waste-pond phosphate no. 915 (table 3) contain less calcium (2.92 to 19.12 percent CaO on the samples) than is required to combine with the fluorine and carbon dioxide and with the phosphoric acid in the ratio required by the calcium phosphate portion of the fluorapatite formula. In soft phosphate no. 580, the marked deficiency of calcium (19.12 percent CaO) together with the high alumina (23.05 percent) and the low total iron (3.28 percent Fe_2O_3) gives conclusive evidence of the presence of considerable aluminum phosphate. A deficiency of calcium also occurs in the "sand" fractions of soft phosphate no. 728 and waste-pond phosphate no. 727 (table 28). Since the original samples of these materials are not deficient in lime, it may be concluded that concentration of the iron or aluminum phosphate has occurred in the "sand" fractions. Similar calculations on the original samples and the mechanical fractions of the other types of domestic phosphates give no indication of the presence of iron or aluminum phosphates.

NONPHOSPHATIC COMPOUNDS

The occasional occurrence of fluorite and the frequent occurrence of calcite in phosphate rock have been pointed out on page 73.

Microscopical examination usually indicates the presence of gypsum (*64*) in sufficient quantity to account for the acid-soluble sulphate in domestic phosphate rocks (table 17). Gale and Richards (*51*) reported the presence of both gypsum and anhydrite in low-grade phosphate from the Crawford Mountains, Utah. The acid-insoluble sulphide, found in significant quantities in Tennessee blue rock and phosphatic limestone, South Carolina land rock, rock from Cokeville, Wyo., and in one sample of Tennessee brown rock (table 17), is present principally in the form of pyrite (FeS_2). All samples of phosphate examined during this investigation also contained organic sulphur, the quantities running as high as 0.8 percent SO_3 in rock from Conda, Idaho.

The state of combination of the iron may vary considerably in different varieties of phosphate. As pointed out in the preceding paragraph, pyrite is an important constituent of several of the domestic types of rock. Analysis of the organic material isolated from several samples also indicates that iron may be present in organic combination (table 20). According to Matson (*122, p. 84*), limonite, $2Fe_2O_3.3H_2O$, is the most common iron-bearing mineral in the Florida phosphate deposits, though glauconite is a constituent of the "bedrock" in the pebble-phosphate region. Matson also states that in many of the deposits iron probably occurs in the form of ferrous silicate at depths where oxidation has not been very effective. The color of Tennessee brown rock and of Conda, Idaho, rock indicates the presence of ferric oxide.

Aside from that occurring as the phosphate, the greater part of the aluminum is probably present in the form of silicates, principally in the submicrocrystalline condition. Microscopical examination of Florida land-pebble phosphate no. 790 by W. H. Fry, of the soil chemistry and physics division of the Bureau of Chemistry and Soils, showed the presence of very small quantities of orthoclase and microcline. Traces of plagioclase were found in Florida land-pebble phosphates nos. 910, 912, and 947, and no. 912 contained very small quantities of muscovite and tourmaline. Mica was identified in Florida hard-rock phosphate no. 771. Coarsely crystalline silicates were not found in samples of the other types of rock. Gale and Richards (*51*) reported the presence of kaolin in samples of phosphate from Idaho, Utah, and Wyoming, and Matson (*122, p. 84*) stated that kaolin is the most prominent aluminum-bearing mineral in the Florida phosphates.

The nature of the compound or compounds accounting for the presence of sodium and potassium in natural phosphates has not been definitely established. The studies of Hausen (*59*) and Borgström (*10*) indicate that at least a portion of the sodium may have replaced calcium in the complex apatitelike compounds which are the principal phosphatic components of natural calcium phosphates. As pointed out by Hendricks and coworkers (*64*), a partial replacement of calcium by sodium is structurally possible because the ionic radii of sodium and calcium are nearly the same. On the other hand, there is a considerable difference in the sizes of the potassium and calcium ions and, consequently, replacement of calcium by potassium in the apatite complex would seem to be improbable. Alkali aluminum silicates account, no doubt, for at least a portion of the sodium and potassium present in many phosphate rocks.

Matson (*122, p. 85*) suggests that the magnesium in the Florida phosphates probably occurs most commonly as magnesite. Results obtained on samples of Florida, Tennessee, and Idaho phosphates (table 23) show, however, that approximately 30 to 100 percent of the total magnesium is insoluble in hot 1 to 1 hydrochloric acid. This indicates the presence of magnesium-bearing silicates.

Quartz is a common constituent of all types of phosphate rock. Most types also contain silica in the form of silicates.

Not enough information is available to justify conclusions as to the states of combination of the small quantities of titanium, manganese, chromium, vanadium, copper, zinc, and arsenic that are present in nearly all types of phosphate rock.

SUMMARY

A brief review of the phosphate deposits and the production and reserves of phosphate rock in the United States is given. The flotation process of concentrating low-grade phosphate ores is discussed with reference to its value in the conservation of the phosphate deposits in the southeastern part of the United States.

The results of an analytical study of 46 samples of mineral calcium phosphates representing nearly all of the more important domestic types and sources of this material are presented. Data are also given on the composition of 11 samples of bone ash, apatites, and foreign phosphate rocks, and on the percentages of fluorine and phosphoric acid in a large number of additional samples from deposits throughout the world.

Phosphoric acid, lime, alumina, iron, silica, carbon dioxide, fluorine, and, in most samples, sulphate are the predominating constituents of domestic phosphate rock. Magnesium, titanium, sodium, potassium, manganese, chromium, copper, zinc, arsenic, chlorine, and iodine are present in nearly all samples, but only in comparatively small quantities. Small percentages of vanadium are also present in many samples.

Phosphate rock from continental deposits usually contains 3 to 4 percent of fluorine, whereas that from insular deposits contains smaller quantities. As a general rule, the fluorine-phosphoric acid ratios in a particular type of rock are approximately constant. Although fresh bones are very low in fluorine, fossil bones frequently contain high percentages of this element. Evidence is presented to show that the fluorine in phosphate rock and fossil bones originates principally from contact of the phosphates with fluorine-bearing waters, and that, to a certain extent, there is a rough correlation between the fluorine content and the geological age of these materials.

The commercial types and grades of domestic phosphate rock contain approximately the following percentages of minor constituents—

MgO, 0.0 to 0.5; TiO_2, 0.03 to 0.15; Na_2O, 0.1 to 0.8; K_2O, 0.05 to 0.65; MnO, traces to 0.3; Cr_2O_3, 0.00 to 0.15; V_2O_3, 0.00 to 0.40; CuO, <0.0005 to 0.01; ZnO, <0.0005 to 0.025; As_2O_3, 0.001 to 0.015; and Cl, 0.00 to 0.10. The iodine content ranges from approximately 1 to 130 parts per million.

Pyrite is a common constituent of Tennessee blue rock and phosphatic limestone, South Carolina land rock, and rock from Cokeville, Wyo.

The organic matter isolated from phosphate rock carries high percentages of nitrogen and sulphur, and the ash of this material is rich in iron.

In comparison with the other types of domestic phosphate rock, Tennessee brown-rock phosphate is characterized by the presence of high percentages of aluminum, iron, and manganese, and by the absence of vanadium. It usually contains more potassium than sodium, whereas the reverse is the rule with the other types.

Tennessee blue-rock phosphate is similar to Tennessee brown rock in that it is comparatively high in iron. It is also high in acid-soluble sulphate, but its outstanding characteristic is its high content of acid-insoluble sulphide, principally pyrite.

Florida land-pebble phosphate has no outstanding chemical characteristic. The percentages of fluorine in the different commercial grades of this material are, however, approximately constant, whereas in the other types of phosphate rock the fluorine content varies, as a general rule, directly with the phosphoric acid.

Florida hard-rock phosphate is characterized by its comparatively high content of iodine and low content of sulphate and chlorine.

In general, the phosphates from deposits in the Rocky Mountain States are comparatively high in chromium and vanadium, and low in iodine. Certain samples, notably those from deposits at Conda, Idaho, and Cokeville, Wyo., are exceptionally high in organic carbon and organic sulphur, whereas rock from the Garrison, Mont., deposit is low in organic carbon and in total sulphur.

In comparison with phosphate rock, Florida waste-pond phosphate is low in phosphoric acid and exceptionally high in silica and alumina. The composition of Florida soft phosphate varies considerably with different samples.

Nearly all of the elements present in phosphate rock occur also in bone ash.

Analyses of the mechanical fractions separated from samples of ground phosphate rock and from Florida soft and waste-pond phosphates showed that, as a general rule, the phosphoric acid, calcium, and fluorine concentrate somewhat in the "sand" and "silt" fractions, whereas the alumina and silica concentrate to a marked extent in the "clay" and colloid fractions, particularly the latter.

Phosphate rock does not contain significant quantities of phosphoric acid soluble in neutral ammonium citrate solution, and less than 30 percent of the total phosphoric acid is soluble in 2 percent citric acid solution. The percentages of phosphoric acid dissolved by these reagents from a particular sample of phosphate increase with increase in the fineness of the particles.

The principal phosphatic component of phosphate rock from continental deposits is fluorapatite, which is present almost entirely in the submicrocrystalline condition. Hydroxy fluorapatite is an important constituent of rock from insular deposits. The available data indicate that domestic phosphate rock may contain small quantities of carbonate apatite and hydroxyapatite.

LITERATURE CITED

(1) Anonymous.
1931. NEW CHEMICAL INDUSTRY FOR THE SOUTH. Manufacturers Rec. 99 (15):38–40, illus.

(2) Aita, A.
1916. RICERCHE SULLA SOLUBILITÀ DEI FOSFATI MINERALI. Ann. Chim. Appl. [Rome] 6:28–44, illus.

(3) ———
1916. CAUSE CHE INFLUISCONO SULLA SOLUBILITÀ IN ACIDO CITRICO DEI FOSFATI DIFFICILMENTE SOLUBILI. Ann. Chim. Appl. [Rome] 6:119–131, illus.

(4) Alexander, L. T., and Jacob, K. D.
1930. MECHANICAL ANALYSIS OF FINELY DIVIDED NATURAL PHOSPHATES. U. S. Dept. Agr. Tech. Bul. 212, 24 p., illus.

(5) Artini, E.
1912. OSSERVAZIONI PETROGRAFICHE SU DI ALCUNE ROCCE FOSFATICHE DELLA PALESTINA. Atti Soc. Ital. Sci. Nat. Milano 50:349–364, illus.

(6) Association of Official Agricultural Chemists.
1930. OFFICIAL AND TENTATIVE METHODS OF ANALYSIS. COMPILED BY THE COMMITTEE ON EDITING METHODS OF ANALYSIS. Ed. 3, 593 p., illus. Washington, D. C.

(7) Bethke, R. M., Kick, C. H., Edgington, B. H., and Wilder, O. H.
1930. THE EFFECT OF FEEDING SODIUM FLUORIDE AND ROCK PHOSPHATE ON BONE DEVELOPMENT IN SWINE. A PRELIMINARY REPORT. Amer. Soc. Anim. Prod. Proc. 1929:29–33.

(8) Blackwelder, E.
1910. PHOSPHATE DEPOSITS EAST OF OGDEN, UTAH. U.S. Geol. Survey Bul. 430:536–551, illus.

(9) ———
1911. A RECONNAISSANCE OF THE PHOSPHATE DEPOSITS IN WESTERN WYOMING. U.S. Geol. Survey Bul. 470:452–481, illus.

(10) Borgström, L. H.
1931. SYNTETISK NACL-APATIT. Finska Kemistsamfundets Meddel. 40: [51]–54, illus.

(11) Branner, J. C.
1896. THE PHOSPHATE DEPOSITS OF ARKANSAS. Amer. Inst. Mining Engin. Trans. 26:580–598, illus.

(12) ——— and Newsom, J. F.
1902. THE PHOSPHATE ROCKS OF ARKANSAS. Ark. Agr. Expt. Sta. Bul. 74, p. [61]–123, illus.

(13) Braun.
1896. UNTERSUCHUNGEN ÜBER DEN FLUORGEHALT VON PHOSPHATEN, SUPERPHOSPHATEN, KNOCHENMEHLEN UND GUANOS. Chem. Indus. [Berlin] 19:181–185.

(14) Bredig, M. A., Franck, H. H., and Füldner, H.
1932. BEITRÄGE ZUR KENNTNIS DER KALK-PHOSPHORSÄURE-VERBINDUNGEN. Ztschr. Elektrochem. 38:158–164, illus.

(15) Carles, P.
1907. LE FLUOR DANS LES EAUX MINÉRALES. Compt. Rend. Acad. Sci. [Paris] 144:37–39.

(16) ———
1907. LE FLUOR DANS LES COQUILLES DE MOLLUSQUES. Compt. Rend. Acad. Sci. [Paris] 144:437–438.

(17) ———
1907. LE FLUOR DANS LES COQUILLES DES MOLLUSQUES NON MARINS. Compt. Rend. Acad. Sci. [Paris] 144:1240.

(18) Carnot, A.
1892. RECHERCHE DU FLUOR DANS DIFFÉRENTES VARIÉTÉS DE PHOSPHATES NATURELS. Compt. Rend. Acad. Sci. [Paris] 114: 1003–1006.

(19) Carnot, A.
1892. RECHERCHE DU FLUOR DANS LES OS MODERNES ET LES OS FOSSILES. Compt. Rend. Acad. Sci. [Paris] 114:1189–1192.

(20) ———
1892. SUR LA COMPOSITION DES OSSEMENTS FOSSILES ET LA VARIATION DE LEUR TENEUR EN FLUOR DANS LES DIFFÉRENTS ÉTAGES GÉOLOGIQUES. Compt. Rend. Acad. Sci. [Paris] 115:243–246.

(21) ———
1892. SUR UNE APPLICATION DE L'ANALYSE CHIMIQUE POUR FIXER L'ÂGE D'OSSEMENTS HUMAINS PRÉHISTORIQUES. Compt. Rend. Acad. Sci. [Paris] 115:337–339.

(22) ———
1893. RECHERCHES SUR LA COMPOSITION GÉNÉRALE ET LA TENEUR EN FLUOR DES OS MODERNES ET DES OS FOSSILES DES DIFFÉRENTS AGES. Ann. Mines (9) 3:155–195.

(23) ———
1894. SUR LA COMPOSITION CHIMIQUE DES WAVELLITES ET DES TURQUOISES. Compt. Rend. Acad. Sci. [Paris] 118:995–998.

(24) ———
1896. SUR LES VARIATIONS OBSERVÉES DANS LA COMPOSITION DES APATITES. Compt. Rend. Acad. Sci. [Paris] 122:1375–1380.

(25) ———
1896. SUR LE MODE DE FORMATION DES GÎTES SÉDIMENTAIRES DE PHOSPHATE DE CHAUX. Compt. Rend. Acad. Sci. [Paris] 123:724–729.

(26) ———
1896. SUR LES VARIATIONS OBSERVÉES DANS LA COMPOSITION DES APATITES, DES PHOSPHORITES ET DES PHOSPHATES SÉDIMENTAIRES. REMARQUES SUR LE GISEMENT ET LE MODE DE FORMATION DE CES PHOSPHATES. Ann. Mines (9) 10:137–231.

(27) Carpenter, F. B.
1894. THE MARLS AND PHOSPHATES OF NORTH CAROLINA. N.C. Agr. Expt. Sta. Bul. 110, p. [455]–504, illus.

(28) Casares, J., and Casares, R.
1930. SOBRE LA INVESTIGACION CUALITATIVA DEL FLUOR EN LOS HUESOS. An. Soc. Españ. Fís. Quím. 28:910–915.

(29) Chazal, P. E.
1904. THE CENTURY IN PHOSPHATES AND FERTILIZERS. A SKETCH OF THE SOUTH CAROLINA PHOSPHATE INDUSTRY. 71 p., illus. Charleston.

(30) Churchill, H.V.
1931. OCCURRENCE OF FLUORIDES IN SOME WATERS OF THE UNITED STATES. Indus. and Engin. Chem. 23:996–998, illus.

(31) Clarke, F. W., Schneider, E. A., Hillebrand, W. F., Melville, W. H., Eakins, L. G., and Stokes, H. N.
1893. REPORT OF WORK DONE IN THE DIVISION OF CHEMISTRY DURING THE FISCAL YEARS 1891–'92 AND 1892–'93. U. S. Geol. Survey Bul. 113, 115 p., illus.

(32) ———
1924. THE DATA OF GEOCHEMISTRY. U.S. Geol. Survey Bul. 770, Ed. 5, 841 p.

(33) ——— and Wheeler, W. C.
1922. THE INORGANIC CONSTITUENTS OF MARINE INVERTEBRATES. U.S. Geol. Survey Prof. Paper 124, Ed. 2, rev. and enl., 62 p.

(34) Condit, D. D.
1924. PHOSPHATE DEPOSITS IN THE WIND RIVER MOUNTAINS NEAR LANDER, WYOMING. U.S. Geol. Survey Bul. 764, 39 p., illus.

(35) ——— Finch, E. H., and Pardee, J. T.
1928. PHOSPHATE ROCK IN THE THREE FORKS–YELLOWSTONE PARK REGION, MONTANA. U.S. Geol. Survey Bul. 795:147–209, illus.

(36) Cristiani, H.
1930. LA PÉRIODE LARVÉE DE L'INTOXICATION FLUORIQUE. Compt. Rend. Soc. Biol. [Paris] 103:292–294.

(37) Dabney, C. W., Jr.
1884. NORTH CAROLINA RESOURCES FOR COMMERCIAL FERTILIZERS. I. PHOSPHATES. N.C. Agr. Expt. Sta. Ann. Rpt. 1883:57–83.

(38) ———
1885. THE PHOSPHATE EXPLORATION. N.C. Agr. Expt. Sta. Ann. Rpt. 1884:44–84, illus.

(39) Dana, E. S.
1914. THE SYSTEM OF MINERALOGY OF JAMES DWIGHT DANA, 1837–1868. Ed. 6, entirely rewritten and much enl., 1134 p., illus. New York and London.

(40) Day, D. T.
1885. FERTILIZERS. PHOSPHATE ROCK. U.S. Geol. Survey Min. Resources U. S. 1883–84:783–794.

(41) ———
1886. FERTILIZERS. PHOSPHATE ROCK. U.S. Geol. Survey Min. Resources U. S. 1885:445–458.

(42) Ditte, A.
1886. RECHERCHES SUR LES APATITES ET LES WAGNÉRITES. Ann. Chim. Phys. (6) 8:502–542.

(43) Dussert, D.
1924. LES GISEMENTS ALGÉRIENS DE PHOSPHATE DE CHAUX. Ann. Mines (12) 6:135–221, 229–325, 333–398, 407–451, illus.

(44) Eldridge, G. H.
1893. A PRELIMINARY SKETCH OF THE PHOSPHATES OF FLORIDA. Amer. Inst. Mining Engin. Trans. 21:196–231, illus.

(45) Fellenberg, T. von
1926. DAS VORKOMMEN, DER KREISLAUF UND DER STOFFWECHSEL DES JODS. Ergeb. Physiol. 25:176–363, illus.

(46) ———
1927. UNTERSUCHUNGEN ÜBER DAS VORKOMMEN VON JOD IN DER NATUR. XI. MITTEILUNG: ZUR GEOCHEMIE DES JODS. II. Biochem. Ztschr. 187:1–6.

(47) ——— and Lunde, G.
1926. UNTERSUCHUNGEN ÜBER DAS VORKOMMEN VON JOD IN DER NATUR. X. MITTEILUNG. BEITRAG ZUR GEOCHEMIE DES JODS. Biochem. Ztschr. 175:[162]–171.

(48) Fieldner, A. C., Selvig, W. A., and Taylor, G. B.
1919. THE DETERMINATION OF COMBUSTIBLE MATTER IN SILICATE AND CARBONATE ROCKS. U. S. Dept. Int., Bur. Mines Tech. Paper 212, 22 p., illus.

(49) Foerste, A. [F].
1913. THE PHOSPHATE DEPOSITS IN THE UPPER TRENTON LIMESTONES OF CENTRAL KENTUCKY. Ky. Geol. Survey (4) 1 (pt. 1):391–439, illus.

(50) Gale, H. S.
1911. ROCK PHOSPHATE NEAR MELROSE, MONTANA. U.S. Geol. Survey Bul. 470:440–451, illus.

(51) ——— and Richards, R. W.
1910. PRELIMINARY REPORT ON THE PHOSPHATE DEPOSITS IN SOUTHEASTERN IDAHO AND ADJACENT PARTS OF WYOMING AND UTAH. U.S. Geol. Survey Bul. 430:457–535, illus.

(52) Garner, W. W., McMurtrey, J. E., jr., Bowling, J. D., jr., and Moss, E. G.
1930. MAGNESIUM AND CALCIUM REQUIREMENTS OF THE TOBACCO CROP. Jour. Agr. Research 40:145–168, illus.

(53) Gautier, A., and Clausmann, P.
1914. LE FLUOR DANS LES EAUX DOUCES. Compt. Rend. Acad. Sci. [Paris] 158:[1389]–1395.

(54) ——— and Clausmann, P.
1914. LE FLUOR DANS LES EAUX MINÉRALES. Compt. Rend. Acad. Sci. [Paris] 158:1631–1640.

(55) Gile, P. L., Middleton, H. E., Robinson, W. O., Fry, W. H., and Anderson, M. S.
1924. ESTIMATION OF COLLOIDAL MATERIAL IN SOILS BY ADSORPTION. U.S. Dept. Agr. Bul. 1193, 42 p.

(56) Grammont, A.
1924. ÉTUDE SUR LES PHOSPHATES NATURELS.—RECHERCHE ET DOSAGE DES MÉTAUX CONTENUS EN PETITE QUANTITÉ DANS CES MINÉRAUX. Bul. Soc. Chim. France (4) 35:405–408.

(57) ———
1924. ÉTUDE SUR LES PHOSPHATES NATURELS.—RECHERCHE ET DOSAGE DES MÉTAUX CONTENUS EN PETITE QUANTITÉ DANS CES MINÉRAUX (2^e NOTE). Bul. Soc. Chim. France (4) 35:1351–1354.

(58) Gray, A. N.
1930. phosphates and superphosphates. 275 p. London.
(59) Hausen, H.
1926. till frågan om apatiternas kemiska formel. Finska Kemistsamfundets Meddel. 35:[9]–18, illus.
(60) Hayes, C. W.
1895. the tennessee phosphates. U.S. Geol. Survey Ann. Rpt. 16 (pt. 4):610–630, illus.
(61) ———
1896. the tennessee phosphates. U.S. Geol. Survey Ann. Rpt. 17 (pt. 2):519–550, illus.
(62) ———
1903. origin and extent of the tennessee white phosphates. U.S. Geol. Survey Bul. 213:418–423.
(62a) Hayes, C. W., and Ulrich, E. O.
1903. description of the columbia quadrangle. U.S. Geol. Survey Geol. Atlas of U.S. Columbia Folio Tennessee no. 95, 6 p., illus.
(63) Headden, W. P.
1910. the occurrence of arsenic in soils, plants, fruits, and animals. Colo. Sci. Soc. Proc. 9:[345]–366.
(64) Hendricks, S. B., Hill, W. L., Jacob, K. D., and Jefferson, M. E.
1931. structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and x-ray diffraction examinations. Indus. and Engin. Chem. 23:1413–1418, illus.
(65) ——— Jefferson, M. E., and Mosley, V. M.
1932. the crystal structures of some natural and synthetic apatite-like substances. Ztschr. Kristallographie 81:352–369, illus.
(66) Hercus, C. E., Benson, W. N., and Carter, C. L.
1925. endemic goitre in new zealand, and its relation to the soil-iodine. Jour. Hyg. [London] 24:321–402, illus.
(67) ——— and Roberts, K. C.
1927. the iodine content of foods, manures and animal products in relation to the prophylaxis of endemic goitre in new zealand. Jour. Hyg. [London] 26:49–83, illus.
(68) Hess, F. L.
1925. cobalt, molybdenum, nickel, tantalum, titanium, tungsten, radium, uranium, and vanadium in 1922. U.S. Geol. Survey Min. Resources U.S. 1922 (pt. 1):557–583.
(69) Hill, W. L., and Jacob, K. D.
1930. determination of silica in phosphate rock. Jour. Assoc. Off. Agr. Chem. 13:112–117.
(70) ——— and Jacob, K. D.
1933. determination and occurrence of iodine in phosphate rock. Jour. Assoc. Off. Agr. Chem. 16: 128–137.
(71) ——— Jacob, K. D., Alexander, L. T., and Marshall, H. L.
1930. chemical and physical composition of certain finely divided natural phosphates from florida. Indus. and Engin. Chem. 22:1392–1396, illus.
(72) ——— Marshall, H. L., and Jacob, K. D.
1932. composition of crude phosphoric acid prepared by sulfuric acid process. Indus. and Engin. Chem. 24:1064–1068, illus.
(73) ——— Marshall, H. L., and Jacob, K. D.
1932. minor metallic constituents of phosphate rock. Indus. and Engin. Chem. 24:1306–1312, illus.
(74) ——— Marshall, H. L., and Jacob, K. D.
1933. occurrence of sulphur, organic matter, nitrogen, and water in phosphate rock. Jour. Assoc. Off. Agr. Chem. 16: 260–276.
(75) Hillebrand, W. F.
1900. distribution and quantitative determination of vanadium and molybdenum in rocks of the united states. U.S. Geol. Survey Bul. 167:49–55.
(76) ———
1919. the analysis of silicate and carbonate rocks. U.S. Geol. Survey Bul. 700, 285 p., illus.

(77) Hillebrand, W. F. and Lundell, G. E. F.
1929. APPLIED INORGANIC ANALYSIS; WITH SPECIAL REFERENCE TO THE ANALYSIS OF METALS, MINERALS, AND ROCKS. 929 p., illus. New York and London.

(78) Hintze, C.
1924. HANDBUCH DER MINERALOGIE. Bd. 1, Lieferung 22, p. 487–572, illus.

(79) Hoffman, J. I., and Lundell, G. E. F.
1929. DETERMINATION OF FLUORINE AND OF SILICA IN GLASSES AND ENAMELS CONTAINING FLUORINE. U.S. Dept. Com., Bur. Standards Jour. Research 3:581–595.

(80) Holmes, F. S.
1870. PHOSPHATE ROCKS OF SOUTH CAROLINA AND THE "GREAT CAROLINA MARL BED," . . . TOGETHER WITH THEIR HISTORY AND DEVELOPMENT. 87 p., illus. Charleston.

(81) Hook, J. S.
1914. THE BROWN AND BLUE PHOSPHATE ROCK DEPOSITS OF SOUTH-CENTRAL TENNESSEE. Resources Tenn.: [451]–83, illus.

(82) ———
1915. THE WHITE PHOSPHATES OF TENNESSEE. Resources Tenn. 5:[23]–33, illus.

(83) Ihlseng, M. C.
1896. A PHOSPHATE PROSPECT IN PENNSYLVANIA. U.S. Geol. Survey Ann. Rpt. (1895–96) 17 (pt. 3, continued):955–957.

(84) Jacob, K. D., Beeson, K. C., Rader, L. F., jr., and Ross, W. H.
1931. THE SOLUBILITY OF PHOSPHATES IN NEUTRAL AMMONIUM CITRATE SOLUTION. Jour. Assoc. Off. Agr. Chem. 14:263–283.

(85) ——— Hill, W. L., and Holmes, R. S.
1930. THE COLLOIDAL NATURE OF SOME FINELY DIVIDED NATURAL PHOSPHATES. Colloid Symposium Annual, v. 7, p. 195–204. New York and London.

(86) ——— Rader, L. F., jr., Marshall, H. L., and Beeson, K. C.
1932. CITRATE-INSOLUBLE PHOSPHORIC ACID IN DI- AND TRICALCIUM PHOSPHATES; SOME FACTORS AFFECTING ITS DETERMINATION. Indus. and Engin. Chem., Analyt. Ed. 4:25–31, illus.

(87) ——— Rader, L. F., jr., and Ross, W. H.
1932. COMPARISON OF TWO PER CENT CITRIC ACID AND NEUTRAL AMMONIUM CITRATE SOLUTIONS, AS SOLVENTS FOR PHOSPHATES. Jour. Assoc. Off. Agr. Chem. 15:146–162.

(88) ——— and Reynolds, D. S.
1928. THE FLUORINE CONTENT OF PHOSPHATE ROCK. Jour. Assoc. Off. Agr. Chem. 11:237–250.

(89) ——— and Ross, W. H.
1932. DETERMINATION OF AVAILABLE PHOSPHORIC ACID BY THE NEUTRAL AMMONIUM CITRATE METHOD. Commercial Fertilizer Yearbook, p. 19–26, 46.

(90) Jenkins, O. P.
1916. PHOSPHATES AND DOLOMITES IN JOHNSON COUNTY, TENNESSEE. Resources Tenn. 6:[51]–106, illus.

(91) Johnson, B. L.
1930. PHOSPHATE ROCK. PART I—GENERAL INFORMATION. U.S. Dept. Com., Bur. Mines Inform. Circ. 6256, 64 p., illus.

(92) Jones, C. C.
1914. THE DISCOVERY AND OPENING OF A NEW PHOSPHATE FIELD IN THE UNITED STATES. Amer. Inst. Mining Engin. Trans. 47:192–216, illus.

(93) Jumeau, L. P.
1905. LE PHOSPHATE DE CHAUX (GISEMENTS CONNUS) ET LES EXPLOITATIONS AUX ÉTATS-UNIS EN 1905. 198 p., illus. Paris.

(94) Knop, J.
1924. DIPHENYLAMINE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE SOLUTION. Jour. Amer. Chem. Soc. 46:[263]–269.

(95) Lacroix, A.
1910. SUR LA CONSTITUTION MINÉRALOGIQUE DES PHOSPHORITES FRANÇAISES. Compt. Rend. Acad. Sci. [Paris] 150:1213–1217.

(96) Lacroix, A.
1910. SUR LE MINÉRAL À STRUCTURE OPTIQUE ENROULÉE CONSTITUANT LES PHOSPHORITES HOLOCRISTALLINES DU QUERCY. Compt. Rend. Acad. Sci. [Paris] 150:1388–1390.

(97) Lamar, J. E.
1926. PRELIMINARY REPORT ON THE ECONOMIC MINERAL RESOURCES OF CALHOUN COUNTY. Ill. Geol. Survey Rpt. Invest. 8, 21 p., illus.

(98) Lapp, M. E.
1932. CHANGES IN THE OFFICIAL AND TENTATIVE METHODS OF ANALYSIS MADE AT THE FORTY-SEVENTH ANNUAL CONVENTION, NOVEMBER 2–4, 1931. Jour. Assoc. Off. Agr. Chem. 15:65–87.

(99) Larison, E. L.
1929. MANUFACTURE OF HIGH-ANALYSIS PHOSPHATES. Indus. and Engin. Chem. 21:1172–1175, illus.

(100) Larsen, E. S., and Shannon, E. V.
1930. THE MINERALS OF THE PHOSPHATE NODULES FROM NEAR FAIRFIELD, UTAH. Amer. Mineralogist 15:307–337, illus.

(101) Lasne, H.
1890. IDENTITÉ DE COMPOSITION DE QUELQUES PHOSPHATES SÉDIMENTAIRES AVEC L'APATITE. Compt. Rend. Acad. Sci. [Paris] 110:1376–1377.

(102) Lawrence, H. M., and Rocca, E.
1931. FLOTATION OF LOW-GRADE PHOSPHATE ORES. II. U.S. Dept. Com., Bur. Mines Rpt. Invest. 3105, 9 p.

(103) Lipman, J. G.
1929. THE FERTILIZING VALUE OF MANY MINERALS . . . Amer. Fert. 70 (1): [19]–25, 55–56, 58, 60, 62.

(104) Lundell, G. E. F., and Hoffman, J. I.
1924. THE ANALYSIS OF PHOSPHATE ROCK. Jour. Assoc. Off. Agr. Chem. 8:184–206.

(105) McCalley, H.
1900. ALABAMA PHOSPHATES ON AND NEAR ELK RIVER, LIMESTONE COUNTY. Ala. Dept. Agr. Bul. 14:15–16.

(106) McCallie, S. W.
1896. A PRELIMINARY REPORT ON A PART OF THE PHOSPHATES AND MARLS OF GEORGIA. Ga. Geol. Survey Bul. 5–A, 98 p., illus.

(107) McClure, F. J., and Mitchell, H. H.
1931. THE EFFECT OF CALCIUM FLUORIDE AND PHOSPHATE ROCK ON THE CALCIUM RETENTION OF YOUNG GROWING PIGS. Jour. Agr. Research 42:363–373, illus.

(108) McHargue, J. S.
1925. THE OCCURRENCE OF COPPER, MANGANESE, ZINC, NICKEL, AND COBALT IN SOILS, PLANTS, AND ANIMALS, AND THEIR POSSIBLE FUNCTION AS VITAL FACTORS. Jour. Agr. Research 30:193–196.

(109) ———
1931. REPORT ON LESS COMMON METALS IN SOILS. Jour. Assoc. Off. Agr. Chem. 14:138–141.

(110) ——— Roy, W. R., and Pelphrey, J. G.
1930. IODINE IN SOME FERTILIZER MATERIALS. Amer. Fert. 73 (10):40, 42, 63.

(111) ——— Young, D. W., and Roy, W. R.
1932. DETERMINATION OF IODINE IN SOILS. A NEW METHOD. Indus. and Engin. Chem., Analyt. Ed. 4:214–216, illus.

(112) Mansfield, G. R.
1916. A RECONNAISSANCE FOR PHOSPHATE IN THE SALT RIVER RANGE, WYOMING. U.S. Geol. Survey Bul. 620:331–349, illus.

(113) ———
1917. THE PHOSPHATE RESOURCES OF THE UNITED STATES. 2nd Pan Amer. Sci. Cong. Proc., sec. 7, v. 8, p. 729–766, illus.

(114) ———
1920. GEOGRAPHY, GEOLOGY, AND MINERAL RESOURCES OF THE FORT HALL INDIAN RESERVATION, IDAHO. U.S. Geol. Survey Bul. 713:9–119, illus.

(115) ———
1925. PHOSPHATE ROCK. U.S. Geol. Survey Min. Resources U.S. 1922 (pt. 2):109–132.

(116) Mansfield, G. R.
1926. PHOSPHATE ROCK. U.S. Geol. Survey Min. Resources U.S. 1923 (pt. 2):239–273.

(117) ———
1927. PHOSPHATE ROCK. U.S. Dept. Com., Bur. Mines, Min. Resources U.S. 1924 (pt. 2):77–112.

(118) ———
1929. GEOGRAPHY, GEOLOGY, AND MINERAL RESOURCES OF THE PORTNEUF QUADRANGLE, IDAHO. U.S. Geol. Survey Bul. 803, 110 p., illus.

(119) ——— and Girty, G. H.
192 . GEOGRAPHY, GEOLOGY, AND MINERAL RESOURCES OF PART OF SOUTHEASTERN IDAHO . . . WITH DESCRIPTIONS OF THE CARBONIFEROUS AND TRIASSIC FOSSILS. U.S. Geol. Survey Prof. Paper 152, 453 p., illus.

(120) Marshall, H. L., Jacob, K. D., and Reynolds, D. S.
1932. OCCURRENCE OF FLUORINE IN NATURAL PHOSPHATES; FURTHER STUDIES. Indus. and Engin. Chem. 24:86–89.

(121) Martini, A.
1929. UEBER DAS VORKOMMEN VON NICKEL IN DEN KNOCHEN. Mikrochemie 7:235.

(122) Matson, G. C.
1915. THE PHOSPHATE DEPOSITS OF FLORIDA. U.S. Geol. Survey Bul. 604, 101 p., illus.

(123) Maynard, T. P.
1913. WHITE ROCK PHOSPHATES OF DECATUR COUNTY, TENN. Resources Tenn., 3:161–169, illus.

(124) Memminger, C. G.
1895. COMMERCIAL DEVELOPMENT OF THE TENNESSEE PHOSPHATE. U.S. Geol. Survey Ann. Rpt. 16 (pt. 4):631–635.

(125) ——— Waggaman, W. H., and Whitney, W. T.
1930. THE CALCINATION OR ENRICHMENT OF PHOSPHATE ROCK. Indus. and Engin. Chem. 22:443–446, illus.

(126) Millar, C. C. H.
1892. FLORIDA, SOUTH CAROLINA, AND CANADIAN PHOSPHATES: GIVING A COMPLETE ACCOUNT OF THEIR OCCURRENCE, METHODS, AND COST OF PRODUCTION, QUANTITIES RAISED, AND COMMERCIAL IMPORTANCE. 223 p., illus. London.

(127) Moses, O. A.
1883. THE PHOSPHATE DEPOSITS OF SOUTH CAROLINA. U.S. Geol. Survey Min. Resources U.S. 1882:504–521.

(128) Murray, J., and Renard, A. F.
1891. REPORT ON DEEP-SEA DEPOSITS, BASED ON THE SPECIMENS COLLECTED DURING THE VOYAGE OF H.M.S. CHALLENGER IN THE YEARS 1872 TO 1876. 525 p., illus. London, Edinburgh, [etc.].

(129) Nelson, W. A.
1913. MINERAL PRODUCTS ALONG THE TENNESSEE CENTRAL RAILROAD. Resources Tenn. 3:[137]–160, illus.

(130) Öpik, A.
1928. GISEMENTS DE PHOSPHATES EN ESTHONIE; DER ESTLAENDISCHE OBOLENPHOSPHORIT. Les réserves mondiales en phosphates: Bur. 14th Cong. Géol. Internat. Espagne, 1926, v. 1, p. 135–192, illus. Madrid.

(131) Orr, J. B., and Leitch, I.
1929. IODINE IN NUTRITION; A REVIEW OF EXISTING INFORMATION. [Gt. Brit.] Med. Research Council, Spec. Rpt. Ser. 123, 108 p., illus.

(132) Papish, J., Hoag., L. E., and Snee, W. E.
1930. SPECTROSCOPIC DETECTION OF FLUORINE. Indus. and Engin. Chem., Analyt. Ed. 2:263–264, illus.

(133) Pardee J. T.
1913. SOME FURTHER DISCOVERIES OF ROCK PHOSPHATE IN MONTANA. U.S. Geol. Survey Bul. 530:285–291, illus.

(134) ———
1917. THE GARRISON AND PHILIPSBURG PHOSPHATE FIELDS, MONTANA. U.S. Geol. Survey Bul. 640:195–228, illus.

(135) Pardee, J. T.
1921. PHOSPHATE ROCK NEAR MAXVILLE, GRANITE COUNTY, MONTANA. U.S. Geol. Survey Bul. 715:141–145, illus.

(136) Parrish, P., and Ogilvie, A.
1927. ARTIFICIAL FERTILISERS, THEIR CHEMISTRY, MANUFACTURE, & APPLICATION. v. 1, 356 p., illus. London.

(137) Penrose, R. A. F., jr.
1888. NATURE AND ORIGIN OF DEPOSITS OF PHOSPHATE OF LIME. U.S. Geol. Survey Bul. 46:21–143, illus.

(138) Phalen, W. C.
1912. BAUXITE AND ALUMINUM. U.S. Geol. Survey Min. Resources U.S. 1911 (pt. 1):923–939, illus.

(139) ———
1915. REPORT ON THE PHOSPHATE ROCKS OF CENTRAL KENTUCKY. 80 p., illus. Frankfort, Ky.

(140) ———
1917. THE CONSERVATION OF PHOSPHATE ROCK IN THE UNITED STATES. 2nd Pan Amer. Sci. Cong. Proc., sec. 7, v. 8, p. 772–808, illus.

(141) Phillips, W. B.
1887. THE FERTILIZER TRADE IN NORTH CAROLINA IN 1886. U.S. Geol. Survey Min. Resources U.S. 1886:611–617.

(142) ———
1901. THE BAT GUANO CAVES OF TEXAS. Mines and Minerals 21:440–442, illus.

(143) Pike, R. D.
1930. VOLATILIZATION OF PHOSPHORUS FROM PHOSPHATE ROCK. I. EXPERIMENTS IN CRUCIBLES AND ROTARY KILN. Indus. and Engin. Chem. 22:242–245, illus.

(144) ———
1930. VOLATILIZATION OF PHOSPHORUS FROM PHOSPHATE ROCK. II. EXPERIMENTS IN THE VOLATILIZATION OF PHOSPHORUS AND POTASH IN A BLAST FURNACE. Indus. and Engin. Chem. 22:344–349, illus.

(145) Pratt, N. A.
1868. ASHLEY RIVER PHOSPHATES. HISTORY OF THE MARLS OF SOUTH CAROLINA AND OF THE DISCOVERY AND DEVELOPMENT OF THE NATIVE BONE PHOSPHATES OF THE CHARLESTON BASIN . . . 42 p., illus. Philadelphia.

(146) Purdue, A. H.
1907. DEVELOPED PHOSPHATE DEPOSITS OF NORTHERN ARKANSAS. U.S. Geol. Survey Bul. 315:463–473.

(147) Reed, O. E., and Huffman, C. F.
1930. THE RESULTS OF A FIVE YEAR MINERAL FEEDING INVESTIGATION WITH DAIRY CATTLE. Mich. Agr. Expt. Sta. Tech. Bul. 105, 63 p., illus.

(148) Reeds, C. A.
1910. A REPORT ON THE GEOLOGICAL AND MINERAL RESOURCES OF THE ARBUCKLE MOUNTAINS, OKLAHOMA. Okla. Geol. Survey Bul. 3, 69 p., illus.

(149) Reith, J. F.
1930. DER JODGEHALT VON MEERWASSER. Rec. Trav. Chim. 49:142–150.

(150) Reynolds, D. S., and Jacob, K. D.
1931. METHOD FOR DETERMINATION OF FLUORINE IN PHOSPHATE ROCK AND PHOSPHATIC SLAGS. Indus. and Engin. Chem., Analyt. Ed. 3:366–370.

(151) ——— and Jacob, K. D.
1931. EFFECT OF CERTAIN FORMS OF SILICA ON DETERMINATION OF FLUORINE BY VOLATILIZATION METHOD. Indus. and Engin. Chem., Analyt. Ed. 3:371–373.

(152) ——— Jacob, K. D., and Hill, W. L.
1929. RATIO OF FLUORINE TO PHOSPHORIC ACID IN PHOSPHATE ROCK. Indus. and Engin. Chem. 21:1253–1256.

(153) ——— Ross, W. H., and Jacob, K. D.
1928. VOLATILIZATION METHOD FOR THE DETERMINATION OF FLUORINE WITH SPECIAL REFERENCE TO THE ANALYSIS OF PHOSPHATE ROCK. Jour. Assoc. Off. Agr. Chem. 11:225–236, illus.

(154) Richards, R. W., and Mansfield, G. R.
1911. PRELIMINARY REPORT ON A PORTION OF THE IDAHO PHOSPHATE RESERVE. U.S. Geol. Survey Bul. 470:371–439, illus.

(155) ——— and Mansfield, G. R.
1914. GEOLOGY OF THE PHOSPHATE DEPOSITS OF GEORGETOWN, IDAHO. U.S. Geol. Survey Bul. 577, 76 p., illus.

(156) ——— and Pardee, J. T.
1926. THE MELROSE PHOSPHATE FIELD, MONTANA. U.S. Geol. Survey Bul. 780:1–32, illus.

(157) Robertson, G. S.
1914. THE SOLUBILITY OF MINERAL PHOSPHATES IN CITRIC ACID. Jour. Soc. Chem. Indus. 33:9–11.

(158) ———
1916. NOTES ON THE NATURE OF THE PHOSPHATES CONTAINED IN MINERAL PHOSPHATES. Jour. Agr. Sci. [England] 8:[16]–25, illus.

(159) ——— and Dickinson, F.
1923. THE VALUATION OF INSOLUBLE PHOSPHATES BY MEANS OF A MODIFIED CITRIC ACID TEST. Jour. Soc. Chem. Indus. 42:59T–66T, illus.

(160) Robinson, W. O.
1914. THE INORGANIC COMPOSITION OF SOME IMPORTANT AMERICAN SOILS. U.S. Dept. Agr. Bul. 122, 27 p.

(161) ———
1922. THE ABSORPTION OF WATER BY SOIL COLLOIDS. Jour. Phys. Chem. 26:[647]–653.

(162) ——— and Holmes, R. S.
1924. THE CHEMICAL COMPOSITION OF SOIL COLLOIDS. U.S. Dept. Agr. Bul. 1311, 42 p.

(163) Rogers, G. S.
1915. THE PHOSPHATE DEPOSITS OF SOUTH CAROLINA. U.S. Geol. Survey Bul. 580:183–220, illus.

(164) Roseberry, H. H., Hastings, A. B., and Morse, J. K.
1931. X-RAY ANALYSIS OF BONE AND TEETH. Jour. Biol. Chem. 90:395–408, illus.

165) Ross. B. B.
1900. PHOSPHATES OF THE ELK RIVER VALLEY IN LIMESTONE COUNTY, ALABAMA. Ala. Dept. Agr. Bul. 14:[5]–15.

(166) Ross, W. H., and Jacob, K. D.
1931. REPORT ON PHOSPHORIC ACID: AVAILABILITY OF THE REVERTED PHOSPHORIC ACID IN AMMONIATED SUPERPHOSPHATES. Jour. Assoc. Off. Agr. Chem. 14:182–196.

(167) ——— Jacob, K. D., and Beeson, K. C.
1932. REPORT ON PHOSPHORIC ACID: COMPOSITION AND FERTILIZER EFFICIENCY OF THE INSOLUBLE PHOSPHATES IN AMMONIATED SUPERPHOSPHATES. Jour. Assoc. Off. Agr. Chem. 15:227–266.

(168) ——— and Merz, A. R.
1931. PHOSPHORIC ACID. *In* Wiley, H. W., Principles and Practice of Agricultural Analysis; A Manual for the Study of Soils, Fertilizers, and Agricultural Products, for the Use of Analysts, Teachers, and Students of Agricultural Chemistry. v. 2. Fertilizers and Insecticides. Ed. 3, rev. and enl., p. [41]–212, illus. Easton, Pa.

(169) Schaller, W. T.
1912. MINERALOGICAL NOTES, SERIES 2. U.S. Geol. Survey Bul. 509, 115 p., illus.

(170) Schoch, E. P.
1918. CHEMICAL ANALYSES OF TEXAS ROCKS AND MINERALS. Tex. Univ. Bul. 1814, 256 p.

(171) Schreiner, O.
1929. THE RÔLE OF THE RARER ELEMENTS IN SOILS, FOODS, AND DRUGS. Jour. Assoc. Off. Agr. Chem. 12:16–30, illus.

(172) Schucht, L.
1926. DIE FABRIKATION DES SUPERPHOSPHATES MIT BERÜCKSICHTIGUNG DER ANDEREN GEBRÄUCHLICHEN DÜNGEMITTEL. Ed. 4, 372 p., illus. Braunschweig.

(173) Schultz, A. R.
1918. A GEOLOGIC RECONNAISSANCE FOR PHOSPHATE AND COAL IN SOUTHEASTERN IDAHO AND WESTERN WYOMING. U.S. Geol. Survey Bul. 680, 84 p., illus.

(174) ———
1919. A GEOLOGIC RECONNAISSANCE OF THE UINTA MOUNTAINS, NORTHERN UTAH, WITH SPECIAL REFERENCE TO PHOSPHATE. U.S. Geol. Survey Bul. 690:31–94, illus.

(175) ——— and Richards, R. W.
1913. A GEOLOGIC RECONNAISSANCE IN SOUTHEASTERN IDAHO. U.S. Geol. Survey Bul. 530:267–284, illus.

(176) Sellards, E. H.
1910. A PRELIMINARY PAPER ON THE FLORIDA PHOSPHATE DEPOSITS. Fla. Geol. Survey Ann. Rpt. 3:[21]–41, illus.

(177) ———
1915. THE PEBBLE PHOSPHATES OF FLORIDA. Fla. Geol. Survey Ann. Rpt. 7:[25]–116, illus.

(178) Shaler, N. S.
1888. REPORT ON THE GEOLOGY OF MARTHA'S VINEYARD. U.S. Geol. Survey Ann. Rpt. (1885–86) 7:303–363, illus.

(179) Shead, A. C.
1923. PHOSPHATE ROCKS IN OKLAHOMA. Okla. Acad. Sci. Proc. 3:97–102, illus. (Okla. Univ. Bul. (n.s.) 271).

(180) ———
1923. PHOSPHATE IN PERMIAN RED BEDS OF OKLAHOMA AND TEXAS. Chem. Age [New York] 31:319–320.

(181) Shepard, C. U., jr.
1880. SOUTH CAROLINA PHOSPHATES. 29 p., illus. Charleston, S.C.

(182) ———
1880. SOUTH CAROLINA PHOSPHATES AND THEIR PRINCIPAL COMPETITORS IN THE MARKETS OF THE WORLD. S.C. Commr. Agr. Ann. Rpt. 1:68–115, illus.

(183) Smith, E. A.
1892. ON THE PHOSPHATES AND MARLS OF ALABAMA. Ala. Geol. Survey Bul. 2, 82 p.

(184) ———
1895. PHOSPHATES AND MARLS OF ALABAMA. Amer. Inst. Mining Engin. Trans. 25:811–822.

(185) ——— and McCalley, H.
1904. INDEX TO MINERAL RESOURCES OF ALABAMA. Ala. Geol. Survey [Bul. 9], 79 p., illus.

(185a) Smith, H. V., and Smith, M. C.
1932. MOTTLED ENAMEL IN ARIZONA AND ITS CORRELATION WITH THE CONCENTRATION OF FLUORIDES IN WATER SUPPLIES. Ariz. Agr. Expt. Sta. Tech. Bul. 43, p. [213]–287, illus.

(186) Smith, R. W.
1926. GEOLOGY AND UTILIZATION OF TENNESSEE PHOSPHATE ROCK. Amer. Inst. Mining and Metall. Engin. Trans. 74:127–146, illus.

(187) Starynkevich-Borneman, I. D.
1924. SUR LA PRESENCE DES TERRES RARES DANS LES APATITES. Compt. Rend. Acad. Sci. Russie (A):39–41.

(188) Stone, R. W.
1920. PHOSPHATE ROCK. U.S. Geol. Survey Min. Resources U.S. 1917 (pt. 2):7–18.

(189) ——— and Bonine, C. A.
1915. THE ELLISTON PHOSPHATE FIELD, MONTANA. U.S. Geol. Survey Bul. 580:373–383, illus.

(190) Stose, G. W.
1907. PHOSPHORUS ORE AT MOUNT HOLLY SPRINGS, PA. U.S. Geol. Survey Bul. 315:474–483.

(191) ———
1914. PHOSPHATE DEPOSITS IN SOUTHWESTERN VIRGINIA. U.S. Geol. Survey Bul. 540:383–396, illus.

(192) Stubbs, W. C.
1885. PHOSPHATE ROCK, ALABAMA. U.S. Geol. Survey Min. Resources U.S. 1883–84:794–803.

(193) Tanakadate, H. S., and Carobbi, G.
1929. SOPRA UN NUOVO GIACIMENTO DI APATITE IN CINA. Rend. Accad. Sci. Fis. e Mat. Napoli (4) 35:116–132, illus.

(193a) Thompson, T. G., and Taylor, H. J.
1933. DETERMINATION AND OCCURRENCE OF FLUORIDES IN SEA WATER. Indus. and Engin. Chem., Analyt. Ed. 5:87–89.

(194) Waggaman, W. H.
1910. A REVIEW OF THE PHOSPHATE FIELDS OF IDAHO, UTAH, AND WYOMING, WITH SPECIAL REFERENCE TO THE THICKNESS AND QUALITY OF THE DEPOSITS. U.S. Dept. Agr., Bur. Soils Bul. 69, 48 p., illus.

(195) ———
1911. A REVIEW OF THE PHOSPHATE FIELDS OF FLORIDA. U.S. Dept. Agr., Bur. Soils Bul. 76, 23 p.

(196) ———
1912. A REPORT ON THE NATURAL PHOSPHATES OF TENNESSEE, KENTUCKY, AND ARKANSAS. U.S. Dept. Agr., Bur. Soils Bul. 81, 36 p., illus.

(197) ———
1913. A REPORT ON THE PHOSPHATE FIELDS OF SOUTH CAROLINA. U.S. Dept. Agr. Bul. 18, 12 p., illus.

(198) ———
1914. THE RESERVE SUPPLY OF PHOSPHATE ROCK IN THE UNITED STATES. Jour. Indus. and Engin. Chem. 6:464–465.

(199) ——— and Easterwood, H. W.
1927. PHOSPHORIC ACID, PHOSPHATES, AND PHOSPHATIC FERTILIZERS. 370 p., illus. New York.

(200) ——— Easterwood, H. W., and Turley, T. B.
1923. INVESTIGATIONS OF THE MANUFACTURE OF PHOSPHORIC ACID BY THE VOLATILIZATION PROCESS. U.S. Dept. Agr. Bul. 1179, 55 p., illus.

(201) Wagner, C. R., and Ross, W. H.
1917. A MODIFIED METHOD FOR THE DETERMINATION OF FLUORINE WITH SPECIAL APPLICATION TO THE ANALYSIS OF PHOSPHATES. Jour. Indus. and Engin. Chem. 9:1116–1123, illus.

(202) Watson, T. L.
1907. MINERAL RESOURCES OF VIRGINIA. 618 p., illus. Lynchburg, Va.

(203) ——— and Gooch, S. D.
1918. VIVIANITE FROM THE LAND PEBBLE PHOSPHATE DEPOSITS OF FLORIDA. Jour. Wash. Acad. Sci. 8:82–88.

(204) ——— and Taber, S.
1913. GEOLOGY OF THE TITANIUM AND APATITE DEPOSITS OF VIRGINIA. Va. Geol. Survey Bul. 3-A, 308 p., illus.

(205) Weller, S.
1907. NOTES ON THE GEOLOGY OF SOUTHERN CALHOUN COUNTY. Ill. Geol. Survey Bul. 4:[219]–233.

(206) Wilber, F. A.
1883. APATITE. U.S. Geol. Survey Min. Resources U. S. 1882:521.

(207) Wilke-Dörfurt, E., Beck, J., and Plepp, G.
1928. ÜBER DAS VORKOMMEN VON JOD IN PHOSPHATLAGERN. Ztschr. Anorg. Allgem. Chem. 172:344–352, illus.

(208) Wright, C. D.
1893. THE PHOSPHATE INDUSTRY OF THE UNITED STATES. U.S. Commr. Labor Spec. Rpt. 6, 145 p., illus.

(209) Wyatt, F.
1892. THE PHOSPHATES OF AMERICA; WHERE AND HOW THEY OCCUR; HOW THEY ARE MINED; AND WHAT THEY COST. . . . Ed. 4, 187 p., illus. New York.

(210) Zies, E. G.
1929. THE VALLEY OF TEN THOUSAND SMOKES. I. THE FUMAROLIC INCRUSTATIONS AND THEIR BEARING ON ORE DEPOSITION. II. THE ACID GASES CONTRIBUTED TO THE SEA DURING VOLCANIC ACTIVITY. Natl. Geogr. Soc. Contributed Tech. Papers (Katmai Ser.) 1, no. 4, 79 p., illus.

(211) Zuccàri, G.
1913. SULLA PRESENZA DELL'ARSENICO COME ELEMENTO NORMALE NELLE TERRE. Gaz. Chim. Ital. 43 (pt. 2):398–403.

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