

Phosphate Deposits

GEOLOGICAL SURVEY BULLETIN 1252-D



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By V. E. McKELVEY

CONTRIBUTIONS TO ECONOMIC GEOLOGY

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*A summary of salient features of the
geology of phosphate deposits, their
origin, and distribution*



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PHOSPHATE DEPOSITS

By V. E. MCKELVEY

Abstract

The earth's crust contains an average of about 0.27 percent P_2O_5 , most of which occurs in species of apatite, $Ca_{10}(PO_4,CO_3)_6(F,Cl,OH)_2$. Common igneous rocks contain 0.005–0.4 percent P_2O_5 , but some of the less common alkalic rocks contain 1 percent or more.

Apatite is slowly soluble in neutral or alkaline waters, and its solubility increases with increasing acidity. It may survive rock weathering to form a phosphate-rich residuum, but it breaks down under prolonged exposure. The PO_4 content of most river and lake waters ranges from about 0.01 to 0.5 part per million (ppm), but may be much higher in soft acid waters and highly saline alkaline lakes. About one-sixth of the phosphate carried to the sea by runoff is in dissolved form. The ocean as a whole is nearly saturated with phosphate, but its distribution within the ocean is not uniform; deep cold waters contain nearly 0.3 ppm PO_4 , but warm surface waters contain only 0.01 ppm or less. Oceanic circulation brings phosphate-rich water to the surface in several environments, and phosphate may be precipitated either inorganically or biochemically, as the pH and temperature increase near the surface. Such nutrient-rich waters support abundant plant and animal life, including large colonies of fish-eating seafowl.

Mineable concentrations of phosphate, containing from 5 to 35 percent P_2O_5 , are formed in all phases of the phosphate cycle. Primary deposits include igneous apatites, sedimentary phosphorites, and guano; secondary deposits form from each of these as the result of weathering. Apatites of igneous origin include hydrothermal veins and disseminated replacements, marginal differentiations near the boundaries of intrusions, and pegmatites, but the largest deposits are intrusive masses or sheets associated with carbonatite, nepheline-syenite, and other alkalic rocks. Most of the world's phosphate production comes from marine phosphorites, many of which are associated with black shale and chert. Secondary processes—including diagenetic phosphatization of calcium carbonate and interstitial precipitation, reworking by waves and currents, and weathering—have often played a prominent part in forming deposits of mineable quality. Guano deposits consist of natural accumulation of the excrement of bats or, more importantly, seafowl, altered to various degrees through dehydration, oxidation, and

leaching. Phosphate leached from guano phosphatizes the underlying rocks in some areas, forming apatite where the host rock is limestone and forming aluminum- or aluminum-iron-phosphate minerals where the underlying rock is a silicate. Individual deposits of both igneous apatite and marine phosphorite commonly contain hundreds of millions or billions of tons. Guano deposits and phosphatized rock derived from them are typically much smaller, but a few contain millions of tons. World resources total hundreds of billions of tons.

INTRODUCTION

Phosphorus is a vital component of every living cell, and it plays several fundamental parts in metabolic processes (Albaum, 1952). It is required for the synthesis of starch, is an integral part of nucleic acids, may be essential to photosynthesis, is a major constituent of bone and teeth, and is important in the shell or shell-forming process of many organisms. Among the essential plant nutrients, phosphorus is one of the less abundant in most soils, and its availability is one of the most critical factors controlling plant growth.

Most virgin soils in temperate climates contain enough phosphorus to support good crop production, but many soils in tropical climates are naturally deficient in phosphorus because it is leached out during the advanced stages of chemical weathering. Phosphorus can be added to deficient soils in the form of natural or artificial fertilizers, and for sustained good yields it must be added to all soils when they are cropped heavily for long periods. Phosphate fertilizers are used extensively now in the developed countries, but in many of the less developed countries their use must be much increased to bring crop production to acceptable levels. Annual consumption of phosphate, for example, is about 20–50 pounds per capita in western European countries, but is under 2 pounds per capita in most of the less developed countries. Deficiencies in plant nutrients, including nitrogen and potash as well as phosphate, are now the major factors limiting crop production in the less developed countries (Parker and Nelson, 1966), and fertilizers will play a key role in the war on hunger in the years ahead.

In the United States about two-thirds of the phosphate consumed is used for agriculture; the remainder is used as chemicals for detergents and other cleaning compounds, leavening agents, food preservatives, insecticides, and many other products.

World demands for phosphate are expected to double within the next decade. Although known supplies are adequate to meet world needs for many years, additional sources are needed in regions that contain no known minable deposits, for phosphate rock is a

low-value commodity and transportation costs may add substantially to its price at the point of final use. New sources are especially needed in many developing countries that have neither known minable deposits nor the ability to pay for imports.

Unlike many other minerals, phosphate rock has not been intensively prospected for in the past; and because it resembles limestone and other common rocks in appearance, it has not always been recognized even where it has been uncovered in the course of other work. Opportunities for new discoveries are good, therefore, and the increasing knowledge about the origin and occurrence of phosphate deposits should aid in prospecting. The salient features of the geology of phosphate deposits are summarized here as background and orientation for those newly concerned with the problem.

MINERALOGY

About 200 minerals are known that contain 1 percent or more P_2O_5 .¹ Most of the phosphorus in the earth's crust, however, occurs in species of the apatite group, $Ca_{10}(PO_4,CO_3)_6(F,Cl,OH)_2$ (Palache and others, 1951, p. 877; Altschuler and others, 1958; Deer and others, 1962, p. 324). The structure of apatite favors a wide variety of minor substitutions (McConnell, 1938). For example, small amounts of VO_4 , As_2O_4 , SO_2 , SO_4 , or CO_3 may substitute for equivalent amounts of PO_4 ; the F position may be partly or completely occupied by F, Cl, or OH; and minor amounts of Mg, Mn, Sr, Pb, Na, U, Ce, and Y and other rare earths may substitute for Ca. Cationic replacements involving loss or gain of valence may be compensated for by anionic replacements of opposite nature. The composition of apatite deposits, therefore, may change on exposure to solutions of different composition from those from which they were deposited. One characteristic change is the substitution of fluorine for hydroxyl in teeth and bone, which results in a decrease in the solubility of apatite. It is this phenomenon that constitutes the basis for fluoridating water to prevent dental caries and that was utilized in demonstrating that the bones of "Piltdown Man" were of modern rather than ancient age (Oakley, 1955; Weiner and others, 1953).

Apatite is the principal primary mineral, but a number of others are common in deposits formed during weathering of phosphate

¹In the trade the phosphate content of phosphate rock and fertilizer is commonly reported as $Ca_3(PO_4)_2$, known as bone phosphate of lime (B.P.L.). To convert P_2O_5 to B.P.L., multiply percentage P_2O_5 by 2.18. To convert to P, multiply percentage P_2O_5 by 0.436.

rock and guano.² Examples are brushite ($\text{HCaPO}_4 \cdot 2\text{H}_2\text{O}$), moneite (HCaPO_4), whitlockite ($\beta\text{-Ca}_3(\text{PO}_4)_2$), crandallite ($\text{CaAl}_2(\text{PO}_4)_2(\text{OH}) \cdot 5\text{H}_2\text{O}$), wavellite ($\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$), taranakite ($\text{K}_2\text{Al}_6(\text{PO}_4)_6(\text{OH})_2 \cdot 18\text{H}_2\text{O}$), millisite ($(\text{Na},\text{K})\text{CaAl}_6(\text{PO}_4)_4(\text{OH})_6 \cdot 3\text{H}_2\text{O}$), variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$), and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$).

GEOCHEMICAL DISTRIBUTION AND BEHAVIOR

The earth's crust contains about 0.27 percent P_2O_5 . Common igneous rocks, such as granite, diorite, gabbro, and peridotite, contain only from about 0.005 to 0.4 percent P_2O_5 , but some of the less common alkalic rocks, such as ijolite and turjaite, can contain more than 1 percent. Variations in phosphate content of igneous rocks generally parallel those of ilmenite and magnetite.

Apatite is slowly soluble in neutral or alkaline waters, and its solubility increases with increasing acidity, decreasing hardness, and decreasing temperature. Apatite may survive rock weathering for a time to form a phosphate-rich residuum, but it breaks down under prolonged exposure. Some of it may be redeposited locally. In high-calcium soils and rocks, apatite is again the mineral formed. Where the terrane consists of igneous rocks, aluminum or iron phosphates such as variscite or strengite are the secondary minerals (Hutchinson, 1952). In subtropical or tropical climates, where clay minerals and hydroxides are the end products of weathering, aluminum phosphates such as wavellite are formed.

Most phosphorus is carried to the sea as phosphate minerals or adsorbed on iron or aluminum hydroxides or clay, but some is carried in particulate or dissolved organic compounds, and about one-sixth of the total is carried in solution. The PO_4 content of most river and lake waters ranges from about 0.01 to 0.5 part per million (ppm). Soft acid waters, such as those in parts of the Florida Peninsula, may contain a few parts per million, however, and the highly saline alkaline lake waters (such as Searles Lake, Calif.) contain 200–900 ppm.

The ocean as a whole is nearly saturated with phosphate, and an amount equivalent to that brought by rivers is precipitated almost continuously (Dietz and others, 1942; Kramer, 1964a, 1964b; Roberson, 1966; Sillén, 1961; Smirnov and others, 1958).

² The term "phosphate rock" is loosely applied to rocks of any origin that contain more than about 20 percent P_2O_5 . The term "phosphorite" is equivalent in meaning, but is commonly applied only to phosphate rocks of marine origin. "Guano" is the term applied to accumulations of animal excrement, altered to various degrees through hydration, oxidation, and leaching.

The phosphate content of the ocean is by no means uniform, however; deep cold waters contain nearly 0.3 ppm PO_4 , but warm surface waters contain only 0.01 ppm or less. Oceanic circulation (mainly a reflection of atmospheric circulation, brought about by solar heating combined with the rotation of the earth) deep plows the sea and brings these phosphate-rich waters to the surface in several environments (Sverdrup and others, 1942, p. 140, 241, 246, 785; Brongersma-Sanders, 1948).

In an idealized ocean (see Fleming, 1957), the main elements of the current system consist of a large circulating gyral in each hemisphere (fig. 1); water cooled in polar latitudes moves toward the equator along the east side of the ocean, and water warmed in equatorial latitudes moves poleward along the west side. In this system, cold nutrient-rich waters are brought to the surface in four situations:

1. Where a current diverges from a coast, or where two currents diverge from each other such as along the equatorial currents and countercurrent (divergence upwelling). The effects of currents moving toward the equator in bringing cold phosphate-rich water along the coast are abetted by the seaward movement of coastal surface water that results from the combined effects of prevailing wind and Coriolis force; for as the surface water moves seaward, deep cold water wells up to replace it.
2. Where two currents meet to produce turbulence.
3. Along the west edge of poleward-moving density currents such as the Gulf Stream, where heavy and usually cold water lies to the left of the observer looking in the direction of flow in the northern hemisphere and lies to the right in the southern hemisphere (dynamic upwelling). In middle and northern latitudes, a cool coastal countercurrent, such as that along the Northeastern United States, is an accompanying feature (Sverdrup and others, 1942, p. 676).
4. In upper latitudes where highly saline water from the tropics tends to sink as a result of winter cooling (convection).

Each of these processes may take place in locations besides those shown in figure 1. For example, upwelling may take place wherever a prevailing wind or current moves surface water away from a coast, and some convection as a result of increase in density of surface water with winter cooling may take place wherever there are pronounced seasonal variations in temperature.

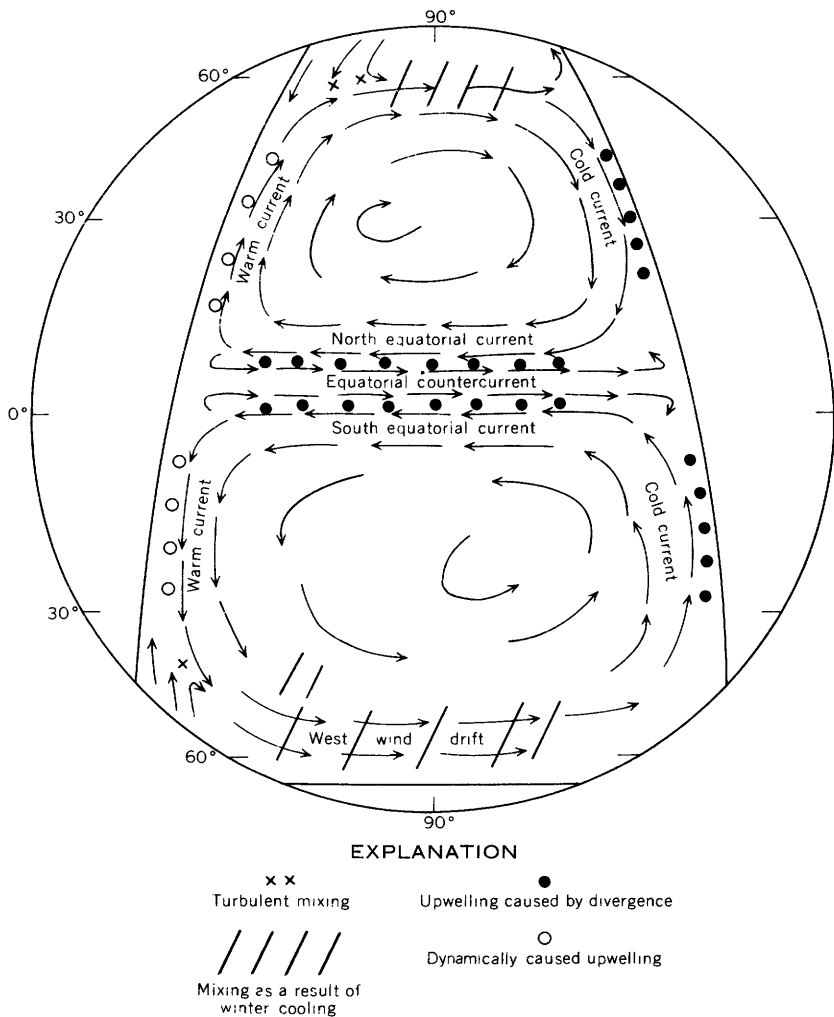


FIGURE 1.—Surface currents in an idealized ocean, showing areas of ascending nutrient-rich water.

Pronounced climatic, biologic, and geologic effects accompany upwelling, especially where it is produced by divergence in coastal areas (fig. 2). The presence of cold waters along coasts produces

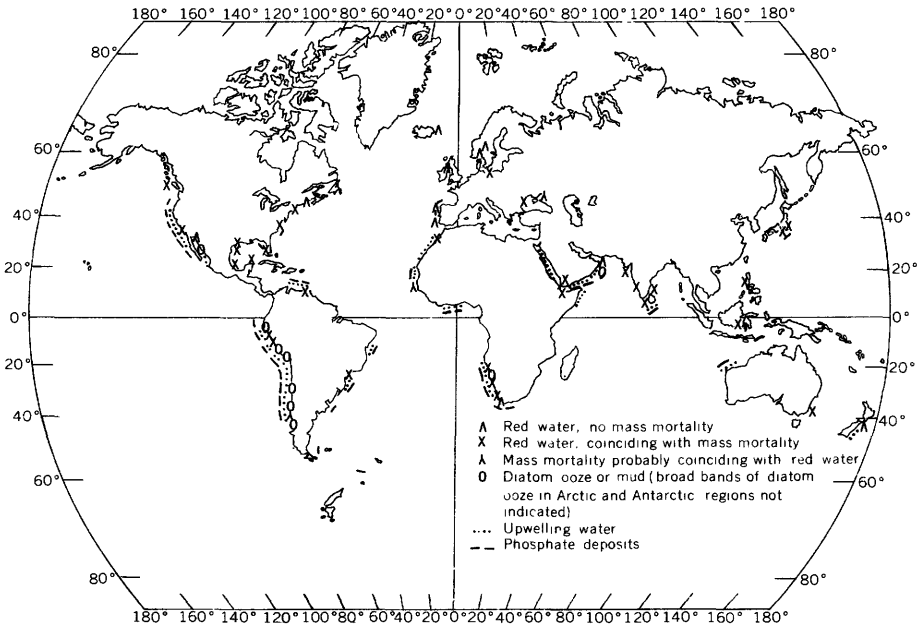


FIGURE 2.—Distribution of upwelling water and related phenomena in modern oceans. Modified from Brongersma-Sanders (1957) to include data on the distribution of phosphate deposits.

coastal fogs and humid-air deserts, such as those of northern Chile and southwest Africa. The nutrient-rich waters that lie alongside these deserts are the lushest gardens of the sea, for the upwelling cold waters there support tremendous quantities of organisms, with diatoms and other phytoplankton at one end of the food chain, and fish, whales, and fish-eating seafoal at the other. Blooms of dinoflagellates (red tides) and diatoms are characteristic biologic phenomena in upwelling areas, as are the mass mortalities of fish that accompany red tides and may be a consequence of them (Brongersma-Sanders, 1948, 1957). Most of the large accumulations of guano are formed by seafoal colonies feeding in these waters, and it is the extremely dry climate created by upwelling that makes the preservation of guano possible (Hutchinson, 1950).

Concentrations of nutrients and accompanying organic growths are also found near the mouths of some large rivers, as well as in estuaries in which the outflow of surface water is replaced by a countercurrent of sea water. The decaying remains of organisms in such estuaries sink from outflowing surface water, and their decay products are trapped in the system by inflowing sea water; nutrients accumulate as a result of this process, and such estuaries often contain a higher phosphate content than adjacent river or sea water. The same process may also tend to enrich the nutrient content of upwelling waters (Redfield and others, 1963, p. 60-66).

The solubility of phosphate in upwelling waters decreases as the temperature and pH increase near the surface (Kazakov, 1937; Kramer, 1964b; Roberson, 1966), and apatite may be precipitated by organic or inorganic processes. Organic skeletons and excrement contribute phosphate in concentrated form to the sea bottom, and organic tissues may carry phosphate to the bottom in moderately soluble organic compounds, from which it may be released before or after burial (van Vloten, 1955, p. 141; Bushinski, 1964). Apatite, generally as carbonate-fluorapatite but under special conditions perhaps also as hydroxyapatite (Kramer, 1964b), may also be precipitated from sea water by inorganic processes; a common textural type of phosphorite composed of unaggregated microcrystalline apatite may have formed in this way (Gulbrandsen, 1960, p. 119).

Fossil shells, such as gastropods and pelecypods, that were nonphosphatic during the life of the organism, are sometimes found to be composed of apatite, giving clear evidence of replacement prior to or after burial. Apatite replacement of calcite has been demonstrated experimentally and has been suggested by Ames (1959) to be the main process by which marine phosphorite is deposited. Evidence for its operation on a large scale, however, is lacking in most deposits. Interstitial accretion probably is a quantitatively more important diagenetic process and may be one of the processes by which the pellets and similar aggregates that are common in many phosphorites are first formed (Sheldon, 1957, p. 123; Bushinski, 1964; Cressman and Swanson, 1964, p. 375; D'Anglejan, 1967).

Although biologic processes are important in enriching the nutrient content of upwelling waters and in precipitating phosphate, they operate within and are basically controlled by the physical and chemical conditions of the system. The phosphorites and their lateral equivalents in the environment of strong upwelling—black shale, chert, dolomite, limestone, and evapo-

rites—are thus depositional products from moving masses of water that change in composition as the result of physical, chemical, and biologic processes (Gulbrandsen, 1960).

Submarine volcanism has been suggested as a local source of the fluorine, phosphorus, and silica of marine phosphorites (Taliaferro, 1933; Mansfield, 1940; Gibson, 1967). No doubt volcanic activity does contribute to the concentration of these and other elements in sea water, but their present distribution in sea water is not controlled by volcanic activity, and the processes described yield deposition from sea water of normal composition (McKelvey, Swanson, and Sheldon, 1953, p. 57; McKelvey and others, 1959, p. 27).

PHOSPHATE DEPOSITS

Minable concentrations of phosphate are formed in all phases of the phosphate cycle through the processes just described. Ordinarily these processes merely concentrate phosphorus a few times over its crustal average, but when they are permitted to operate under unusually favorable conditions, they may yield concentrations 100–125 times those of the crustal average. Particularly effective in forming rich deposits are two or more of these concentrating processes acting in sequence. For example, the oceanographic processes that result in upwelling bring phosphate-rich waters to the zone of photosynthesis where biologic or chemical processes may precipitate phosphate and form concentrations of a few percent P_2O_5 . Biologic, chemical, and mechanical processes may subsequently upgrade these deposits by oxidizing carbonaceous matter, forming pellets or nodules through diagenetic addition or reorganization of phosphatic material within the sediment, and winnowing away lighter and smaller particles, such as carbonaceous matter and clay (Altschuler and others, 1964). The phosphorites that result from these successive processes may contain as much as 25–30 percent P_2O_5 . They, along with rocks containing lesser concentrations, may be upgraded still further by weathering; in fact, the bulk of the world's production of phosphate, particularly rock containing more than 30 percent P_2O_5 , comes from deposits that have been enriched by weathering.

The principal kinds of phosphate deposits (McKelvey, Cathcart, Altschuler, Swanson, and Buck, 1953), classed according to the process responsible for their primary localization, are igneous apatites, sedimentary phosphorites, and guano. Secondary deposits form from each of these as the result of weathering.

APATITE DEPOSITS OF IGNEOUS ORIGIN

Apatite deposits of igneous origin occur as intrusive masses or sheets, as hydrothermal veins or disseminated replacements, as marginal differentiations along or near the boundaries of intrusions, or as pegmatites.

The intrusive masses are the largest of these deposits. They are commonly associated with alkalic igneous rock complexes, many of which—such as those in Africa, Brazil, and Sweden—are associated with rift valley structures. Carbonatite, ijolite, nepheline-syenite, and pyroxenite are common members of the rock assemblage. Many of these complexes have a ringlike structure, with carbonatite as the central core (Pecora, 1956). Apatite or apatite-magnetite deposits occur as inclined sheets, in some places roughly interleaved around the core. Their thickness ranges from tens to hundreds of feet, and some are traceable for hundreds of feet or even a few miles. Their P_2O_5 content is as much as 36 percent, and lower grade deposits rich in magnetite are easily beneficiated. Deep weathering, as at Sukulu, Uganda, may yield a phosphate-rich residuum at the surface during decomposition of calcite, dolomite, and other more soluble minerals. Alkalic complexes known to contain apatite or to be favorable for its occurrence are much more numerous than was believed prior to World War II. Some of the largest deposits are found in the Kola Peninsula, U.S.S.R. (Fiveg, 1937), in eastern Uganda (Davies, 1947), and in Palabora in the Republic of South Africa (Russell and others, 1954).

Most of the other apatite deposits are either less extensive or lower in quality and hence of less economic importance. Examples include the disseminated deposits of hydrothermal apatite-ilmenite (nelsonite) in Nelson County, Va. (Ross, 1941), the apatite veins in Norway, the apatite-magnetite marginal deposits associated with alaskite in the eastern Adirondacks, and the apatite-pegmatite deposits of southern Ontario.

SEDIMENTARY PHOSPHORITE AND WEATHERING DERIVATIVES

Most of the world's phosphate production comes from marine phosphorites. The richest and largest of these form at low latitudes (Sheldon, 1964b) in areas of upwelling associated with divergence, chiefly along the west coasts of the continents or, in large mediterranean seas, along the equatorial side of the basin. Lesser but significant concentrations form along the west sides of poleward-moving warm currents along the eastern coasts of continents (figs. 1, 2).

The rock assemblage in the cold-current environment is the product of deposition on a shoaling bottom over which shoreward

moving waters are progressively warmed (Kazakov, 1937; Macpherson, 1945, p. 34-41). The typical lateral sequence of rocks, in a shoreward direction, consists of dark carbonaceous shale, phosphatic shale, phosphorite, and dolomite; chert or diatomite; several facies of carbonate rock; and saline deposits and red or light-colored sandstone or shale (McKelvey and others, 1959). These rocks were deposited synchronously, and they grade laterally into each other or intertongue. Because the environments in which these rocks are deposited shift laterally with epeirogenic movements of the sea bottom, the rocks are found in vertical sequence in nearly this same or reverse order. The thickest accumulations of phosphorite form in areas of geosynclinal subsidence, and in such areas phosphorite is generally associated with carbonaceous shale and chert (McKelvey, Swanson, and Sheldon, 1953). The phosphorite is typically carbonaceous and pelletal, but nodules as well as skeletal matter and phosphatic shells may be present in lesser quantities. Individual beds may be several feet thick, can contain 30 percent or more P_2O_5 , and extend over hundreds of square miles. Phosphorites formed on adjacent platforms or stable areas are generally associated with cherty carbonate rock and light-colored sandstone or shale. The phosphorite is not appreciably carbonaceous and is likely to contain phosphatized shells as well as naturally phosphatic organic remains. It may consist largely of nodules, but phosphatic sandstone is a common textural type. Individual beds are generally only a few feet thick and contain less than 30 percent P_2O_5 . Thicker and richer deposits may occur locally but are highly lenticular. In Israel (Bentor, 1953) and Egypt (Youssef, 1965) such deposits are localized in synclines that evidently represented shallow depressions at the time of deposition. Examples of phosphorites deposited from upwelling associated with divergence are found in the Permian Phosphoria Formation in Idaho and adjacent States (Mansfield, 1927; Emigh, 1958; McKelvey and others, 1959; Sheldon, 1963; Cressman and Swanson, 1964), Miocene Monterey Formation of California (Gower and Madsen, 1964; Dickert, 1966), Mississippian and Triassic deposits of northern Alaska (Patton and Matzko, 1959), Jurassic La Caja and La Casita Formations in north-central Mexico (Rogers and others, 1961), Miocene deposits in the Sechura Desert of Peru (Harrington and others, 1966), and extensive deposits of Cretaceous and Eocene age in western and northern Africa and the Middle East (British Sulphur Corporation, 1964). Phosphate deposits are abundant on the present sea bottom in most areas of upwelling; some of those off the California coast are being consid-

ered for mining by dredging (Dietz and others, 1942; Emery, 1960; Mero, 1965).

Phosphate deposits that formed in the warm-current environment along the eastern coasts of the continents generally consist of phosphatic limestone or sandstone. Chert, black shale, and salines are not associated with these deposits, and they are less extensive and lower in grade than the deposits formed from cold currents. In fact, only where these deposits have been either extensively reworked by submarine currents and (or) subjected to weathering are they rich enough to be mined, and even then most of them need to be beneficiated artificially. Examples include deposits in the Pliocene Bone Valley Formation of Florida (Cathcart, 1963; Altschuler and others, 1964), the Miocene of south-central Georgia and northern Florida (Sever and others, 1967), the Miocene Pungo River Formation of North Carolina (Brown, 1958; Kimrey, 1965), and the Upper Cretaceous Gramme Formation near Recife, Brazil (Harrington and others, 1966). Phosphate in this general environment may be the product of dynamic upwelling or the cool countercurrent associated with warm density currents (compare Gibson, 1967, p. 644), but the distribution of some of the deposits suggests estuarine deposition (Altschuler and others, 1964; Bushinski, 1964) and may have resulted from processes of estuarine circulation and nutrient enrichment (Redfield and others, 1963; Pevear, 1966).

Secondary processes have played a prominent part in concentrating the richest of the marine deposits. For example, the highest grade phosphate beds in the Phosphoria Formation appear to have been extensively washed by marine currents; in addition, leaching of carbonates and sulfides together with oxidation of carbonaceous matter has raised their P_2O_5 content from about 27–30 percent at depths of a few hundred feet to 32–35 percent near the surface. Similarly, the Bone Valley deposits originated through submarine reworking of phosphatic residuum developed during deep weathering of phosphatic marls in the Miocene Hawthorn Formation; leaching related to recent weathering has upgraded some of the deposits still further (Altschuler and others, 1964). The common occurrence of phosphorite at unconformities also reflects the combined effects of weathering and submarine reworking (Goldman, 1922).

Weathering in the present cycle accounts for the formation of enriched residual and replacement deposits from phosphatic deposits not otherwise minable. The Tennessee "brown rock" phosphate deposits consist of present-day residuum developed through decomposition of phosphatic limestones of Ordovician

age (Smith and Whitlatch, 1940). The "river pebble" deposits prominent in the early history of phosphate mining in Florida and South Carolina are mostly placers formed by alluvial concentration of phosphatic pebbles eroded from the phosphatic formations of the adjacent terrain.

The Tennessee "white rock" and Florida "hard rock" deposits were formed by redeposition of phosphate derived from the decomposition of apatite under more advanced weathering. The same decomposition-phosphatization process accounts for the formation of calcium aluminum phosphate and aluminum phosphate in the "leached zone" of the Bone Valley field and the deeply weathered Cretaceous and Eocene deposits of west Africa (Capdecemme, 1953).

In addition to the marine phosphorites described above, carbonate-fluorapatite has been found recently in thin lake beds of Eocene age in Wyoming (Love, 1964), and noncommercial deposits of sodium phosphate minerals are found locally in or associated with saline deposits formed in the highly alkaline saline lakes (Fahey, 1962). Glauconite, associated with the marine phosphorites in many places, contains from 1 to 5 percent P_2O_5 , and because it also contains potash it has had some use as a fertilizer (Mansfield, 1922). Some sedimentary iron ores contain a few percent P_2O_5 (Geijer, 1962; Davidson, 1963), and the basic slag (Thomas meal) made from these ores (as well as that made from apatite-rich magnetite deposits of igneous origin) contains 8 percent or more P_2O_5 and is locally used as a fertilizer.

GUANO AND RELATED DEPOSITS

Most of the large accumulations of guano are formed at the surface by seafowl, but smaller quantities are formed by bats and to a lesser extent by other cave-dwelling mammals and birds (Hutchinson, 1950). The bat guanos are most abundant in the cave districts of temperate and tropical regions. Although many bat-guano deposits have been found and mined, most of them have been measured in hundreds or thousands of tons, and only sporadic production is obtained from them now. Seafowl deposits are mainly confined to islands and coastal regions in low latitudes. The largest lie along the west coasts of Lower California, South America, and Africa, and on islands near the equatorial currents. Many used to be several hundred thousand tons in size, and although most of the fossil accumulations have been mined out, production from the current crop is continuing in some areas.

Fresh seafowl droppings contain about 22 percent N and 4 percent P_2O_5 . Decomposition proceeds rapidly, and the phosphate content increases as the nitrogen (and total organic matter) decreases. Modern guano contains 10–12 percent P_2O_5 , but leached guano contains 20–32 percent. The mineralogy of guano is complex. Slightly decomposed deposits contain soluble ammonium and alkali oxalates, sulfates, and nitrates, and a variety of magnesium and ammonium-magnesium phosphates. Largely decomposed guano consists chiefly of calcium phosphates (for example, monetite or whitlockite).

In areas where rainfall, however slight, is a normal event, the soluble phosphates of guano are carried to underlying rocks, where they may be deposited as cavity fillings or replacements. Through this process, phosphate from guano has accumulated over long periods of geologic time, and it has formed some comparatively large deposits. For example, reserves on Nauru, an island in the equatorial region of the western Pacific Ocean, were originally about 90 million tons of rock averaging about 39 percent P_2O_5 (Hutchinson, 1950, p. 221). The mineralogy of phosphatized rocks derived from guano depends on the composition of the host rock. Where it is limestone, as on many of the coral atolls, the phosphate mineral is apatite; but where the underlying rock is a silicate, as in islands of volcanic origin, the phosphate minerals are aluminum or aluminum-iron phosphates.

GUIDES TO PROSPECTING

The geologic relations described above provide the basis for prospecting for new deposits, at least to the extent of defining provinces and terranes worthy of field reconnaissance. The relation of alkalic rocks to the rift zones helps focus on areas favorable for their occurrence, and the identification of individual alkalic complexes defines specific targets worthy of more detailed examination and exploration. The location of areas of modern upwelling (and associated features) is a prime clue to the presence of phosphorite on the modern sea bottom and in adjacent coastal plain sediments. Probably not many nitrogenous guano deposits remain to be found, but known deposits and oceanographic features point to areas in which phosphatized rocks may occur. In older sedimentary rocks the presence of black shale and chert—the companions of phosphorite in geosynclinal deposits—are helpful clues. Other members of the phosphorite family (red beds and salines, for example) may be used to define favorable areas through regional lithofacies analysis, and, perhaps most important, the presence of phosphate even in small amounts may identify horizons that elsewhere contain richer primary or se-

condary deposits (McKelvey, 1963; Sheldon, 1964a). Paleogeographic and paleoclimatologic reconstruction, based on paleomagnetic and other studies, may make it possible to identify probable areas of upwelling in low latitudes and thus to define potential phosphogenic provinces (Sheldon, 1964b).

Because nearly all marine phosphorites contain from 0.005 to 0.02 percent U, they are radioactive enough to be identified in gamma-ray well logging and, under favorable circumstances, by aerial radiometric reconnaissance. With experience, one can recognize the phosphate rock itself by its resinous luster and its white "bloom" on the surface of weathered outcrops or fragments. A few drops of concentrated hydrochloric acid on rocks containing more than 5–10 percent P_2O_5 will produce a white spot, the density of which is roughly proportional to the phosphate content (Gardner, 1944). A simple chemical test is also available for semiquantitative analysis in the field (Shapiro, 1952).

BENEFICIATION, PROCESSING, AND USE

Because apatite is slightly heavier than some of the impurities commonly associated with it and because the "matrix" of many phosphorites is finer grained than the phosphatic particles, many impure phosphatic rocks can be upgraded by inexpensive washing or other hydraulic techniques. Noncarbonaceous deposits are effectively upgraded by flotation (Ruhlman, 1958; Service and Popoff, 1964).

A relatively small part of the phosphate mined is used directly as a fertilizer, and on acid soils in tropical or subtropical regions this may be the most efficient means of application. For most soils and for chemical uses, phosphate rock must be processed to a more soluble or purer state (Waggaman and Ruhlman, 1960). Three basic methods are used for this purpose: acidulation, electric furnace reduction to the elemental state, and fusion. Rock containing 31 percent or more P_2O_5 is generally required in acid treatment; depending on the kind and amount of acid used, a wide variety of products are made by acidulation, including superphosphate (a mixture of phosphate rock and sulfuric acid containing 16–20 percent P_2O_5), phosphoric acid, triple superphosphate (a mixture of rock and phosphoric acid containing 42–48 percent P_2O_5), and ammonium and potassium phosphates (made by combining phosphoric acid with potash or ammonia). Feed for the electric furnace contains about 24 percent P_2O_5 ; the elemental phosphorus produced by this method is used mainly for chemicals, prominent among which are detergents and other cleansing products. Fusion methods combine high-

grade phosphate rock with alkali salts, silica, or magnesium silicate and generally produce a partly defluorinated, moderately soluble slag usable as fertilizer without further treatment.

Most phosphate rock contains from 3 to 4 percent F; and much of it contains uranium, rare earths, and other minor elements (Davidson and Atkin, 1953; McKelvey and Carswell, 1956; Altschuler and others, 1958; Sheldon, 1959; Gulbrandsen, 1966; Altschuler and others, 1967). Some fluorine is now recovered, mostly for fluorosilicates used in insecticides, and processes are under development for manufacture of calcium fluoride. Uranium and vanadium have been recovered as a byproduct of phosphoric acid manufacture at times, and small quantities of other metals are recovered in ferrophosphorus, a byproduct of the production of elemental phosphorus. Some of the black shales associated with marine phosphorites contain potentially recoverable amounts of vanadium, zinc, and other metals (Gulbrandsen, 1960, 1966; Love, 1961; Lotspeich and Markward, 1963).

PRODUCTION

United States production of phosphate rock in 1966 was 39 million short tons, of which about 50 percent was used in agriculture, 25 percent in industry, and the remainder exported or stocked (Lewis, 1967). About 74 percent came from the Florida field, 11 percent from Tennessee, and 15 percent from Idaho and adjacent States. Some 40 countries in the same year contributed to world production, which totaled about 98 million tons. Of this, about 18 million came from Africa, 32 million from U.S.S.R. and Europe, 5 million from Asia, and 3 million from Oceania. Total production from Latin America, Asia and Africa (except Morocco, Senegal, Republic of South Africa, Togo, Tunisia, and Egypt) amounted to about 19 million tons, or less than one-fifth of the total.

About 74 percent of the world total was produced from marine phosphorites and their weathering derivatives, 24 percent from igneous apatite deposits, and 2 percent from guano or phosphatized rock derived from guano.

RESERVES

World reserves were estimated in 1953 (Jacob, 1953) to be on the order of 45 billion tons, but since then large deposits have been discovered in North Carolina, Georgia, Alaska, Baja California, Peru, Venezuela, Brazil, the Republic of South Africa, Uganda, several countries of west and north Africa, Israel, Jordan, China, and the U.S.S.R.; promising new prospects have also

been found in a number of other countries. Moreover, advances in beneficiation and processing technology now make it possible to recover economically many lower grade deposits that were formerly not considered minable. Although they are irregularly distributed, resources of phosphate rock in presently known deposits that are within reach of developed technology are probably on the order of hundreds of billions of tons.

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