

DEPARTMENT OF THE INTERIOR

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BULLETIN

OF THE

UNITED STATES

GEOLOGICAL SURVEY

No. 46



WASHINGTON  
GOVERNMENT PRINTING OFFICE  
1888



UNITED STATES GEOLOGICAL SURVEY

J. W. POWELL, DIRECTOR

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NATURE AND ORIGIN

OF

DEPOSITS OF PHOSPHATE OF LIME

BY

R. A. F. PENROSE, Jr.

WITH AN

INTRODUCTION BY N. S. SHALER



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GOVERNMENT PRINTING OFFICE  
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# INTRODUCTION.

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By N. S. SHALER.

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The circumstances which have led to the preparation of the sub-joined report on mineral phosphates are as follows, viz: In 1870 the present writer was employed by the Superintendent of the Coast Survey, the late Benjamin Peirce, to examine the phosphate beds of South Carolina with a view to determining the limits of that field; it was also deemed desirable to ascertain, if possible, the conditions which led to the formation of the deposits.

It was at that time the intention of Professor Peirce to have the geology of the belt of country within the limits of the Coast Survey maps carefully determined, so that they might be shaped in a way that would better serve the commercial interests of the country and also have a greater scientific value. After a time it appeared that there were legal difficulties in the way of publishing these studies in the reports of the Coast Survey and this work was suspended. It was the hope of Professor Peirce to secure a modification of the law, but before this was accomplished he retired from the post of Superintendent and his successor deemed it best to abandon the project. During the two years in which I was engaged in this work on the geology of the coast line I became very much interested in the problems connected with the origin and distribution of phosphatic deposits. From 1873 to 1880, while employed as State geologist of Kentucky, I had a chance to see a good deal of the somewhat phosphatic limestones of the Cambro-Silurian sections, a set of beds which, by their decay, have given great fertility to the soils that lie upon them. The researches of Dr. Robert Peter, the chemist of that survey, made it plain that the phosphatic contents of the soils are among the first materials to be exhausted by the careless tillage which characterizes our American agriculture, and that they are the most costly to restore to the soil.

Extending the general inquiry to the grain-producing districts which lie to the north and west of Kentucky, it became evident that all those States, which are now the granary of this country and the chief source of supply for European markets as well, are rapidly exhausting their soils and will soon be in grave need of phosphatic manures. The im-

portance of such manures has so far been well recognized only by the cotton growers of this country, yet it is evident that in a short time this class of fertilizers will be equally in demand for all forms of grain crops.

These considerations have led me to the conclusion that the geological history of phosphatic deposits should receive more deliberate attention than has yet been given to it.

When I began my work in the U. S. Geological Survey, I asked permission of the Director to continue my studies on phosphatic deposits. There was at the time no money available for these studies; it was therefore necessary that they should be carried on without other expense to the Survey than that involved in the small share of my time which could be given to the supervision of the work. It was my good fortune, however, to find in one of my students of geology, Dr. R. A. F. Penrose, jr., a person who was willing at his own cost to undertake a preliminary study of the whole field as far as our knowledge extends and thus to prepare the problems concerning American phosphate deposits for detailed inquiry. This work he has pursued with great intelligence and energy during the two years in which he has been engaged in it. In this task he has examined all the known phosphate deposits of the United States and Canada and has made a careful inquiry into the literature of the subject, as is shown by the extended bibliography which is appended to this report.

The object of this work being to make a necessary preparation for the further study of the American phosphatic deposits, Dr. Penrose's studies were not designed to be encyclopedic in their scope, but rather to afford a synopsis of what is known of the deposits in this and other countries. So little is yet generally known of the several conditions under which these deposits may occur that it would be very blind work to search for them in this country without a careful endeavor to bring together the experience which has been gained in other countries. It will be evident to the reader of Dr. Penrose's report that the workable deposits of phosphates are found in a greater variety of circumstances than those which contain most mineral substances that have an economic value. It is not likely that we have as yet exhausted the inquiry into the modes of occurrence of this substance; but this synopsis of the experience in this and other countries, which is much more extensive than any other which has been published, will, I believe, serve as a guide to the further search for sources of supplies of phosphatic manures. It will also be evident to the reader that the conditions of occurrence of these deposits in Europe make it plain that the search for them in this country may advantageously be directed to many districts in which they have not as yet been found.

So far the vein deposits of apatite, such as those which are so abundant north of the St. Lawrence, have not been found in workable quantities within the limits of the United States, though the general geo-

logical conditions of the Laurentian area exist in the Adirondack district and in the southern parts of the Appalachian system as well as in several districts of the Rocky Mountains. It would be remarkable if extensive deposits of this nature, so common in Canada and in the equivalent rocks of northern and southern Europe, should not be found at many points in our American Archæan formations. It is on this account that so much space in this report is given to the description and illustration of the Canadian apatite deposits. So, too, we may hope to find in the ancient rocks of this country deposits analogous to the great Logrosan and Cáceres veins in the province of Estremadura, Spain.

The Cretaceous deposits of Belgium (which at the present time are, next after the phosphate beds of South Carolina, the most productive in the world) present a type of beds not yet found in paying quantities in the United States, though deposits of the same age, formed under about the same conditions, abound in this country. It is not to be expected that phosphatic deposits will exactly repeat themselves in strata of the same age in widely separated regions; yet it is clear from the summary account of the geological distribution of these phosphates in Europe and North America that in the case of these, as well as in that of other substances of value in the arts, there are certain guiding principles which we may base on the stratigraphy of the deposits to aid our search. The known workable deposits of a phosphatic nature are limited to certain portions of the geological section. Beginning at the surface of the deposits now forming, these zones are, in descending order, as follows:

(1) Superficial deposits, including (a) those formed in the manner of guanos; (b) the deposits formed in the bottoms of fresh-water swamps, sometimes in connection with deposits of bog iron ore (hematite); and (c) deposits which are the result of the long-continued decay of rocks containing a small portion of lime phosphate intermingled with lime carbonate, as, for instance, the deposits of North Carolina. This superficial group of deposits has no other common feature save that they are on the surface and are due to causes now or recently in action.

(2) Deposits of the Tertiary and Upper Cretaceous. These deposits are generally the result of reactions which took place on ancient land surfaces, the phosphatic matter being such as formed in swamp beds or in ablation deposits like those of the Carolinas or of eastern England. Below the level of the Cretaceous no important deposits of phosphate have been found in the vast section of rocks which lies between that era and the Devonian horizons.

(3) In the horizons below the level of the Upper Silurian bedded rock phosphates and apatite deposits occur. These infra-Devonian bedded rock phosphates seem to have derived their phosphatic matter from the animals, brachiopods and small crustaceans, which separated that substance from the sea insects or other food which the old oceans afforded.

These phosphate-bearing invertebrates appear to have been particularly abundant in the early Paleozoic seas.

(4) Below the level of the Silurian the phosphatic deposits which have been worked probably belong altogether to the class of apatites or crystallized lime phosphates, and are probably all new deposits. They evidently occur through a large part of the Laurentian section, though, so far, the known deposits of economic importance are possibly limited to one portion of that vast series of rocks.

The apparent absence of phosphatic deposits of economic importance in the section between the Devonian and the Cretaceous is remarkable. It is possible that it may be due to our lack of knowledge as to the chemical character of the deposits in those parts of the earth's crust. It is more likely, however, that such deposits do not there exist, owing to the fact that the invertebrate species of animals which secrete phosphatic matter in their skeletons became relatively less abundant in the middle portion of the geological section; while the vertebrate species, the birds which accumulate guanos and the fishes which afford an abundance of bones and teeth to littoral deposits, as well as the mammalia whose skeletons occasionally form a considerable element in the later deposits, did not begin to contribute phosphatic matter to the rocks until comparatively modern times.

The absence of phosphatic deposits in the Upper Paleozoic and Lower Mesozoic strata is well shown by the fact that, while in the Carboniferous and the Triassic beds there are abundant land surfaces which have been carefully explored, no phosphatic deposits of economic importance have been found in them, while on the relatively very limited areas of the Tertiary and Cretaceous formations where old land areas have been explored a large number of deposits of beds of nodular phosphate have been found.

From the facts set forth in Dr. Penrose's report and the unpublished results of certain studies on swamps, we may draw certain general conclusions as to the best method of prosecuting the search for unknown deposits of American phosphates. These conclusions are essentially as follows:

First, as regards the superficial and recently formed deposits of phosphates. We are driven to the conclusion that this class of deposits may reasonably be sought for wherever soft calcareous beds containing a certain amount of lime phosphate have been subjected to long continued leaching by waters containing the share of carbonic acid gas which belongs to all rain-water after it has passed through the mat of decayed vegetation. As long ago as 1870 I became convinced that it was to the leaching out of the carbonate of lime by the carbonated water of the soil bed that we owe in the main the concentration of the nodular phosphates of South Carolina.<sup>1</sup> Although it is still necessary to explain

<sup>1</sup> See Proc. Boston Soc. Nat. Hist., vol. 13, 1871, p. 222.

many of the details of this process to adapt it to the peculiar circumstances of particular deposits, it seems to me that it is the key to the most common forms of superficial accumulations of nodular phosphates. In an admirable description of the phosphate beds in the neighborhood of Mons, in Belgium, by Mr. F. L. Cornet,<sup>1</sup> that distinguished author has independently propounded this simple hypothesis, and several other writers on the subject have apprehended the importance of this leaching action.

It is evidently essential to this process of concentration that the surface of the deposits which are leaching away should have been preserved from the action of mechanical erosion, which would have prevented the formation of phosphatic concentrates.

Inquiry into the conditions of the swamp deposits of this country has satisfied me that beneath the surface of many of our fresh-water marshes, and probably in a lesser degree beneath the marine deposits of the same nature, there is a more or less important concentration of lime phosphates constantly going on. The effect of this action is seen in the remarkable fitness of these fresh-water swamp soils for the production of grain crops. For instance, in the case of the Dismal Swamp district in Virginia and North Carolina we find that the soils on which the swamp deposit rests are extremely barren, while in the mud that has accumulated beneath the swamp we have a rich store of phosphates, potash, and soda, which causes the soil of these swamps to be extremely well suited to grain tillage as soon as it is drained. In a similar way in the swamps of New England and elsewhere we find the bog-iron ores which are frequently accumulated in their bottoms very rich in phosphatic matter. The evidence is not yet complete that this phosphatic material becomes aggregated into nodules in the swamp muds, but the number of cases in which nodules have been found in this position makes it quite likely that the nodulation of the material may go on in that position. The present condition of the inquiry goes, in a word, to show that wherever we have a region long overlaid by swampy matter we may expect a certain concentration of lime phosphates in the lower part of the marsh deposit. Wherever the swamp area lies upon somewhat phosphatic marls which have been slowly washed away by the downward leaching of the waters charged with the acids arising from decayed vegetation, or where the swamp deposits, even when not resting on such marls, are in a position to receive the waste from beds containing phosphates, we may expect to find a considerable concentration of phosphatic matter in the swamp bed. By the erosion of these swamps we may have the nodules of phosphate concentrated in beds such as occupy the estuaries of the rivers near Charleston, S. C.

The area of swamp lands which fulfill these conditions is very large. They exist in numerous areas in more than half the so-called Southern

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<sup>1</sup> See Quart. Jour. Geol. Soc. London, vol. 42, 1886, p. 325.

States. At present it can only be said that they afford the conditions which, so far as the theory goes, should lead to the accumulation of phosphatic deposits of greater or less importance. It will be a simple matter to explain these deposits, though it is a task requiring a patient study of a large field. Although it is likely that the phosphatic materials will be found aggregated into nodules at many points in this area it will not be safe to assume that they will be found in the same form as those which occur about Charleston, S. C. The nodules found in the beds about the last named point, though in my opinion originating beneath swampy deposits, have apparently been, in part at least, swept from their original beds by the rivers which enter the sea at that point and have thus been concentrated in estuarine deposits.

Although local concentrations of phosphatic nodules other than those now known may well be sought for in the Southern States, I do not think that the precise conditions or character of the deposits as found at Charleston should be expected to repeat themselves elsewhere. It is characteristic of the process of concentration of phosphatic, as well as of other matter into nodules that the material takes on a great variety of aspects, each proper to a particular site, and this although the surrounding circumstances of the several localities may apparently be identical.

Next lower on the geologic section we have, in the Tertiary region of the Mauvais Terres, extensive deposits of vertebrate remains which may possibly yield some commercially important supplies of bone phosphates. Although none of the existing sources of supply of these materials come from deposits of the nature of those found in Nebraska, the conditions of that remarkable region are so peculiar that it will not be well to pass it by without inquiry.

While the American Cretaceous deposits are, as a whole, decidedly different from those of the Old World, the Greensand beds of the section in the two countries present considerable likeness in their characters. It is probable that in this country, as in Europe, considerable parts of the Cretaceous section are somewhat phosphatic, and that those beds containing disseminated phosphatic matter have been in many places exposed to the process of leaching in former geologic periods. Therefore we may reasonably search in the Cretaceous beds of this country for the same class of phosphatic deposits which have proved so important in the northern parts of Europe.

Although some peculiar deposits of phosphate have been found in the Devonian rocks of Nassau, it may safely be assumed that below the line of the Cretaceous we have no facts to guide us in our search for phosphates until we come to the horizon of the Upper Silurian limestones, at about the level of the uppermost beds of the Upper Silurian, as far as that level can be determined by the perplexing assemblage of fossils. There occurs in Bath County, Ky., a thick bed of much decayed, very phosphatic siderite. This deposit covers but a small area and con-

sists of a patch of limestone about fifteen feet thick, which has been converted into siderite by the leaching of iron-bearing waters from the ferruginous Ohio (Devonian) shales which formerly overlaid the bed. Since the escarpment of the Ohio shales retreated beyond this bed it has been subjected to oxidation and is now in the main converted into a much decayed limonite. Beneath this limonite there is a greenish, argillaceous sand which contains frequent nodules of lime phosphate. These nodules are smooth-surfaced and not unlike some of the nodules from the Carolina district. They contain as much as 92 per cent. of lime phosphate. It seems likely that these nodules were formed by the leaching out of the lime phosphate from the overlying ferruginous layers, which has completely removed the lime carbonate, but has not removed the whole of the less soluble lime phosphate (Fig. 1).

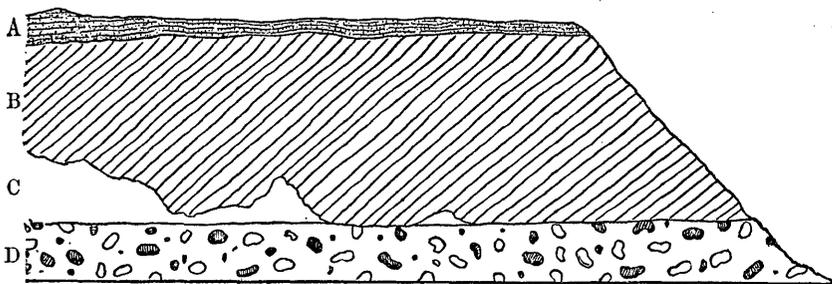


FIG. 1. Section at Olympia, Bath County, Ky. (Preston ore bed). A, soil; B, limonite iron ore; C, siderite iron ore; D, phosphatic nodules. Scale: 1 inch = 12 feet.

Although this deposit of nodules is not of sufficient abundance to have any economic value, it is clear that we have in it an indication of a method where, by a slight variation of the conditions, important beds of nodular phosphates might be found.

In the horizons of the Cambro-Silurian section, or, as it is generally called, the Lower Silurian, there is much greater reason to expect the occurrence of workable phosphates than in the beds immediately above. It is likely that the most important of the Spanish deposits belong in strata of this period, and the Welsh deposits of this general age are of noteworthy extent. We know, moreover, that the commoner marine animals of this part of the geological section were particularly adapted for the secretion of lime phosphate.

The search of this portion of the section for phosphates should be directed to two ends: first, to finding beds of very phosphatic limestone; and, second, to discovering veins formed by a segregation of lime phosphates either in the form of the Spanish deposits referred to by Dr. Penrose or in the condition of nodular accumulations. The area of rocks of these Lower Silurian and Cambrian periods in this country is very extensive, and so far there has been no search of them for phosphatic materials. The little work done in Kentucky during the above-men-

tioned geological survey served only to show that the proportion of lime phosphate in the rocks is extremely variable, and that in certain beds it is so considerable that the material might advantageously be used in a local way for fertilizing purposes.<sup>1</sup>

The search for phosphatic materials in the stratified rocks demands a method of inquiry that has not yet been applied to the study of our rocks. It seems to me that the method, or rather methods, should be as follows:

First, there should be a careful inquiry to determine the share in which the several important groups of rock-making organic forms contribute phosphatic matter to strata. This can be accomplished by carefully comparing the chemical character of particular strata with the fossils the beds contain. When this determination is made we shall have one means of guiding our inquiries, which will surely be of great value in the search for bedded phosphates.

Secondly, we should have a carefully executed chemical survey of our stratified rocks. Enough can be gathered from the scattered records of chemical analysis to make it plain that certain features of the chemical character of particular beds or divisions of strata often extend laterally for great distances. This is shown in a general way by the character of the soils formed of the waste of particular horizons; for instance, the deposits of the horizon on which lies the Cincinnati group of this country and the equivalent deposits of Europe are nearly always well suited to grasses and grains and have a great endurance to tillage. It is now desirable to take these beds which promise to afford mineral manures and subject each stratum to analyses which shall determine the quantity of phosphoric matter, soda, and potash which they contain, so that their fitness for use as mineral manures may be ascertained.

Below the level of the Silurian and Cambrian strata, and partly in those sections where they have been much metamorphosed, lies the field of the vein phosphates. It is more than likely that in this vast thickness of rocks with their development in this country there are many extensive sources of this class of phosphates which await discovery. As yet no careful search has been made for such veins in any part of the United States. The regions most likely to contain such deposits are found in the central parts of the Appalachian system of mountains,

<sup>1</sup> Among the analyses recently made by the chemists of the Kentucky geological survey is one which indicates the presence of phosphoric acid in considerable quantities in the limestones of Corniferous age exposed at Stewart's mill, on Lulbegrud Creek, in Clark County. This partial analysis, for which I am indebted to Mr. John R. Proctor, the present director of the Kentucky survey, is as follows, viz:

Lime carbonate.....	21.380
Magnesia.....	3.055
Phosphoric acid.....	9.710
Potash.....	.830
Soda.....	.228
Siliceous nodules insoluble in acids.....	27.580

especially in the section from Virginia southward; in the Archæan district of Missouri and Arkansas, and in the vast region of highly metamorphic rocks of the Cordilleran district, extending from the Rocky Mountains to the Pacific Ocean. It is true that at present the economic value of phosphatic deposits in the western part of the continent would probably be small, on account of the great cost of transportation to the seaboard districts; but the growing use of phosphatic manures in the Mississippi Valley and the rapid exhaustion of the soils of that district will soon give commercial importance to any sources of supply of phosphates that may be found in any parts of the Cordilleras which are convenient to transportation.

A proper study of the mineral manures of this country can best be carried on by means of a well considered co-operation between geological explorers and the experiment stations of the several States. At present the methods of using mineral phosphates are extremely costly: not only is the material brought into the soluble condition by saturation in sulphuric acid, but it is then mingled with ammoniacal and other matter to increase its effect as a fertilizer. The result is that, although a ton of Carolina phosphate now costs but \$6, the average price of the manufactured product to the consumer at the phosphate factories is about \$30 per ton. It is probable that the essential value of the phosphatic ingredients to the plants of most soils is not enhanced by this costly treatment, though an incidental but dearly purchased gain, in the case of some crops, is obtained from the ammoniacal matter. The only effect of the superphosphatizing on the phosphatic matter is to make it more immediately absorbable by the plants. If placed on the soil without any other preparation than grinding, lime phosphate will slowly pass into a condition in which it may be absorbed by plants, while if treated with sulphuric acid it is for a time at least in a soluble state. That this treatment is not essential is well shown by the fact that the phosphatic matter derived from the rocks is brought into a condition for absorption by the ordinary process of decay in soils. Our present costly method of applying phosphates has come about through the commercial history of artificial manures, which is as follows:

Before guanos were brought into use the English farmers had learned that they could profitably use the phosphatic marls of their Tertiary and Cretaceous deposits without any artificial preparation. If guanos had not existed it seems likely that mineral phosphates would have always been used in this way. When the Peruvian guanos came into use they afforded a much more stimulating material than any other purchasable manures, and in a short time they established the type of commercial fertilizers. When the sources of supply of these guanos became in part exhausted, artificial compounds, formed on a basis of rock phosphates or apatites, were devised to take their place. These were made to imitate the effect of the guanos as closely as possible. Like them, they

gave a quick though temporary stimulus to the soil, enabling the farmer to obtain the greater part of the return for his investment in the season following the application of the high-priced manure. Very generally the fertilizer, guano or compounded material, was applied with the seed or dibbled in the soil alongside the young plant, so that it would be immediately available in the first stages of its growth, and, what is a more important consideration, that it might take less of the substance to give the effect than if it were sown broadcast over the surface or mingled with the soil of the whole field.

In this way a habit has been established in the art of using phosphates, as well as in the composition of the material, which, like all commercial habits, is hard to overcome. The question to be determined is as to the utility of phosphates with other modes of treatment than those which are applied to the imitation guanos. At present this treatment requires the commingling of the lime phosphate with a number of costly substances. The manufacture can only be advantageously carried on at points remote from the districts where the materials are produced and remote from the fields where they are used, so that the costs of transportation are great. The problems to be solved by the agricultural stations are as follows:

(1) As to the effect, immediate as well as permanent, arising from the application of ground phosphatic rock commingled with other materials on soils used for the production of different crops.

(2) As to the degree of comminution of the material which is most advantageous. It seems possible that fine pulverizing may take the place in a measure of superphosphatizing.

(3) As to the effect of mingling the powdered rock with ordinary barn yard manure, peat, and other similar substances.

(4) As to the effect of lime phosphate used alone on soils containing different mineral constituents, as, for instance, those having considerable proportions of lime carbonate and those having but little of that substance.

(5) As to the proportion of the lime phosphate which it is necessary to apply in order to produce different degrees of effect upon the fertility of soils.

It is desirable that these and other experiments should be tried at a number of stations in different parts of the country, in order that the needs of various crops may be considered and the effect of the fertilizers on different classes of soils ascertained.

The effect of a small amount of lime phosphate on the fertility of the soil is clearly great, but so far we do not know with accuracy the amount necessary to produce a given effect. The range in phosphoric acid contents in the soils of Kentucky, as determined from many hundred analyses, varies from 0.540 to 0.061.<sup>1</sup> In most cases the fitness of the

<sup>1</sup> See report of Dr. Robert Peter in Repts. Geol. Survey Kentucky, new series, vol. 5, 1878, N. S. Shaler, Director:

soil for grain tillage is measurably proportionate to the phosphatic contents. It seems almost certain, though not yet demonstrated, that the greater part of the phosphatic matter in the soil is in the state known as *insoluble*, and that it only becomes in small part, year by year, soluble, or, in other words, fitted for assimilation by plants. Whenever the soil contains the quantity of lime which characterizes the better class of Kentucky soils it is supposed that even if soluble phosphatic manures are applied the superphosphate becomes again insoluble by taking up a molecule of lime. It is therefore an interesting question as to the means by which the lime phosphate enters the plants. It may be that the solution is effected through the action of the various humic acids of the soil or it may arise from some specific change which takes place at the contact of the soil with the roots. It is evident that this point requires precise determination, for on it will depend further experiments as to the methods of applying phosphatic manures.

There is yet another point on which we need experiments. Many of our rock phosphates, especially those which are distinctly bedded, contain low percentages of phosphatic matter. Many of our lime phosphates contain crystals of apatite and calcite so intermingled that it is not possible to separate them; yet from these deposits it will be easy to produce a mixture of lime carbonate and lime phosphate containing from 10 to 20 per cent. of phosphoric acid. The value of such material for manure has never been determined. If it can be used in a way which will give to the fields the full value for both the lime and the phosphorus it will open a way for an extensive production of cheap fertilizers.

The foregoing considerations give the general results of the preliminary inquiry into phosphatic manures of which Dr. Penrose's work forms a part. Before we go further into these studies I much desire to have the criticism and advice of others who have considered this subject. It is with this view that I have ventured to give in the foregoing pages an account of the aim of the inquiries I have in hand. The questions are at once chemical and geological, and demand much co-operation for their solution. Much of the work of searching for the unknown phosphatic deposits of this country will necessarily have to be undertaken by local students of geology or by commercial explorers in search of such deposits. Unfortunately, the unfamiliar aspect of the various forms of phosphatic deposits will make this task under any circumstances difficult. There is no substance of equally wide diffusion among those of considerable commercial importance which, in the present state of popular knowledge, so readily escapes detection as lime phosphate. It may be hoped that the following memoir may make it easier for explorers to recognize this class of deposits.

My own as well as Dr. Penrose's acknowledgments are due to many persons who have given him aid in the prosecution of his work. To Prof. Charles U. Shepard, jr., of Charleston, S. C., Dr. Penrose is par-

ticularly indebted for much information and access to a great deal of valuable matter contained in his unpublished notes on American and foreign phosphatic deposits.

In justice to Harvard University it should be said that the following report, although designed as a memoir of the U. S. Geological Survey, was used in manuscript form by Dr. Penrose as his thesis for the degree of doctor of philosophy in that institution.

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# NATURE AND ORIGIN OF DEPOSITS OF PHOSPHATE OF LIME.

By R. A. F. PENROSE, JR.

## IMPORTANCE OF PHOSPHATE OF LIME IN NATURE.

Phosphorus is one of the most universally distributed of all the elements. It is found in all animal and vegetable matter, as well as in most eruptive and sedimentary rocks. Phosphoric acid composes over 40 per cent. of the ashes of bones and in the vegetable kingdom it is especially abundant in the seeds of plants. Thus the ash of wheat contains over 49 per cent. of phosphoric acid.

It has been estimated that for each cow kept on a pasture through the summer there are carried off, in veal, butter and cheese, not less than fifty pounds of phosphate of lime. Consequently it will be seen that phosphoric acid is one of the most important elements of plant food, and no soil can be productive which is destitute of it. The necessity of restoring phosphoric acid to an exhausted soil has been acknowledged from very ancient times, though the cause of its stimulating effect was unknown until a comparatively late date. In the days of the Romans the excrements of birds, from pigeon-houses and bird-cages, brought a high price, and Edrisi relates that the Arabians, as early as 1154 A. D., used the guano deposits found along their coast for agricultural purposes. Garcilaso de la Vega (*Comentarios Reales*, lib. V, 1604) says that the Peruvians, in the twelfth century, used the guano beds on their islands as fertilizers. Of such importance did they esteem the material of these beds that the penalty of death was imposed by the early Incas on any one found killing the birds that made these precious deposits. It was not, however, until the early part of this century, when Liebig and others showed the important part played by phosphoric acid in vegetable life, that artificial phosphatic manures came into use, and it is only in the last twenty years that the mining of natural phosphates with their conversion into superphosphates has assumed its present great and steadily increasing importance.

## CLASSIFICATION OF DEPOSITS OF PHOSPHATE OF LIME.

The classification of deposits of phosphate of lime is a matter attended with many difficulties, not only on account of the great variety of forms in which phosphate of lime occurs, but also because many varieties grad-

usually blend into one another, thus often rendering it uncertain to which class a special deposit should be referred. The classification given below is based mainly on the chemical composition of the deposits. These are grouped under two principal headings, namely, *mineral phosphates* and *rock phosphates*.<sup>1</sup> The former includes all deposits of phosphate of lime which, besides having the other properties inherent in a true mineral, have a definite chemical composition or at least show a strong tendency toward such properties and composition. The latter includes those deposits which, having no definite chemical composition and lacking the homogeneous nature and other fixed characteristics of a true mineral, cannot be classed with mineral phosphates. These two classes are again subdivided as follows:

Mineral phosphates.	{	Apatites.	{	Fluor-apatites.
				Chlor-apatites.
		Phosphorites.		
Rock phosphates.	{	Amorphous nodular phosphates.	{	Loose nodules.
				Cemented nodules or conglomerates.
		Phosphatic limestone beds.		
		Guanos.	{	Soluble guanos.
				Leached guanos.
		Bone beds.		

The various phosphate deposits of North and South America, Europe, Africa, and other localities will be treated under the different divisions of the above classification, each deposit being described under the heading to which it belongs. Mineral phosphates will be taken up first, and then the various representatives of rock phosphates will be described. Special attention will be given to the phosphate deposits of the United States and Canada, which were visited and studied by the writer.

## MINERAL PHOSPHATES.

### APATITES.

Apatite is found in both stratified and crystalline rocks, but is much more plentiful in the latter, especially in metamorphic limestone, syenite, garnetiferous, hornblendic, and pyroxenic, gneiss, mica-schist, and igneous and volcanic rocks.

The mineral occurs in both the massive and the crystalline form. It belongs to the hexagonal system of crystallization, has a vitreous or subresinous luster, is translucent and sometimes transparent, has a hardness of 5, a specific gravity of 3.17 to 3.25, is brittle, of a white, yellow, green, or red color, gives off phosphorescent light when heated,

<sup>1</sup> It will be seen that the determination which phosphate shall be classed under minerals and which under rocks must in certain cases be somewhat arbitrary, but the classification is intended simply as a matter of convenience in describing the various deposits, and as such answers its purpose sufficiently well.

and becomes electric by application of heat or friction. It occurs principally in the early crystalline rocks and is found in New York, New Jersey, Maine, Canada, and other places in North America. In Europe it is found in England, France, Saxony, Tyrol, Bohemia, Spain, Norway, and many other regions. The only deposits of economic importance as yet discovered are in Canada, Norway, and Spain.

Prof. J. D. Dana gives as a formula of apatite  $\text{Ca}_3\text{O}_8\text{P}_2 + \frac{1}{3}(\text{Cl}_2\text{F}_2)$ , in which the fluorine and the chlorine may replace each other in any proportion. When there is more fluorine than chlorine present the mineral is called fluor-apatite, and when less it is called chlor-apatite.<sup>1</sup> The apatites of Canada and of Spain, as well as most of those from Norway, are essentially fluor-apatites, though they almost always contain 0.01 to 0.5 of chlorine. Occasionally apatites are found free from chlorine, as some of those of Nassau and the Tyrol, but they are never found entirely free from fluorine. The apatite of Snarum, Norway, contains more chlorine than any other known apatite, amounting, as it does, to 2.71 per cent. of that element.<sup>2</sup> The apatite deposits of Canada, being at present more extensively worked than any others and consequently better known, will be described first; after them the apatites of Norway and Spain.

#### APATITES OF CANADA.

Phosphates were discovered in considerable quantities in Canada before the middle of this century, and were described by Dr. T. Sterry Hunt in the Canadian Geological Survey Reports for 1848. Shortly afterwards they were mined in the counties of Lanark and Leeds, Ontario. But the first regular mining operations of any considerable importance were begun in 1871, in the townships of Buckingham and Portland, Ottawa County, Quebec, where apatite had been discovered several years later than in Ontario. The first company to operate on a large scale here was known as the Buckingham Mining Company. It worked successfully until 1875, when a sudden fall in the prices of the phosphate market led to a stoppage. For several years after this the mines were worked by private parties, until, in the years 1881 to 1883, the large mining companies which now control the richest properties in Canada were organized. Many of the phosphate properties in Ontario have been worked by the so-called "contract system." Under this system the farmers of the neighborhood, whenever they are without employment, blast out a little phosphate. The result of such a method is, of course, that the whole of a property is soon cut up with small pits and trenches, rarely exceeding twenty feet in depth, and often interfering considerably with later and larger mining operations.

There are two principal districts in Canada where apatite occurs in considerable quantities. The first is in Ottawa County, Province of Que-

<sup>1</sup> J. D. Dana: *Manual of Mineralogy and Lithology*, 1885, p. 213.

<sup>2</sup> O. Ramon T. Muños de Luna: *Estudios químicos sobre economía agrícola en general, y particularmente sobre la importancia de los abonos fosfatados.*

bec. It consists of a belt running from near the Ottawa River, on the south, for over sixty miles in a northerly direction, through Buckingham, Portland, Templeton, Wakefield, Denholm, Bowman, Hincks, and other townships. The belt probably stretches still farther to the north, but the country in that direction has been but little explored, and is scarcely known, except to trappers and Indians. The belt averages in width from fifteen to twenty-five miles.

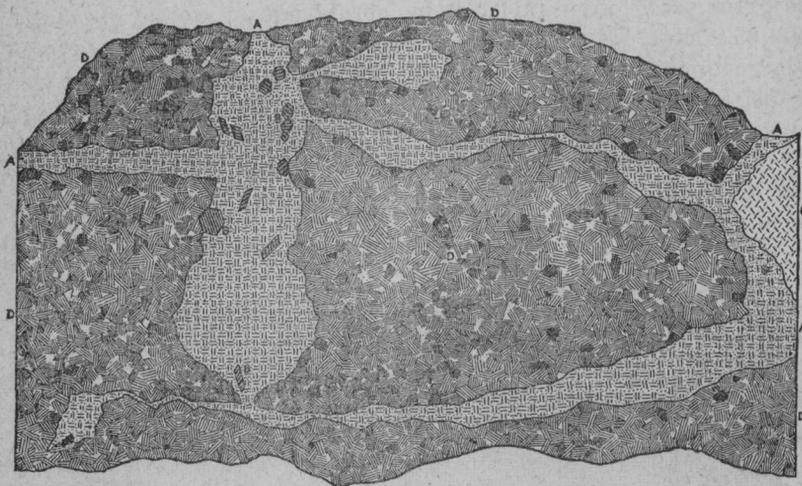


FIG. 2. Apatite in the Bonanza pit, Union mine, Portland, Ottawa County, Quebec, Canada. A, apatite; B, mica; C, white feldspar; D, pink and white feldspar, mica, and pyroxene. Scale: 1 inch = 16 feet.

The second phosphate district is in Ontario, principally in the counties of Leeds, Lanark, Frontenac, Addington, and Renfrew. This district is much larger than that of Quebec. But the apatite is much more scattered, and, though special deposits are in some places much more continuous than those of Quebec, the mineral has not yet been discovered in such large pockets as occur in the latter district. The belt which contains the deposits runs from about fifteen miles north of the St. Lawrence River in a northerly direction to the Ottawa River, a distance of about one hundred miles. It varies from fifty to seventy-five miles in breadth.

The above-mentioned districts are the regions where apatite has been found most plentifully, but it also occurs in other places, though, so far as has been discovered, in much smaller quantities.<sup>1</sup>

The apatite occurs in the upper part of the Lower Laurentian formation, the horizon being characterized by large quantities of pyroxene rock. The principal phosphate-bearing band consists of quartzites, gneisses, schists, feldspar, and pyroxenic and calcareous rocks, having an aggregate thickness, according to Vennor, of twenty-six hundred to

<sup>1</sup> Lately it has been found that apatite is very generally distributed in Pontiac County, Quebec.

thirty-nine hundred feet. All the beds are more or less completely metamorphosed, being sometimes indistinctly stratified and at other times massive and with no traces of bedding. The rocks, often contorted, all dip at a vertical or almost vertical angle. Sometimes the gneiss contains large quantities of mica and has a distinctly foliated structure. At other times it is impregnated with large quantities of pyroxene, as in the Quebec district. In the Ontario district this pyroxene is often replaced by hornblende of a dark-green, lustrous character. A highly garnetiferous gneiss is also often found in large quantities in some of the apatite localities. In the Quebec district there is a series of trap dikes running in a general east and west direction. By some they are supposed to be connected with the occurrence of the apatite. But the trap is, probably, of a later date than the apatite, as it is sometimes found passing through pockets of that mineral (Fig. 4).

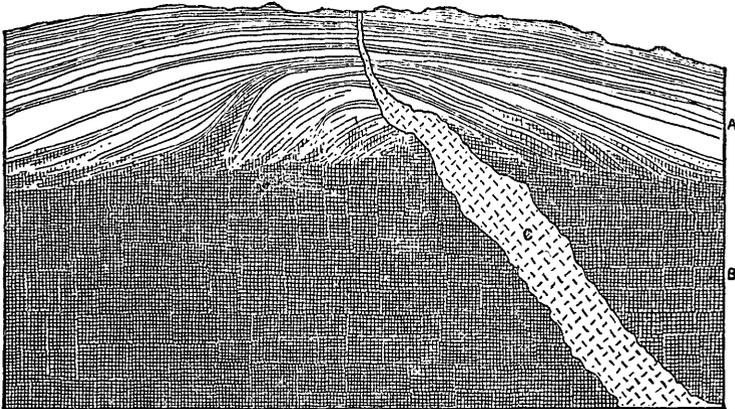


FIG. 3. Section on south side of hill on north side of Rheanmo Lake, Templeton, Ottawa County, Quebec, Canada. A, stratified rock; B, pyroxene; C, feldspar. Scale: 1 inch = 16 feet.

The principal difference between the country rock of the Quebec district and that of the Ontario district is that the rocks in the latter region are often much more hornblendic than those in the former, and are often found in the form of a more or less hornblendic gneiss. The country in the Quebec apatite district is rough and mountainous. The hills are of a remarkably uniform height, rarely rising over five hundred to six hundred feet above the level of the neighboring Du Lièvre River. In Ontario, on the other hand, the land in Leeds, Lanark, Frontenac, and Addington Counties is low, and sometimes shows a smooth, glaciated surface, covered by a thin layer of soil. In Renfrew County, however, the land is more hilly, and resembles that of the Ottawa district. As before remarked, the apatite occurs, almost without exception, in association with pyroxenic or hornblendic rocks. This rule holds especially true in the Quebec district,

where the phosphate has never yet been found without being associated with pyroxene rock, possibly often of vein origin. This, called pyroxenite by Prof. T. Sterry Hunt, occurs in ridges, running in a general northeast and southwest direction, following the general course of

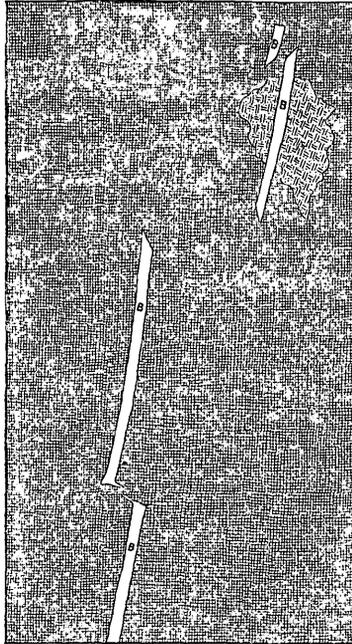


FIG. 4. Dike at Union mine, Portland West, Ottawa County, Quebec, Canada. A, apatite; B, trap; C, pyroxene.

the strike of the country gneisses. It forms, together with lilac-colored orthoclase, quartzite, and trap, the mass of many of the hills in the phosphate district, while the stratified and massive gneisses are often seen bordering the sides of the ridges, as shown in Fig. 5.

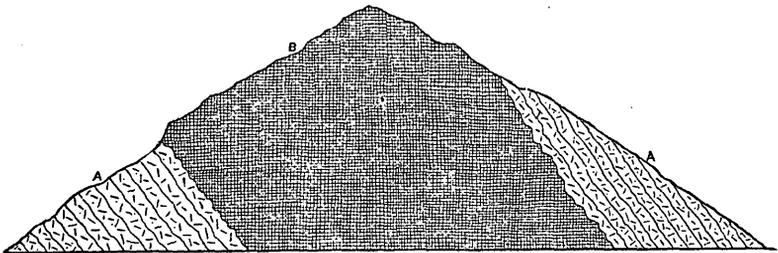


FIG. 5. Ideal section southeast and northwest through the Emerald mine hill, Buckingham, Ottawa County, Quebec, Canada. A, country quartzite, gneiss, etc.; B, pyroxene. Scale: 1 inch = 180 feet.

The pyroxene rock is never found distinctly bedded, though occasionally a series of parallel lines can be traced through it, which, while possibly the remains of stratification, are probably often joint planes. Sometimes, when the pyroxenite has been weathered, apparent signs of bed-

ding are brought out, which are often parallel to the bedding of the country rock. Thus at Bob's Lake mine, in Frontenac County, a rich-green pyroxenite occurs which exhibits this structure. For 10 feet down from the surface this apparent bedding can be distinguished. It gradually grows fainter, until it disappears in the massive pyroxenite below. A similar phenomenon has been observed at the Emerald mine, Buckingham Township, Ottawa County, Quebec, and at several other places (Fig. 6). It can also be seen in the crystalline rocks on Newport Island, opposite Tiverton, R. I. There, for a depth of from one to two feet, an apparent stratification can be seen, and the rock below gradually becomes more massive, until it merges into the apparently homogeneous mass of the hill.

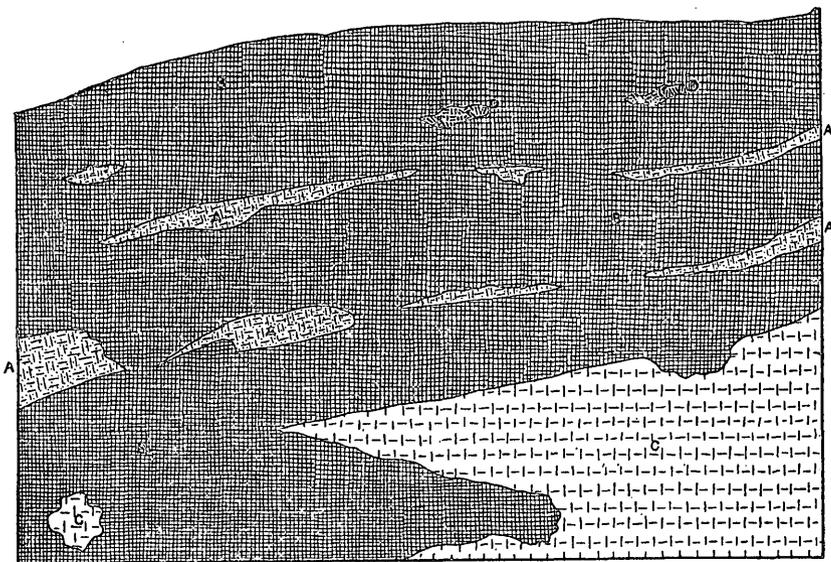


FIG. 6. Section in a pit near the Emerald mine (looking west), Buckingham, Ottawa County, Quebec, Canada. A, apatite; B, pyroxene; C, feldspar; D, pyrite. Scale, 1 inch = 6 feet.

The pyroxene occurs in several different forms. Sometimes it is massive, of a light or dark green color, and opaque or translucent; at other times it is granular and easily crumbled. Occasionally it occurs in a distinctly crystalline form, the crystals being in color of different shades of a dull green, generally opaque or translucent, but sometimes, though rarely, almost transparent. The massive variety is the most common, and composes the greater part of the pyroxenites found in the phosphate districts.

The associated feldspar is generally a crystalline orthoclase, varying in color from white to pink and lilac; occasionally, as in Denholm and Bowman Townships, Ottawa County, Quebec, it occurs as a whitish-brown, finely crystalline rock. The trap is of the dark, almost black, variety. Thin sections under a microscope show it to have a very

variable composition—a net-work of striated blades of triclinic feldspar, brownish augite, black opaque grains of magnetite, and, commonly, small quantities of a green, chloritic mineral.<sup>1</sup> The quartzite is white, gray, or blue. The blue variety often contains specks of felsite. These pyroxenes, feldspars, and quartzites are often mixed up in a perfect net-work, very similar to that seen at Marblehead, Mass., and at

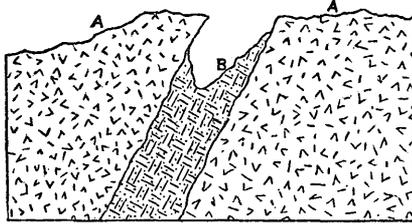


FIG. 7. Section of apatite vein near Smith's mine, Oso, Frontenac County, Ontario, Canada. A., country syenite; B, red and green apatite. Scale: 1 inch = 8 feet.

many places in the metamorphic rocks of Mount Desert Island. Often whole hills are formed of these rocks, mixed in various proportions (Figs. 8 and 9). The gneiss in some places has no distinct line of separation from the pyroxene, but seems to have been impregnated with some of it, forming for a few feet from the line of contact a more or less pyroxenic gneiss, which is easily decayed and eroded by weathering (see Fig. 3).

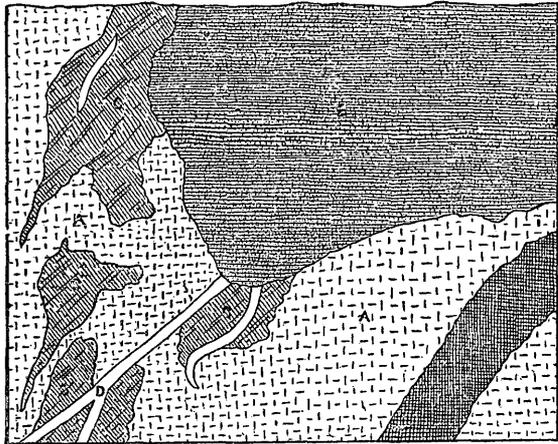


FIG. 8. Horizontal view of surface rock at Turner's Island, Clear Lake, Canada. A, feldspar; B, pyroxenite; C, hornblende; D, feldspar dykes; E, soil. Scale: 1 inch = 6 feet.

In the Ontario district, as mentioned before, the pyroxene is often replaced by hornblende. Thus at Bell's mine, in Frontenac County, little or no pyroxene is met with, and in its place large quantities of dark green hornblende occur. The apatite here is found in a rock consisting

<sup>1</sup> B. J. Harrington: Geol. Survey Canada, Rept. Progress, 1877-'78.

of green hornblende and white feldspar, which forms a ridge about one hundred yards wide parallel to the strike of the country gneiss. To complete the list of rocks found in the apatite districts it is necessary to mention the large veins of crystalline calcite, which often contain serpentine and chrysotile. In the occurrence of these veins this Canadian apatite region is in marked contrast with that of Norway, where little calcareous matter is found.

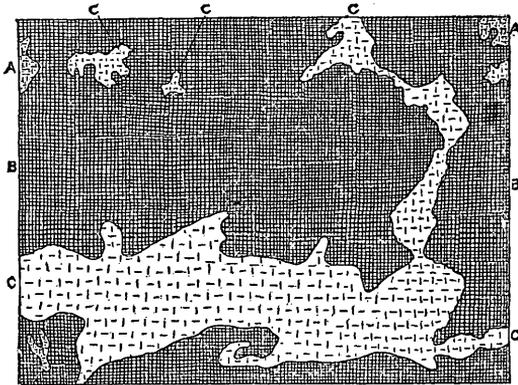


FIG. 9. Pyroxene surface, Star Hill, Union mine, Portland, East Ottawa County, Quebec, Canada. A, apatite; B, pyroxene; C, feldspar. Scale: 1 inch = 8 feet.

The apatite of Canada is found occurring in a great variety of ways. Prof. T. Sterry Hunt regards most of the workable deposits as veins, but he thinks there are also some deposits which occur in beds. He has discovered small masses of apatite marking the lines of stratification in

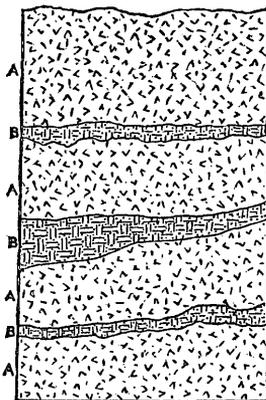


FIG. 10. Opening in west side of a hill near Smith's mine, Oso, Frontenac County, Ontario, Canada. A, country syenite; B, apatite. Scale: 1 inch = 24 feet.

the pyroxene.<sup>1</sup> An instance of this was seen by the writer in an old pit in Buckingham Township, Ottawa County, Quebec, where the apparent lines of stratification were marked by bands of apatite (see Fig. 6).

<sup>1</sup> Geol. Survey Canada, Rept. Progress for 1863.

Professor Hunt thinks that most of the deposits of apatite are concretionary vein stones and have resulted from a hot-water solution. He bases his belief upon several characteristic facts concerning Canada apatite, such as the rounded form of many of the apatite crystals, which

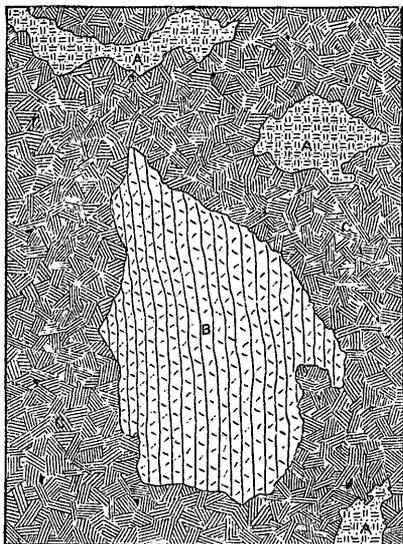


FIG. 11. Boulder of country rock embedded in pyroxene etc., High Rock mine, Portland West, Ottawa County, Quebec, Canada. A, apatite; B, country gneiss; C, mica, pyroxene, and feldspar. Scale: 1 inch = 6 feet.

he regards as due to the action of partial solution after deposition, and not of fusion, as suggested by Dr. Emmons.<sup>1</sup> Another argument is that one mineral in the vein is often found incrusting or containing frag-

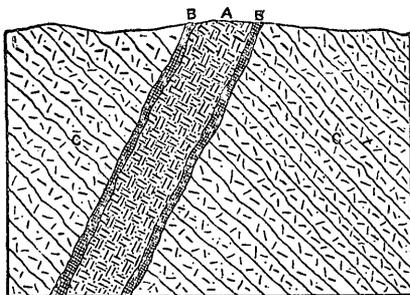


FIG. 12. Section of one of the northwest and southeast veins at Foxton's mine, Loughboro', Frontenac County, Ontario, Canada. A, apatite; B, pyroxene; C, country gneiss. Scale: 1 inch = 7 feet.

ments of another. Thus it is very common to find masses of crystalline calcite rounded into pebbles and buried in the centers of apatite crystals, which are themselves worn and rounded, showing, as Dr. Hunt

<sup>1</sup>Nat. Hist. New York, pt. 4, Geology, 1843, pp. 57, 58. Some of the dike stones of eastern Massachusetts, especially those in the town of Somerville, contain phosphate crystals which are similarly rounded.—N. S. S.

thinks, that the erosive action in the veins has taken place in at least two different epochs. The appearance in the veins of drusy cavities and the parallel deposition of the different minerals observed in many veins are also arguments for the theory of concretionary structure. Professor Dawson thinks that many of the deposits of the Ontario district are true beds.<sup>1</sup>

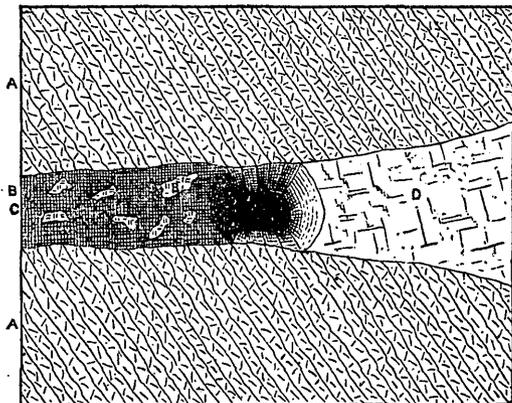


FIG. 13. Horizontal section showing natural cavity in vein, Loughboro', Frontenac County, Ontario, Canada. A, country gneiss; B, apatite; C, pyroxene; D, calcite. Scale: 1 inch = 7 feet.

Prof. B. J. Harrington<sup>2</sup> thinks that most of the phosphate deposits will come under the heading of fissure veins and pockets. He shows that many of the deposits cannot be beds, because they cut across the strata of the country rock.

Many of the veins are of considerable length. A very continuous vein, composed of hornblende, calcite, and apatite, mixed in varying proportions and associated with sphene, zircon, mica, scapolite, etc., is found in Renfrew County, Ontario. This vein, or what may be a series of similar and parallel veins, was traced by the writer for a distance of three miles, and it is said by the native prospectors to be traceable for 27 miles. It runs in a N. 40° E. direction, widening and contracting at intervals and varying from three to thirty feet in thickness. It can best be examined on Turner's Island, in Clear Lake, Renfrew County, Ontario, where several small openings have been made in it for the purpose of mining the rich apatite found there.<sup>3</sup> The island is three-quarters of a mile long and from one hundred feet to a quarter of a mile wide. The vein runs through its longer axis from one end to the other. The apatite occurs in crystals, sometimes in considerable quantities and composing the greater part of the vein matter and at other times

<sup>1</sup> Quart. Jour. Geol. Soc. London, vol. 32, 1876, p. 239.

<sup>2</sup> Geol. Survey Canada, Rept. Progress for 1877-'78-'79.

<sup>3</sup> The same or a similar vein is seen to great advantage on the land of Xavier Plaunt, on the south side of Clear Lake. It widens and contracts at intervals and runs in the same general direction as the Turner's Island vein.

scattered sparingly through a mass of the crystalline minerals which accompany it. Apatite crystals of immense size have been found here. One prism is said to have weighed seven hundred pounds; a crystal of zircon, almost a foot in diameter, is also said to have been found in the same vein. A crystal of sphene from this locality in the Harvard Mineral Cabinet measures over a foot in length. The country rock on the island consists of a confused mass of feldspar, coarse-grained, unstratified gneiss, and of a rock composed of feldspar and hornblende. Small quantities of green pyroxene are also found (see Fig. 8). The vein is said to change into pure calcite at its extremities. It shows no signs, as far as seen, of banded or concretionary structure, but consists of a mass of crystallized minerals mixed in an apparently indiscriminate manner.

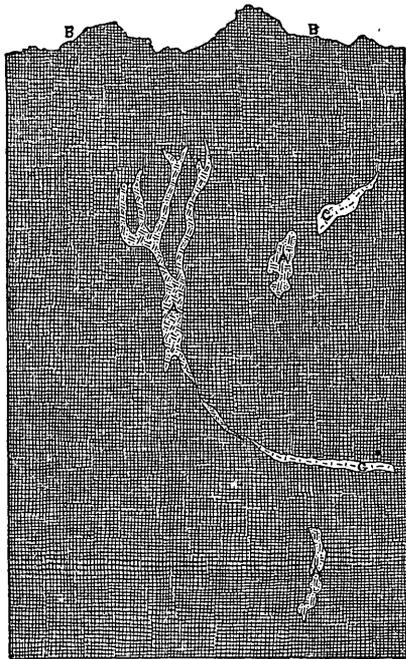


FIG. 14. Northeast side of a pit in the North Star mine, Portland East, Ottawa County, Quebec, Canada. A, apatite; B, pyroxene; C, feldspar. Scale: 1 inch = 10 feet.

Like most apatite deposits in Canada, the vein has no sharp line of division from the country rock, but gradually blends into it. The hornblende in the country rock becomes more perfectly crystalline and occurs in larger masses as the vein is approached, until finally, when the vein is met, the hornblende and the feldspar crystallize out separately among the other minerals. "Such a blending of a vein with the walls," says Professor Dana, "is a natural result when its formation in a fissure takes place at a high temperature during the metamorphism or crystallization of the containing rock."<sup>1</sup> This blending of the country rock with the vein matter does not, however, always happen, as sev-

<sup>1</sup> Dana's Manual of Geology, 1875, p. 733.

eral cases were found where the apatite and associated minerals came into direct and sharp contact with the country rock (see Figs. 7 and 20). Thus, on the land of the Sly brothers, in Oso, Frontenac County, Ontario, there is a vein two feet wide in a gneissic rock. The boundary lines of the vein are sharply defined and white, red, and transparent calcite is associated with grass-green hornblende and brown apatite, in a mass apparently devoid of any banded structure (see Fig. 7). The vein dips at an angle of  $85^{\circ}$  N. and strikes E. and W. The country rock strikes N.  $20^{\circ}$  E. and dips  $40^{\circ}$  to  $45^{\circ}$  ESE. A somewhat similar instance is seen in the same township at Boyd Smith's mine. Here were three veins apparently occupying joint planes, and parallel to one another (see Fig. 10). The veins are composed principally of apatite and hornblende, and their general character is very similar to that of the last vein described. They strike N.  $15^{\circ}$  W. and dip at  $10^{\circ}$  NE. The strike of the country gneiss is N.  $35^{\circ}$  E., dip  $60^{\circ}$  SE., so that it is evident that the deposits cannot be beds. They can be traced for 50 yards along the side of the hill.

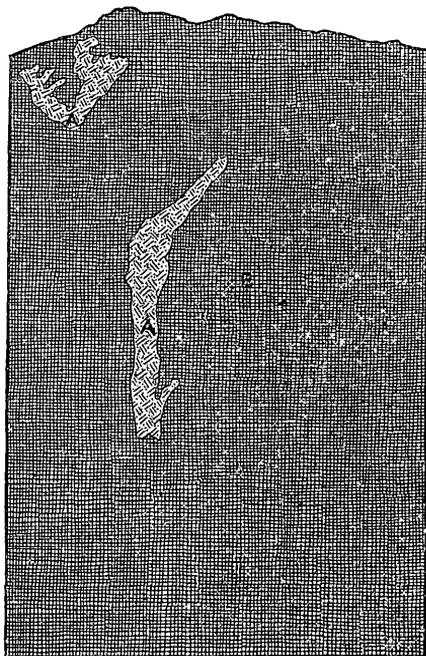


FIG. 15. Southwest side of a pit at North Star mine, Portland East, Ottawa County, Québec, Canada. A, apatite; B, pyroxene. Scale: 1 inch = 10 feet.

Some of the veins of apatite show a distinctly banded structure. On the land of James Foxton, in Frontenac County, township of Loughboro', there is a series of gash-veins running in a general northwest and southeast direction. They are of all sizes, from small ones not two inches thick to large ones three to six feet wide. The general character of all of them is the same. They occur in the country gneiss and occupy an al-

most vertical position. Fig. 12 shows a section of one of them, and most of the others are like it. It will be seen that the pyroxene lines both sides of the vein and the apatite comes in the middle. The strike and the width of nine of these veins were found to be :

- N. 11° W., six inches wide. Red apatite.
- N. 10° W., eighteen inches wide. Red apatite.
- N. 8° W., one to three feet wide. Red apatite.
- N. 20° W., one foot wide. Red apatite.
- N. 8° W., one foot wide. Red apatite.
- N. 35° W., six inches to one foot wide. Red apatite.
- N. 36° W., one foot wide. Red apatite.
- N. 45° W., one foot wide. Red apatite.
- N. 30° W., one foot wide. Red apatite.

The country gneiss is much contorted and strikes in various directions. It has an almost vertical dip. On the same properties there are also other veins running in various directions, but they are generally of small extent. In one place a vein was seen composed on one side of a band of apatite and on the other of a band of pyrites of iron containing masses of talc.

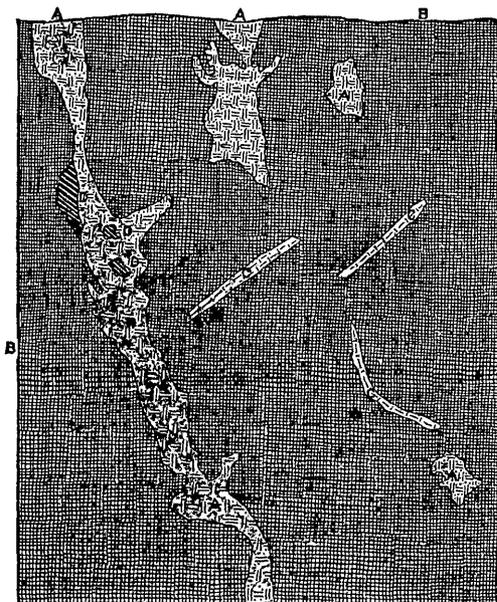


FIG. 16. Southeast side of a pit at North Star mine, Portland East, Ottawa County, Quebec, Canada. A, apatite; B, pyroxene; C, feldspar; D, mica. Scale: 1 inch = 10 feet.

Another instance of a banded vein occurs at Mud Lake, Templeton Township, Ottawa County, Quebec, where apatite, mica, and pyroxene form the contents of the vein.<sup>1</sup> But it is generally in the Ontario district that the banded structure is most often seen.

In the township of North Burgess, Lanark County, Ontario, are many examples of phosphate-bearing veins, some of which can be traced for

<sup>1</sup> B. J. Harrington: Geol. Survey Canada, Rept. Progress for 1877-'78-'79.

over half a mile, while others are short and amount to little more than pockets. In places the ground is literally cut up by a net-work of these veins, varying from a few inches to over ten feet wide. Occasionally they

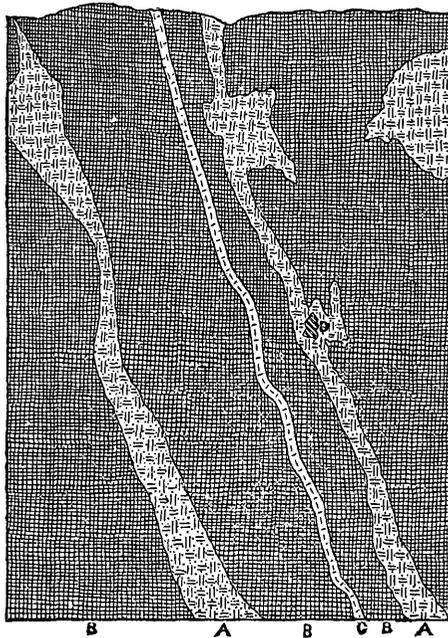


FIG. 17. Northwest side of a pit at North Star mine, Portland East, Ottawa County, Quebec, Canada. A, apatite; B, pyroxene; C, feldspar; D, mica. Scale: 1 inch = 10 feet.

are found widening into bunches almost twenty feet across. The veins often show a banded structure and consist of mica and pyroxenite on the outside and apatite in the center. The outside bands of the veins are in some cases composed of a dark, almost black, talcose material.

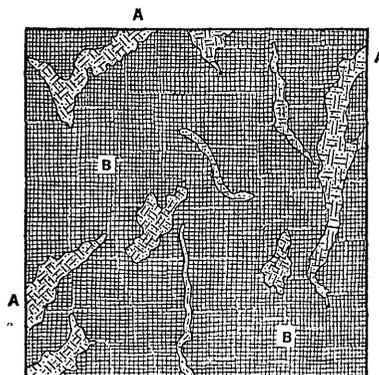


FIG. 18. Part of the northeast wall of McLaurin's mine, Templeton, Ottawa County, Quebec, Canada. A, apatite; B, pyroxene. Scale: 1 inch = 5 feet.

In other places the contents of the vein consist of apatite, mica, pyroxenite, and white and flesh or salmon colored calcite, indiscriminately

mixed and associated with small quantities of scapolite, zircon, sphene, talc, hornblende, specular iron ore, zeolites, and other minerals. Veins also occur which are almost entirely composed of apatite crystals scattered in a matrix of granular quartzite.

On the land of the Anglo-Canadian Phosphate Company, at Otty Lake, North Burgess, where some of these veins have been opened to a depth of seventy to eighty feet, the mode of occurrence of the apatite is well seen. The prevailing country rock here is quartzite and garnetiferous gneiss. In some cases the line of division between the vein matter and the country rock is sharply drawn, while in others they gradually blend. Both of these phenomena, as well as the banded and the unbanded structure, are often seen in different parts of the same vein. The apatite occurs in bunches, sometimes connected by seams of the same mineral. From a single one of these bunches over a thousand tons have been taken.

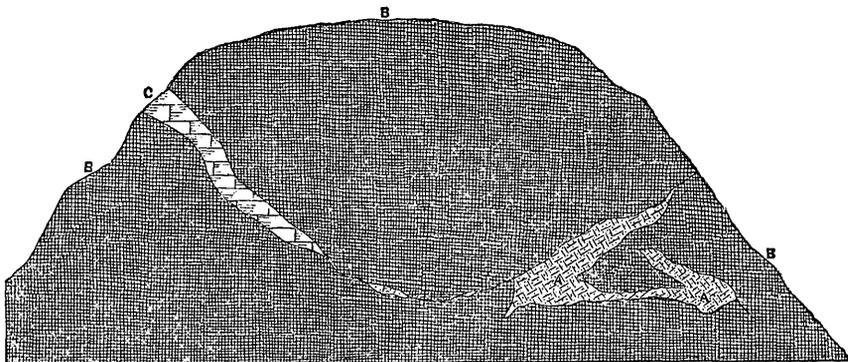


FIG. 19. Section at McKenzie's opening, looking ENE., Bowman, Ottawa County, Quebec, Canada. A, apatite, with pyroxene crystals; B, pyroxene; C, limestone. Scale: 1 inch = 50 feet.

The contents of the phosphate-bearing veins are often very variable at different points in the same vein, sometimes consisting mostly of apatite, scapolite, feldspar, and pyroxene, and at others being composed of crystalline limestone bearing crystals of the above minerals. Such a formation is seen on Henry Barr's land, in Renfrew County. At the McKenzie mine, in Bowman Township, Ottawa County, Quebec, there is a vein in a hill of lilac-colored feldspar and pyroxenite. One part of the vein is composed of massive apatite, holding crystals of pyroxene and scapolite, while another about fifty feet distant assumes a totally different character, being composed of a pink, crystalline calcite, bearing crystals of apatite. In some places the calcite has been worn away by the infiltration of water, and then the structure of the vein can be seen. The cavity is lined with crystals of scapolite and pyroxene, which come next to the country rock, while the calcite, bearing the crystals of apatite, comes in the middle (Fig. 19). This formation of drusy cavities in limestone leads is very common, especially in the Ontario district. Often the calcareous matter has been washed away, and crystals of apatite and their fragments are scattered over the bottom of the hollow. The

formation of cavities seems especially apt to take place at the point of junction of the limestone and a harder mineral in the vein. Thus in the township of Loughboro', Frontenac County, Ontario, was seen the cavity represented in Fig. 13, where a mass of limestone in a vein came in contact with a mass of apatite-bearing pyroxenite. From this opening several hundred pounds of loose apatite crystals were taken. Though it will thus be seen that the apatite of Canada often occurs in well defined veins, yet the largest deposits yet discovered occur in irregular masses in the pyroxenic and feldspathic rocks (see Figs. 2, 14, 15, 16, 17, 18, and 21). They seem to occur at some places in fissures and at others as simple segregations. As a general rule it may be said that the vein character is best developed in the Ontario district, while the segregation and pocket formations are more common in the Quebec district. A very characteristic section, showing the occurrence of pockets of apatite is given in Fig. 18. It is a figure from the side of McLaurin's mine in Templeton, Ottawa County, Quebec. The mineral seems to lie in no definite vein, but to have been formed by the segregation of apatite from the including rocks. This seems especially probable, as the surrounding pyroxene often contains 10 to 15 per cent. of apatite and seems to increase in richness as the pocket is approached. It is also well known that phosphate of lime has, more than any other mineral, the property of forming into concretionary and segregated masses. Thus Professor Rogers found, in the materials dredged in the Challenger expedition, numerous phosphatic concretions scattered over many parts of the sea bottoms. Again, in the phosphorite deposits of southwestern France and of Estremadura, in Spain, the concretionary form is one of the most common conditions of the phosphate, while in the phosphate region of South Carolina the nodular phosphates, especially those from Bull River, show sometimes a distinctly concretionary structure. At Crown Point, N. Y., phosphate of lime occurs in radiating and botryoidal masses forming the eupyrcroite of Emmons, and even in the guano beds of Peru concretionary nodules of phosphate of lime have been found.<sup>1</sup>

The pockets and fissures of apatite are of variable size (see Figs. 2, 14, 15, 16, 17, 18, and 21), sometimes being only a fraction of an inch in diameter and sometimes consisting of immense bodies of massive or crystalline apatite, measuring many feet in thickness. Such pockets are to be seen at the Emerald, Battle Lake, North Star, High Rock, Union, and other mines on the Du Lièvre River. The apatite is, generally, not sharply divided from the pyroxenite, but gradually blends with it. The pockets show sometimes a banded structure, such as that of a cavity lined with pyroxene and the central part occupied by apatite. Occasional large boulders of country rock are found embedded in the

<sup>1</sup> In the introduction to this report yet other instances of concretionary forms are noted, as well as the fact that many are probably at present forming in the muds beneath certain swamps.—N. S. S.

apatite (see Fig. 12). Nearly all these pockets and fissure veins seem to take their distinctive characters from the including rocks. Thus where the including rock is pyroxenic, feldspathic, and calcareous, the crystals associated with the apatite are generally pyroxene, feldspar, and calcite; and where the country rock contains large amounts of hornblende, as at Bell's mine, Storrington, Frontenac County, at Barr's mine, and on Turner's Island in Clear Lake, in Renfrew County, Ontario, there are always found large quantities of this mineral in the vein matter. The few veins, however, in which the lines of separation from the country rock are sharply drawn, do not seem to be so dependent on the including rocks for their component minerals.

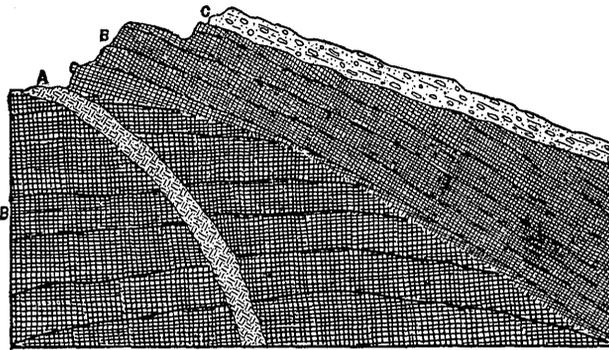


FIG. 20. Section in a pit near the Emerald mine, Buckingham, Ottawa County, Quebec, Canada. A, apatite; B, schistose pyroxene; C, drift. Scale: 1 inch = 6 feet.

The depth to which the apatite extends is probably, for all practical purposes, unlimited. Some bunches of the mineral run out, but others are found at a greater or less distance below. The deepest openings in Canada are the North Star mine, township of Portland, county of Ottawa, Quebec, and the Battle Lake mine, township of Templeton, of the same county. In September, 1886, they had reached the depths, respectively, of 350 feet and 210 feet. In both shafts large bunches of apatite were found, separated by pyroxenic or micaceous rocks containing smaller seams and bunches of that mineral.

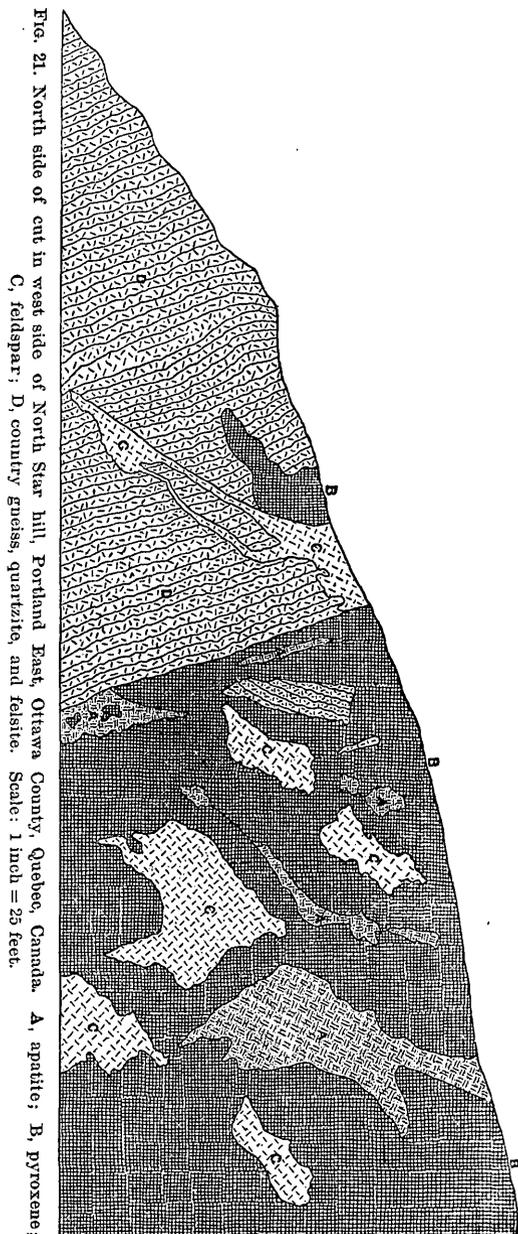
The apatite of Canada varies considerably in its physical character. Its color is green, red, brown, white, blue, purple, or black. The black color is generally caused by the decomposition of the associated iron pyrites and is seen in Ottawa and Frontenac Counties. Apatite occurs in the crystalline, subcrystalline, massive, or granular form. The granular variety, known as "sugar apatite," is of a white or pale-green color and looks like coarse sand, more or less coherent. It occurs principally at the Little Rapids mine, township of Portland, and McLaurin's mines, township of Templeton, Ottawa County, Quebec, and is one of the purest forms of apatite mined. It is uncertain what could have

caused the apatite to assume this granular condition. Some shipments from Ottawa County have analyzed 88 per cent. of tribasic phosphate of lime. The apatite varies very much in its ability to withstand weathering. When it is free from pyrites it endures it very well and is almost as resistant to corrosion as quartz; but when pyrite is present it quickly crumbles away. In some places where pyrites of iron and copper are found the apatite is brown and rusty for a depth of several feet.

Below is given a list of some of the more important minerals of the Canada apatite districts. The crystals often occur of immense size and in a state of great perfection. The zircons, sphenes, scapolites, pyroxenes, apatites, and micas are especially fine, and probably are found nowhere else in such quantities and in such perfection:

Apatite.	Opal.
Calcite.	Chalcedony.
Fluor-spar.	Albite.
Pyroxene.	Scapolite.
Hornblende.	Wilsonite.
Phlogopite.	Talc (steatite).
Garnet.	Chlorite.
Epidote.	Prehnite.
Idocrase.	Chabasite.
Tourmaline.	Galena.
Titanite.	Sphalerite.
Zircon.	Molybdenite.
Orthoclase.	Graphite.
Quartz.	

The apatite, after being blasted out, is put through the process of "cobbing," which consists in breaking it with a hammer from the adhering impurities.



The highest grade which is shipped rarely averages over 85 per cent. tribasic phosphate of lime, and none of the mines ship much phosphate which does not average at least 70 per cent. Eighty per cent. apatite is considered first quality and sells for 11 to 12 pence a unit.<sup>1</sup> The principal market for the Canada apatite is Europe. Great Britain and Germany consume over three-fourths of the total product, which, in 1885, amounted to 23,908 tons. The market is unlimited and the output is yearly increasing, so that phosphate mining bids fair, in a few years, to be one of the most important industries of Canada. The annexed tables will show the output of the mines in past years, as well as the present markets.

According to the Canadian Mining Review, January, 1886, the product for the past five years has been :

	Tons.
1881 .....	15,601
1882 .....	17,181
1883 .....	17,840
1884 .....	22,143
1885 .....	23,908
Total for five years.....	96,673

Shipments to different ports (same authority):

	Tons, 1884.	Tons, 1885.
Liverpool .....	8,557	9,563
London .....	4,389	7,683
Hamburg .....	2,970	3,524
Bristol .....	1,824	2,056
Glasgow .....	3,083	482
Barrow .....		350
Penarth Roads.....	100	100
Cardiff .....		65
Sharpness.....		45
Hull.....		40
Dublin .....	210	.....
Sunderland .....	60	.....
Bristol Channel.....	50	.....
United States.....	200	.....
Consumed in Canada.....	700	.....
Total.....	22,143	23,908
From Ontario district, 1885.....		1,500
From Quebec district, 1885.....		22,408

The origin or chemical history of these Laurentian phosphates has been a matter of considerable dispute. Dr. T. S. Hunt says that phosphates, like silica and iron oxide, were doubtless constituents of the primitive earth's crust, and that the production of apatite crystals in granite veins or in crystalline schists is a process as independent

<sup>1</sup> The expression 11 to 12 pence a unit is the commercial method of signifying the value of the apatite. It means 11 to 12 pence for each per cent. Thus 80 per cent. phosphate at 11 to 12 pence per unit would be worth \$17.60 to \$19.20 per ton.

of life as the formation of crystals of quartz or of hematite.<sup>1</sup> Prof J. W. Dawson,<sup>2</sup> on the other hand, thinks the Canada apatites are of animal origin, and bases his belief on the presence of cozoön and of graphite in the associated beds and of the fluoride of lime in the apatite. He says: "The probability of the animal origin of the Laurentian apatite is, perhaps, further strengthened by the prevalence of animals with phosphatic crusts and skeletons in the primordial age, giving a presumption that, in the still earlier Laurentian, a similar preference for phosphatic matter may have existed, and, perhaps, may have extended to still lower forms of life, just as, in more modern times, the appropriation of phosphate of lime by the higher animals, for their bones, seems to have been accompanied by a diminution of its use in animals of lower grade."<sup>3</sup> Messrs. Brögger and Reusch,<sup>4</sup> in their description of the Norwegian apatites, think that they are of purely eruptive origin.

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<sup>1</sup> Chem. and Geol. Essays, 1875, p. 311.

<sup>2</sup> Quart. Jour. Geol. Soc. London, vol. 32, 1876, p. 290.

<sup>3</sup>The reader should note the fact that since the admirable researches of Möbius it is doubtful whether cozoön be of organic origin.—N. S. S.

<sup>4</sup>Zeitschr. Deutsch. geol. Gesell., Berlin, vol. 27, 1875.

Table giving analyses of apatites of Canada by Christian Hoffman, Geological Survey of Canada, 1877-'78.

[I is from Storrington, province of Ontario ; II is from Buckingham, province of Quebec ; III is from North Burgess, province of Ontario ; IV is from Fortland, province of Quebec ; V is from Longhoro, province of Ontario ; VI is from Portland, province of Quebec ; VII is from Buckingham, province of Quebec ; VIII is from Templeton, province of Quebec.]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Phosphoric acid (1) .	40.373	41.080	39.046	41.139	40.868	40.518	34.032	40.812
Fluorine (2).....	3.311	3.474	3.791	3.863	3.731	3.377	2.855	3.554
Chlorine (3).....	0.438	0.260	0.476	0.229	0.428	0.086	0.101	0.040
Carbonic acid (4) ...	0.026	0.370	0.096	0.223	0.105	0.855	2.848	0.518
Lime .....	47.828	49.161	46.327	49.335	48.475	49.041	44.198	49.102
Sulphur (5) .....							3.507	
Calcium .....	3.732	3.803	4.258	4.195	4.168	3.603	3.062	3.763
Magnesia .....	0.151	0.158	0.548	0.180	0.158	0.205	0.422	0.620
Alumina .....	0.609	0.705	1.190	0.566	0.835	0.267	1.979	0.565
Nickel, cobalt, and copper .....							Not det.	
Iron .....							5.370	
Sesquioxide of iron .....	0.151	0.125	1.290	0.094	0.905	0.083	0.120	0.125
Alkalis .....	?	?	?	?	?	?	?	?
Insoluble residue...	3.890	0.370	3.490	0.060	1.150	1.630	2.050	0.630
<b>Total .....</b>	<b>100.509</b>	<b>99.506</b>	<b>100.512</b>	<b>99.884</b>	<b>100.823</b>	<b>99.665</b>	<b>100.544</b>	<b>99.729</b>
(1) Equal to tribasic phosphate of lime.	88.138	89.682	85.241	89.810	89.219	88.455	74.295	89.098
(2) Equal to fluoride of calcium.....	6.796	7.131	7.731	7.929	7.658	6.932	5.860	7.295
(3) Equal to chloride of calcium....	0.685	0.406	0.744	0.358	0.669	0.134	0.158	0.062
(4) Equal to carbonate of lime.....	0.059	0.840	0.218	0.507	0.239	1.943	6.473	1.177
(5) Equal to pyrrhotite.....							8.877	

Analysis of apatite of Canada, by Dr. C. U. Shepard, jr.

Phosphoric acid .....	IX. 39.80
(Equal to bone phosphate, 86.88.)	
Sand .....	5.91

#### APATITES OF NORWAY.

Under the heading of apatites come the phosphate deposits of Norway. They are found on the southern coast, and extend from Lange-sund Fjord to Arendal. They are also found scatteringly in Kongsberg, in the parish of Snarum. Most of them are fluor-apatites, though they all contain some chlorine, and the apatite from Snarum contains 2.71 per cent. of this element.<sup>1</sup> The apatite occurs in both the crystalline and the massive form, and varies from white and yellow to green

<sup>1</sup> A dark-blue or greenish-blue variety of crystalline apatite is found at Arendal, and is known as moropite.

or red. Some of it is the richest phosphate at present mined, averaging at times over 90 per cent. of phosphate of lime.<sup>1</sup> (See analyses, p. 45).

The mineral occurs in veins in the country gneisses, granites, quartzites, and schists, and also in a rock called by Brögger and Reusch spotted gabbro (*gefleckter Gabbro*), which is composed of brown hornblende and white or gray labradorite. It is generally supposed to be of eruptive origin. From its description it is very similar to the rock, including the apatite, at Bell's mine, Storrington, Ontario, described above, which is composed of green hornblendes and white feldspar, and occurs as an apparently eruptive mass in the country gneiss. The apatite seems to occur indifferently in this hornblende rock and in the other country rocks, though, wherever it has been discovered in the latter, the spotted gabbro is generally found in the neighborhood. The apatite is associated most commonly with micas, enstatite, hornblende, pyroxene, albite, tourmaline, copper and iron pyrites, and other minerals, including many other species of rarer occurrence which are hereafter enumerated. As in the Canadian deposits, the contents of the veins are variable, being in some places composed almost entirely of either mica or enstatite, or both, and in others consisting of apatite with only a few micaceous and pyroxenic impurities. The veins are markedly different from the Canada veins in the fact that they contain only very little carbonate of lime. The large calcareous veins containing apatite, which are so common in the Canadian apatite districts, are never found in the apatite districts of Norway. The apatite veins in Norway are often very numerous and run in all directions, forming a perfect network all through the rock. Thus at Oedegården there is an area of 58 square rods which is cut up by innumerable veins of all sizes. The principal one of these has been worked to a considerable extent; it dips at 45°, has a thickness of one foot to four feet, and a length of about five hundred yards. Dr. C. U. Shepard, jr., who visited it in 1874, says: "It was found in the face of a low, rocky ledge, occurring in mica and a clay slate."<sup>2</sup> The veins often show a banded structure, having the mica and hornblende on the outside and the apatite in the center, though in other places they also show, as is generally the case in Canada, a confused mass of crystallized minerals. At Regårdsheien there are five parallel veins, one of them one and a half feet thick and one hundred to one hundred and fifty feet long; four dip at 30°, while the fifth is almost vertical (Brögger and Reusch). At Kragerøe there is a large vein seven feet wide. It occurs in granitoid and schist rocks, though from the summit of the hill, from which it crops out, there protrudes the eruptive gabbro. The vein matter is com-

<sup>1</sup> Some of the phosphate deposits of Norway, especially at Kragerøe, partake very much of the nature of phosphorites, but they are all classed together here, as both varieties are so intimately associated that they cannot be conveniently separated.

<sup>2</sup> Dr. C. U. Shepard, jr., MS.

posed largely of hornblende and apatite in varying proportions, with crystals of rutile occasionally scattered through the mass. The hornblende often contains cavities lined with crystals of the same substance, and of quartz, apatite, and other minerals. At Nestesvåg the apatite vein occurs in quartzite. The minerals found in the Norway apatite are:<sup>1</sup>

Quartz.	Enstatite.
Apatite.	Phlogopite and green magnesian mica.
Calcite.	Chlorite.
Talc.	Aspasiolite.
Orthoclase.	Titanite.
Albite.	Hematite.
Oligoclase (and albite).	Rutile.
Esmarkite (anorthite?).	Menaccanite.
Scapolite (and paleo-albite).	Magnetite.
Tourmaline.	Copper pyrite.
Hornblende.	Magnetic pyrite.
Pyroxene.	Iron pyrite.

The apatite of Norway was mined as early as 1854. The first deposits worked were those of Kragerøe, from which, between the years 1854 and 1858, 13,000 tons were taken and sold for \$110,000. The Oedegården deposits were discovered in 1874 by Axel Esmark, a Norwegian mineralogist. They have since been worked on a small scale. The difficulty of mining Norwegian apatite has been so great, however, that the yearly output has never exceeded a few thousand tons, and the mineral at present has been almost driven out of the market by the Canada, Curaçoa, and other high-grade phosphates.

As regards the origin of the Norwegian apatites, Brøgger and Reusch think they are of eruptive origin. The banded structure of the veins they ascribe to the way the minerals solidified from a state of fusion. The country rocks are almost absolutely destitute of phosphoric acid in any form, and, consequently, they infer that the vein matter is in no way dependent on the surrounding rocks. Another argument which they bring up in support of the eruptive theory is that veins are often seen to be fine-grained on the outside and coarse and crystalline in the center.

*Table giving analyses of apatite of Norway, by Dehern.*

	Yellowish brown.	Brown.	Black.	General sample.	Poor quality.
Phosphoric acid .....	34.82	33.25	26.25	34.88	17.56
Equivalent to bone phosphate..	76.01	72.58	57.30	76.14	38.33
Sand .....	7.07	7.81	21.01	4.95	35.89

<sup>1</sup> Zeitschr. Deutsch. geol. Gesell., vol. 27, 1875, pp. 672, 673.

Table giving analyses of high-grade Norwegian apatite, by Dr. C. U. Shepard, jr.

	I.	II.
Phosphoric acid .....	38.79	37.66
Equivalent to bone phosphate .....	83.68	82.21
Insoluble siliceous matter.....	8.13	7.39

*Analysis of apatite from Arendal, Norway, by G. Rose.*

Phosphoric acid (1).....	42.229
Fluorine (2).....	3.415
Chlorine (3).....	0.512
Lime .....	49.960
Calcium .....	3.884
	100.000
(1) Equal to tribasic phosphate of lime.....	92.189
(2) Equal to fluoride of calcium.....	7.010
(3) Equal to chloride of calcium.....	0.801

## APATITES OF SPAIN.

The only other apatite deposits which have yet become of commercial importance are in Spain. At Malpartida de Cáceres are the mines of Señor Grappin. The mineral occurs in granite, and about six thousand tons annually have been shipped in good years. Considerable deposits of apatite are found at Zarza la Mayor, and at Ceclavin, in the district of Alcantara, near the Portuguese frontier, and about twenty miles from the Tagus. Crystalline apatite is also found in the volcanic rocks at Jumilla, in the province of Murcia, which averages 86 per cent. phosphate of lime.<sup>1</sup> It is also found in the provinces of Alentejo and Zamora.<sup>2</sup> The Jumilla apatite is often of the yellowish-green variety, known as asparagus stone or Spargelstein.

The Spanish apatite deposits are limited in quantity, compared with the phosphorite deposits of that country, and they have never produced more than a very few thousand tons annually. At present, on account of the disturbed political condition of the country, no apatite is exported.

A description of the other Spanish deposits is given under the subject of phosphorites.

*Analyses of Spanish apatite.*

[I. Apatite from Zarza la Mayor, by Dr. C. U. Shepard, jr., MSS.]

Tribasic phosphate of lime.....	79.16
Sand.....	7.09

<sup>1</sup> O. Ramon T. Muños de Luna: Estudios químicos sobre economía agrícola en general, y particularmente sobre la importancia de los abonos fosfatados. Madrid, 1868.

<sup>2</sup> Naranjo y Garza et Lino Peñuelas: Bull. Soc. géologique France, 1860, p. 157.

## (II. Apatite from Marcia, by G. Rose.)

Phosphoric acid (1).....	42. 172
Fluorine (2).....	3. 434
Chlorine (3).....	0. 566
Lime.....	49. 894
Calcium.....	3. 934
	100. 000
(1) Equal to tribasic phosphate of lime.....	92. 066
(2) Equal to fluoride of calcium.....	7. 049
(3) Equal to chloride of calcium.....	0. 885

## PHOSPHORITES.

"The name phosphorite was used by Kirwan for all apatite, but in his mind it especially included the fibrous, concretionary, and partly scaly mineral from Estremadura, Spain, and elsewhere."<sup>1</sup> In this latter sense it is used here, but it will also include certain vitreous and earthy forms which are often so intimately associated with the above-mentioned varieties and which often run into them by such gradations that they are best described together.

The phosphatic deposits of Nassau, in Germany; those of the southwest of France, commercially known as "Bordeaux phosphates," and those of Estremadura and Cáceres, in Spain, come under this head.

## PHOSPHORITES OF NASSAU.

The phosphorite deposits of Nassau were discovered in 1864 by Herr Victor Meyer, of Limburg, though as early as 1850 Dr. Sandberger had discovered apatite in the manganese mines of Kleinfeld.

The principal phosphorite deposits occupy an irregular area, bounded on the northeast by the town of Weilburg, on the northwest by the Westerwald, on the east by the Taunus Mountains, and on the south by the town of Dietz. The general appearance of the country is that of a broad plain, intersected by the Lahn and its tributaries. The phosphorite is found in cavities in a hard, massive, dolomitic limestone of the Devonian age. The following section,<sup>2</sup> in an ascending order, will show the geologic relations of the deposits:

- (1) Porphyry, dark to light gray and green, containing cavities of calcareous matter.
- (2) Slaty and shaly beds, much contorted.
- (3) Dark-red sandstone, containing beds of hematite.
- (4) Dolomitic limestone, white, blue, or pink in color, resting unconformably on the underlying bed.
- (5) Phosphorite deposits.
- (6) Brown clay, supposed to be Tertiary.

The phosphorite is sometimes found on the surface and sometimes under as much as two hundred feet of clay. The hollows containing the phosphorite are generally much worn and have all their edges rounded off, as if they had been exposed to the action of water for a long time before the phosphorite was deposited in them (Figs. 22, 23).

<sup>1</sup>J. D. Dana: A System of Mineralogy, 1873, p. 531.

<sup>2</sup>D. C. Davies; Geol. Mag., vol. 5, London, 1868, p. 262.

The phosphatic deposits vary from six inches to six feet in thickness and seem to attain their greatest continuity in a belt running in a northeast and southwest direction, thinning out gradually at both extremities. They seem to occur only with the limestone, and are no longer found when that rock disappears. This would seem to indicate that they depend on the limestone for their origin.



FIG. 22. Section at Cubach, Nassau, Prussia. After D. C. Davies: *Geological Magazine*, London, 1868.  
A, clay; B, phosphate of lime; C, manganese; D, dolomite.

The phosphorite is found in a great variety of forms. It is generally massive, fibrous, earthy, porous, jasper-like, kidney-shaped, stalactitic, or nodular. Occasionally there are found in it minute crystals of apatite (Davies). Sometimes, also, it occurs as an incrustation, and it is then known as staffelite, from its abundance near the town of Staffel.

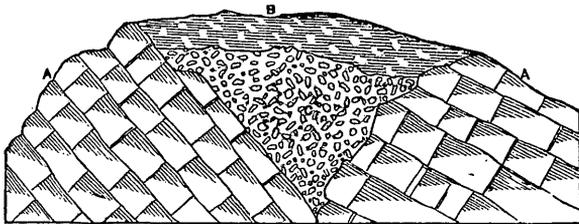


FIG. 23. Section at Staffel, Nassau, Prussia. After D. C. Davies: *Geological Magazine*, London, 1868.  
A, dolomite; B, clay; C, phosphate of lime.

This mineral is, generally, white, yellow, green, or brown in color, and occasionally translucent. The other varieties are of almost all colors, white, yellow, red, gray, blue, green, brown, or black. Occasionally a brecciated variety is found, but the larger part of the deposit is of the massive kind.<sup>1</sup> The hardness varies from 1 to 5. With the phosphorite occasionally occur deposits of crystalline hematite and manganese ore. These minerals are most common on the outside edges of the phosphate-bearing area, but are also found with it in the same deposit. The amount of phosphate of lime in the phosphorite is very variable, averaging from 60 to 92 per cent. (see analyses). It is generally richest when associated with the least hematite and manganese and, when free from the former mineral, it makes an excellent superphosphate. Among the other minerals associated with this deposit are wavellite, calcite, quartz, wollastonite, jasper, and chalcedony.

<sup>1</sup> Dr. C. U. Shepard, jr., MS.

There are no signs of organic remains in the Nassau phosphorites, but they are generally believed to be of animal origin. Dr. Mohr thinks they were formed by the concentration of the phosphate of lime from the underlying limestones. At present not much phosphorite is exported on account of the difficulty of freeing it from the associated iron and the expense of mining it. Several years ago, however, large quantities were sent to England, and in 1867 the total output of all the mines amounted to 30,000 tons, which sold, according to its quality, for \$5 to \$8 per ton. It is still used in considerable quantities along the Rhine.

*Table of analyses of Nassau phosphorites.*

	Fresenius and Foster.	Fresenius.	Wicke.
	Pure staf- felite.	General sample.	General sample.
Lime .....	45.79	47.31	42.31
Magnesia .....	0.16	0.12	0.23
Sesquioxide of iron .....	6.42	3.77	8.22
Alumina .....	1.08	1.67	2.23
Potash .....	0.58	0.66	1.26
Soda .....	0.42	0.52	0.09
Phosphoric acid .....	34.48	33.84	30.63
Carbonic acid .....	1.51	2.75	2.78
Silicic acid .....	4.83	5.04	6.61
Fluorine .....	3.45	2.11	3.74
Water .....	2.45	2.74	3.00
Sulphuric acid .....			1.07
	101.17	100.53	102.17
Deduction for oxygen .....	1.45	0.84	1.57
	99.72	99.69	100.60

PHOSPHORITES OF SOUTHWESTERN FRANCE.

The phosphorites of the southwest of France are in the departments of Lot, Tarn-et-Garonne, and Aveyron. The region is limited by the valleys of the rivers Lère, Cellé, and Aveyron, and the phosphorite is found in largest quantities near Caylus and at St. Antonin, Limogne, Cajarc, Figeac, Villeneuve, Bozouls, and other places on the southwestern side of the central plateau. The material occurs in fissures and cavities in the surfaces of hard, compact, gray limestone plateaus which belong to the Oxfordo-Coralline group of the Jurassic formation. The deposits are of two kinds.<sup>1</sup> The first occurs in irregular cavities, never over a few yards long, and partaking more or less of the character of pockets; the second, in the form of elongated leads, with sides which are nearly vertical and which run in a generally parallel direction, widening and narrowing at intervals. They are generally shallow and

<sup>1</sup> Mr. Daubrée: Comptes rendus Acad. sci., Paris, vol. 73, 1871.

thin out very rapidly at a short distance from the surface. They often, however, continue for some distance longitudinally. Thus, at Pendaré, the surface of the phosphate lead is three to ten yards wide and has been followed in a straight line for 100 yards. Any sudden turn or curve in the fissure is, according to Mr. Rey-Lescure,<sup>1</sup> almost sure to make the lead thin and poor. The richest leads are those which run in a straight line and have walls which are smooth and tend toward a vertical position. According to Mr. Daubrée,<sup>2</sup> the fissures seem to follow certain definite directions. Thus, at Pendaré and Mas-Merlin, they run ENE. and WSW. At the same time there is another series of leads running at right angles to these. The phosphatic material of the leads running in different directions is of very different character, as will be hereafter shown.

The phosphorite occurs in a great number of forms. Sometimes it has a rounded, concentric, and radiated structure; at others it occurs in nodular and mammillated masses. Often it is found in agate-like zones, forming twenty to thirty layers in a thickness of a centimeter. Sometimes it occurs as geodes,<sup>3</sup> and at other times it is found in fibrous masses, very much resembling aragonite. The phosphorite varies very much in hardness, compactness, and general appearance. The purest form is as hard as apatite, has a resinous or subvitreous luster and a yellowish-brown color. Sometimes the color is of a light blue, possibly due to the presence of phosphate of iron. The impure varieties are white, yellow, or red, and are often soft and earthy. The phosphorite which occurs in the form of nodules is often hollow in the interior, containing loose stones in the cavities (Daubrée). The whole mass is mixed with siliceous pebbles, clay (more or less ferruginous), loose blocks of calcareous rock, and pisolites of iron, all solidified into a mass varying very much in compactness and generally containing numerous cracks and cavities. Often pyrolusite is associated with the phosphorite, occurring in thin layers or in the form of dendrites. The presence of iodides has been detected, in which respect it resembles the phosphorite of Amberg in Bavaria. Minute quantities of bromides are also found. The presence of pisolites of iron is most frequent near beds of iron ore; and the iron, according to Rey-Lescure,<sup>4</sup> probably has been derived from such beds.

Mr. Trutat has found that in the leads which run ENE. and WSW. the phosphorite is compact, vitreous, agate-like, and, rarely, geodic. In the leads at right angles to these the mass of phosphatic material consists apparently of geodes filled with carbonate of lime or ferruginous clay. The geodes are, however, generally broken and in fragments, so that their contents cannot be observed. The leads of the first variety

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<sup>1</sup> Bull. Soc. géologique France, 3d series, vol. 3, 1875, p. 398.

<sup>2</sup> Comptes rendus Acad. sci., Paris, vol. 73, 1871.

<sup>3</sup> Mr. Leymerie: Note sur les phosphorites du Quercy, Toulouse, 1872.

<sup>4</sup> Bull. Soc. géologique France, 3d series, vol. 3, 1875.

generally consist of long fissures with parallel walls, while those of the second variety represent the irregular pockets described by Daubrée. Trutat thinks that the ENE. and WSW. leads were formed first, and that those at right angles to them were formed later, by the action of carbonic acid, which dissolved part of the original leads and redeposited it in new hollows and crevices.

The phosphorite deposits are usually capped by a deposit of ferruginous clay, containing pisolites of iron, bones of land animals, and numerous land and fresh-water shells. Among the bones are the remains of many carnivorous, herbivorous, and omnivorous animals, all mixed together. The bones are well preserved and not affected by chemical action. The deposits of Cregols and Beduer have afforded immense quantities of bones of carnivorous animals, and in the deposits of Raynal, Servanac, and Mouillac are found the remains of many skeletons of anthracotherium, palæotherium, and rhinoceros of several varieties. The bones are also occasionally found embedded in the phosphatic matter itself.<sup>1</sup> Thus, near La Mandine there are so many remains of palæotherium (*P. medium*) that from one cubic decimeter of phosphatized marl four or five fragments of different jawbones and many other bones were obtained. Remains of hyænodon and many land and fresh water mollusks, among them *Planorbis* and *Limnæa*, as well as turtle remains, are found in many deposits. Bones of cainotherium and anoplottherium are of frequent occurrence. Though the rock which contains the phosphorite deposits is of Jurassic age, the phosphate itself is generally believed to be of early Tertiary (Eocene) age. The way in which the phosphorite came to occupy its present position, however, has been a much more disputed point than the time in which the deposit was formed. Daubrée,<sup>2</sup> Rey-Lescure,<sup>3</sup> Leymerie,<sup>4</sup> and others are of the opinion that the phosphate came from mineral springs, rising from the bottom of the fissures. The phosphate was dissolved by the action of hot water containing carbonic acid, and, when it came into the fissures, the carbonic acid was lost and the phosphate was deposited. They think the bones are too few to have anything to do with the origin of the phosphate.

Filhol<sup>5</sup> urges against this theory that in all the deposits which have been worked out, and thus afforded a chance of examining the sides of the crevasse, he has found that the phosphate does not run into other leads by narrow necks and veins, as Rey-Lescure asserts, but that the leads are in no way connected with each other and that the crevices show no openings through the limestone which could have served as an exit for the phosphatic solution. Consequently he concludes that

<sup>1</sup> Mr. Daubrée: Comptes rendus Acad. sci., Paris, vol. 73, 1871.

<sup>2</sup> Alph. Peron: Bull. Soc. géologique France, 3d series, vol. 2, 1874.

<sup>3</sup> Bull. Soc. géologique France, 3d series, vol. 3, 1875.

<sup>4</sup> Note sur les phosphorites du Quercy, Toulouse, 1872.

<sup>5</sup> Annales sci. géol., vol. 7, 1876; Recherches sur les phosphorites du Quercy, pp. 1-220.

the deposits were formed by a solution of phosphate of lime in carbonic acid, running from the surface downward into the fissure. When all the fissures were filled the solution often spent its strength in phosphatizing the marl of the neighborhood. Thus at La Mandine Basse they find a calcareous marl containing 25 to 30 per cent. phosphate of lime.

Mr. Combes<sup>1</sup> thinks the phosphate bed was formed by phosphatic vapors rising up through the Jurassic limestone and phosphatizing it. He thinks a similar action is going on at the present time. Mr. Malinowski<sup>2</sup> thinks that the beds are of purely animal origin and that volcanic eruptions of Auvergne killed all the animals of the period and thus furnished the phosphate to fill up the fissures. Mr. Delfortrie<sup>3</sup> thinks the deposit is of Quaternary age and derived from altered guano.

Mr. Peron<sup>4</sup> has shown that the phosphate deposits only occur where the Tertiary deposit now exists or where it has existed in time past. Thus on the Jurassic plateau at Bach, Mouillac, and Malpérie, the Tertiary formation which covers it at Lavaurette, Monpalach, and Lasalle, in Tarn-et-Garonne, has been eroded. Yet both districts are rich in phosphate. On the other hand, at Laussiers and Anglars, where he supposes the Tertiary has never existed, there is no phosphate. He thinks the phosphate deposits are synchronous with the Lower Tertiary of Aude and Tarn. The waters of the Eocene, he supposes, came suddenly over the Jurassic plateau, overwhelming the numerous land animals of the region and sweeping the remains of these and masses of guano into crevices and cavities, together with quartz pebbles, land and fresh-water shells, and other débris. Then the action of time and carbonated waters partially metamorphosed the phosphate and converted it into concretions and other forms of phosphorite in the midst of the clay and bones. At a later time the superficial deposits of bones were laid down.

The strongest arguments of the advocates of the hydrothermic theory are the presence in the phosphorite deposits of iodine and manganese, and of pisolites of iron, which are generally of hot spring origin.

Peron thinks these latter were formed during the deposition of the Lower Tertiary formation. He also calls attention to the fact that phosphorite has nowhere been found in the southwest of France at a greater height above the sea than 320 meters. This he explains by supposing that the waters of the early Tertiary did not extend above this height.

The phosphorites of the southwest of France were discovered in 1865, on the plateau of Quercy, in the department of Lot, by Mr. André Pournarède. Five years later the deposits of Lot-et-Garonne, Tarn-et-Garonne, and Aveyron were discovered and worked until the last few years,

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<sup>1</sup> Phosphorites du Quercy, *Revue scientifique*, 1872, No. 12.

<sup>2</sup> *Traité spécial des phosphates de chaux natifs*, Cahors, 1873.

<sup>3</sup> *Les gîtes de chaux phosphatée dans le départ. du Lot*, Bordeaux, 1873.

<sup>4</sup> *Bull. Soc. géologique France*, 2d series, vol. 2, 1874.

when the exports ceased. The best deposits had given out and the others contained so much iron and alumina that the material was very undesirable as a source of superphosphate. For several years, from 1870 to 1875, an average of 20,000 tons per annum was exported.<sup>1</sup> Some of the mines are still worked, but the phosphate is used only in a raw state and for local purposes.

Soon after mining had begun in this region, Guillier estimated that the total contents of all the mines would not exceed 100,000 tons. This estimate was much too small, but it serves to show that the deposit is a very limited one. The phosphate was formerly collected in loose boulders from the fields for the purpose of building walls. At the Pearl mine, near Cajarc, the phosphorite crops out at the surface.<sup>1</sup> At the depth of 75 feet the lead becomes very thin and uncertain. The mass of the phosphorite is, in some places, 10 feet thick, but ordinarily it consists of several more or less parallel bands, which end abruptly.

One of the largest mines is at Larnagol, in the department of Lot. It is situated on the summit of an Oxfordian plateau over a thousand feet high. The first quality rock is cleaned by hammer and hand, and the second quality in a simple horizontal washer, driven by steam. The phosphorite contains both chlorine and fluorine, but in much smaller quantities than exist in apatite. As has been said before, it also contains iodine, and in some specimens traces of bromine have been detected.

*Table of analyses of phosphorites from southwestern France.*

[I. Analyses by Bobierre.]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Siliceous sand .....	1.00	4.70	12.70	12.06	3.00	1.00	1.40	0.93
Phosphoric acid .....	38.00	32.94	36.48	35.84	36.80	37.10	37.00	38.32
Total lime .....	51.47						51.50	48.92
Water volatilized at red heat, fluorine, chlorine, carbonic acid, and oxides of iron and manganese.....	9.53						10.10	11.83
Lime in excess of phosphoric acid, and combined with carbonic acid, fluorine, and chlorine.....	6.87						8.10	3.94
	100.00						100.00	100.00

<sup>1</sup> Dr. C. U. Shepard, jr., MS.

Table of analyses of phosphorites from southwestern France—Continued.

[II. Analyses by C. U. Shepard, jr.]

	High-grade phosphorite, from Mas-Merlin.	Low-grade phosphorite, from Larnagol.
Phosphoric acid .....	38.64	21.46
Equal bone phosphate .....	84.35	46.85
Sand .....	1.00	14.58

Superphosphates made from 12 parts (by weight) of rock and 9 parts of sulphuric acid (1.50 specific gravity) gave:

High grade .....	14.98 per cent. soluble phosphoric acid.
Low grade .....	5.04 per cent. soluble phosphoric acid.

[III. Analyses of commercial Bordeaux phosphate by C. U. Shepard, jr.]

	I.	II.
Phosphoric acid .....	35.46	34.45
Equal bone phosphate .....	77.41	75.20
Sand .....	4.35	8.55

Superphosphates made in the same way as the last case gave:

	I.	
Soluble phosphoric acid .....	15.00	12.48

## PHOSPHORITES OF SPAIN.

The phosphorite deposits of Spain are situated near the towns of Logrosan and Cáceres, in Estremadura. The two localities differ somewhat in the mode of occurrence of the phosphorite as well as in its physical properties, and will therefore be treated separately.

*Logrosan deposits.*—The country in which these occur is a broad tableland composed of a clay slate and studded here and there with conical peaks rising abruptly from the level of the plain, and often reaching the height of three hundred to six hundred feet above the surrounding surface. There also occur numerous long, flat ridges, rising, like the peaks, abruptly from the surface of the plateau. The slate is of very variable character, being composed sometimes of a dark-blue, fissile schist, sometimes of a micaceous or a talcose schist, and at other times of alternating beds of talc and feldspar.<sup>1</sup> No fossils are found in this formation, but in a very similar deposit near Almaden, and about eighty miles from the town of Logrosan, are found numerous fossils,

<sup>1</sup> Charles Daubeny and Captain Widdrington: Jour. Roy. Agric. Soc., 1845.

such as *Spirifer attenuatus* and trilobites. Consequently the slate formation of Logrosan and Cáceres has been referred by some French and Spanish geologists to the Silurian formation. Le Play<sup>1</sup> refers it to an older formation than the fossiliferous slates of the neighborhood of Almaden. The conical peaks rising up from this formation are granitic intrusions. They are very feldspathic and often much weathered. In this latter respect they differ from the long, flat ridges spoken of above. These are beds of quartzite interstratified with the country rock, which has a quite regular, almost vertical dip. The quartzite is sometimes very compact and homogeneous and at others it is granular and often resembles a sandstone. It has resisted the erosive action, which has worn down the more easily attacked parts of the slate formation and now stands out in bold, angular ridges. The section (Fig. 24) from Truxillo to Logrosan, a distance of seven Spanish leagues, will show the general character of the country. Besides the rocks already mentioned, large veins of dark limestone are occasionally found cutting through the slate formations.



FIG. 24. Section from Truxillo to Logrosan, Spain, after Daubeny and Widdrington. A, granite; B, slate; C, phosphorite.

The phosphorite occurs in true veins and in pockets. Occasionally it occurs as a vein at the line of junction of the granite with the country slate. It is of a variable character, occurring sometimes in an amorphous and compact form, at others in a fibrous or concretionary state, often inclosing pebbles of white or ferruginous quartz. It varies in color from white and yellow to a rich, jasper-like red. It is often covered with dendrites of manganese, and occasionally agate-like varieties are found in which the phosphate is interstratified with bands of lilac amethyst. The palmated variety is generally the purest and the most abundant. It has a hardness of 5.5, and a specific gravity of 3.12. When heated in a darkened room it gives off a bright phosphorescent light.<sup>2</sup>

At Logrosan there are six principal deposits of phosphorite. They are known as Costanaza, Jungal, Castillon, Angustias, Terrenos Colorados, and La Cambre Bojera. The Costanaza vein is by far the largest phosphorite vein known in all Spain, and perhaps in the world (Shepard).<sup>3</sup> It extends for about two and a half miles from the foot of Mt. Boyales, on the north, in a southeasterly direction past Mt. Cristobal. The vein dips at an angle of 60° to 90° toward the east (Garza and

<sup>1</sup> Annales des mines, 1836.

<sup>2</sup> Sur la phosphorite de Logrosan, Estremadura, Messrs. Naranjo y Garza and Lino Peñuelas: Bull. Soc. géologique France, 1860, vol. 17, p. 157.

<sup>3</sup> Foreign Phosphates, 1879, p. 25.

Peñuelas), and cuts obliquely through the country slate, which has a strike of north  $15^{\circ}$  to  $45^{\circ}$  east, and a dip of  $70^{\circ}$  southwest. The vein has been worked principally where it crosses hills, and especially near the chapel of Nuestra Señora del Consuelo. It varies from ten to twenty feet in width and contains streaks of quartz and horses of country rock. The walls of the slate show signs of considerable decomposition and disintegration. The vein thins out at each end, and also grows narrow at a depth; though, as the excavation is only about forty feet deep, the bottom has not yet been reached.<sup>1</sup>

The second vein, Jungal, is at the entrance of the town of Logrosan, on the road to Truxillo. It has a mean width of 32 inches and a length of one thousand to twelve hundred feet. In most respects it resembles the Costenaza vein, but is on a much smaller scale.

The Castillon vein runs under the town for a considerable distance and varies in width from five to six and three-fourths feet. It presents a mass of phosphorite of great purity.

The Angustias lead is on the side of the hill Nuestra Señora del Consuelo and runs towards Mt. Boyales. It is not so valuable as some of the other leads, because of being much cut up by quartz veins and horses of country rock.

The Terrenos Colorados vein is 330 feet long and averages six and two-thirds feet wide. It is parallel to the Cambre Bojera lead, which is about the same size.

The general direction of all these veins is northwest and southeast, with a dip of  $60^{\circ}$  to  $90^{\circ}$ .

The Logrosan phosphate has a subcrystalline structure; some specimens are fibrous and radiating and often resemble feathers. It is soft and chalky to the touch, easily broken, but difficult to grind into a fine powder. An examination under the microscope exhibits conchoidal figures interrupted with spherical grains, devoid of color and opaque (Shepard). It is infusible before the blowpipe; but, on being subjected to long-continued heat, a luminous disk, perceptible in the dark, makes its appearance at the point of contact of the mineral and flame, and a green phosphorescence appears when it is heated for a short time. It is readily soluble in hydrochloric, nitric, or sulphuric acid.

The highest-grade material is rosy white or yellowish white in color, soft, concentric, often brilliantly radiated, with a mamillary or conchoidal surface. Red spots from iron and beautiful dendrites of manganese are not infrequent. The poorer qualities are milky white, vitreous, hard, and, though free from limestone, contain considerable silica.

The shipment of phosphate from Logrosan involves great trouble and expense. The mineral is drawn by ox or mule teams to the nearest railroad, a distance of 30 miles, and is shipped at Villanueva de la Serena. This carriage costs about 20 cents per cwt., and the carts make two

<sup>1</sup> Dr. C. U. Shepard, jr., MS.

trips a week, carrying 40 to 50 cwt. each trip. This, with the expense of getting it to Lisbon and thence to England, makes it cost about \$15 a ton to land in London. First-class phosphorite (80 to 85 per cent.) sold there, in 1875, for \$25 a ton.

In the Cáceres district, which supplies most of the phosphorite shipped from Spain, the mode of its occurrence differs from that in the Logrosan district. While in the latter it occurs in veins, sometimes of considerable length, at Cáceres it occurs in pockets in great veins of quartz and dark limestone, which are found cutting through the country slate. The principal mines are united in the Fraterjidad Company, and are known as the Esmeralda, Estrella, San Eugenio, Abundancia, Cacereña, San Salvador, and La Perla.<sup>1</sup> The first four, being the only mines of much importance, will alone be described. As will be seen from the ground plan (Fig. 25), the limestone and quartz veins, in which the phosphate is found, occur in both the granite and the slate rocks.

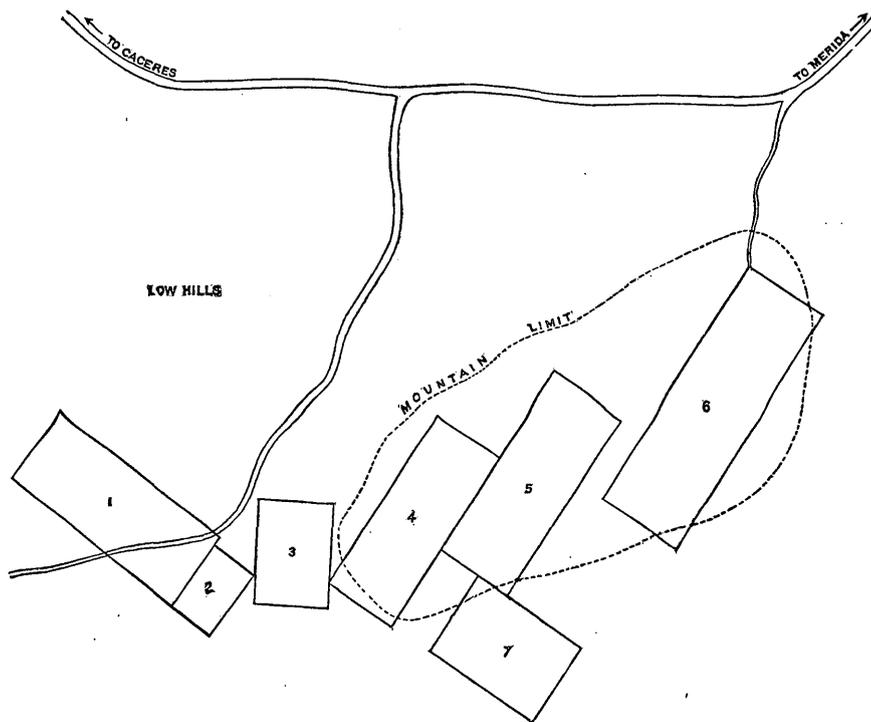


FIG. 25. Ground plan of the Cáceres mines in 1875; after Dr. C. U. Shepard, jr. (MS). 1. Abundancia mine; 2. Carcereña mine; 3. San Eugenio mine; 4. San Salvador mine; 5. Estrella mine; 6. Esmeralda mine; 7. La Perla mine.

The Esmeralda mine is considered the largest and best of the Cáceres mines. There are two veins penetrating the side of a hill in a north

<sup>1</sup> C. U. Shepard, jr., MS.

and east direction, respectively, at an angle of about  $45^{\circ}$ . The vein to the north has a thickness of ten to twenty feet, and contains a variable quantity of limestone and siliceous rock. The immediately surrounding rock is limestone of a hard, brown character, which has been excavated for a depth of some one hundred feet (1875). The leads appear to narrow as they are followed into the hill. The exterior of the mass of phosphate is hard, white, and compact, while toward the center it becomes soft, crumbly, and of a rosy color (Shepard). There is less hard, siliceous rock here than in the other mines.

At the Estrella mine the lead enters the hill in which the Esmeralda mine is situated at an angle of  $45^{\circ}$ . The total thickness of the deposit is ten to twenty feet. It is very irregular in shape and grows thinner as it enters the hill. It contains less of the rich, pulverulent variety of phosphorite and more of the compact, vitreous variety than the last mine. Like the Esmeralda mine, it is in a limestone vein (Fig. 26).

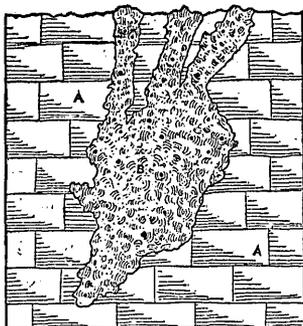


FIG. 26. The Estrella deposit in Estremadura, Spain; after C. U. Shepard, jr. (MS.). A, limestone; B, phosphorite.

The San Eugenio mine is smaller than either the Esmeralda or the Estrella. The lead is almost vertical and the phosphorite in some places is of a very high grade, but in others it is very siliceous and impure.

The Abundancia mine has been abandoned on account of the trouble from water. It is simply a round open pit 75 feet deep and 100 feet in diameter. It once gave large quantities of excellent phosphorite, but what is now left is siliceous and contains only 50 to 65 per cent. phosphate of lime, while the best Spanish phosphate will average 80 to 85 per cent. (See analyses pp. 58, 59.) The Cáceres phosphate is massive and amorphous and of two varieties: (1) Somewhat granular, easily crumpled, and of a white or rosy color; (2) dense, vitreous, hard, and white, with occasional streaks of quartz or limestone.

Cáceres is 43 miles north of Merida, a station on the railroad between Madrid and Lisbon, and near the Portuguese frontier. The cost of transportation between the two places varies from  $12\frac{1}{2}$  to 20 cents per cwt. Thence to Lisbon costs \$4.55 per ton, making the total cost to Lisbon amount to \$5 to \$8 per ton. The Cáceres mines were not opened

until 1860, and from that time until 1875 the mines had exported only 124,156 tons of phosphorite.

The Logrosan deposits were the first phosphorites found in Spain. The earliest mention of them is by William Bowles in 1782.<sup>1</sup> He says that at the base of the Guadalupe Mountains, and near the town called Logrosan, the royal road is traversed by a vein of phosphoric stone, running in a north and south direction. It was also mentioned by La Play, Proust, and others in the early part of this century. But the deposit did not attract much attention until Professor Daubeny, of Oxford, and Captain Widdrington<sup>2</sup> visited the Logrosan country in 1844 and made a thorough study of the one vein then known. Later, in 1849, Mr. Naranjo y Garza, by order of the Spanish government, made a survey of the basin of the Guadiana and gave a description of the Logrosan phosphate deposits.<sup>3</sup>

The Cáceres deposits were discovered in 1860 by Mr. R. De Luna.

Ever since about 1855 the Spanish phosphorites have been worked at intervals. The phosphorite is of excellent quality, commands a high price, and makes as good a superphosphate as any phosphate known. But the expenses of transportation and the occasionally unsettled political condition of the country have been great detriments to the development of the mines.

*Analyses of phosphorites of Spain.*

[I. Logrosan phosphate, by De Luna.]

Water .....	0.40
Bone phosphate of lime .....	82.10
Phosphate of iron .....	5.20
Phosphate of magnesia .....	0.30
Fluoride of lime .....	7.31
Carbonate of lime .....	1.74
Chloride of lime .....	0.40
Silica .....	2.55
	100.00

[II. Logrosan phosphorite, by Professor Daubeny.]

Silica .....	1.70
Protoxide of iron .....	3.15
Fluoride of lime .....	14.00
Phosphate of lime .....	81.15

[III. Logrosan phosphate, by Messrs. Pelletier and Donadei.]

Phosphoric acid .....	40.12
Silica and clay .....	3.10
Hydrochloric acid .....	0.06
Hydrofluoric acid .....	2.27
Lime .....	53.50
Peroxide of iron .....	0.61
Loss .....	0.79

<sup>1</sup> Natural History and Physical Geography of Spain, Madrid, 1782.

<sup>2</sup> Quart. Jour. Geol. Soc. London, vol. 1, 1845, pp. 52-55.

<sup>3</sup> La Gazette de Madrid, July 22, 1849. Revista Minerva (March and July, 1855).

[IV to VII. Logrosan phosphate, by Dr. C. U. Shepard, jr., and Dr. Wamer.]

	IV. White and hard.	V. Yellowish white and hard.	VI. Rosy white and compact.	VII. White, soft, and mammillary.
Phosphoric acid .....	36.97	37.55	42.17	41.72
Equal bone phosphate .....	89.71	82.97	92.06	91.09
Sand and insoluble matter .....	12.63	7.40	Trace	4.32

[VIII to XIV. Cáceres phosphate, by Dr. C. U. Shepard, jr., and Dr. Wamer.]

	VIII. Rosy and pulverulent.	IX. White and hard.	X. Rosy and pulverulent.	XI. White and hard.	XII. San Eugenio.	XIII. Abundancia.	XIV. Mina Rosa, at Alalpárvida de Cáceres.
Phosphoric acid .....	37.38	32.06	38.07	29.09	39.07	27.00	36.18
Equal bone phosphate ...	81.60	69.99	83.11	63.50	85.29	58.94	78.98
Sand .....	3.40	22.97	6.30	2.70	9.19	3.76	Trace

[XV. Cáceres phosphate, by Bobierre and Friedel.]

Insoluble siliceous matter .....	21.05
Water expelled at red heat .....	3.00
Tribasic phosphate of lime .....	72.10
Loss, oxide of iron, etc .....	3.85
	<hr/> 100.00

[XVI. Phosphate from Montanchez, by Bobierre and Friedel.]

Tribasic phosphate of lime .....	85.03
Carbonate of lime .....	10.35
Water expelled at red heat .....	2.40
Silica, oxide of iron, etc .....	2.22
	<hr/> 100.00

Phospherites include, besides those deposits already mentioned under that heading, the minerals staffelite, epiphosphorite, pyrophosphorite, eupyrcroite, hydro-apatite, monite, monetite, and other forms, all of which occur either in scattered pockets, incrustations, and concretions, or as radiated, botryoidal, and subcrystalline masses. Some of them occur scattered through certain phosphorites and rock phosphates, and are mentioned in connection with those deposits. They are rarely of any commercial importance.

Fibrous and concretionary phosphorites have been mined in small quantities at Amberg, Bavaria.

Thin seams of soft, whitish phosphorite, called osteolite, occur at Hanau, in Germany, but, as yet, the mineral has not been found there in sufficient quantities to be of commercial value.

#### ROCK PHOSPHATES.

This class of phosphates includes, as already mentioned, those deposits which, having no definite chemical composition and lacking the homogeneous nature and other fixed characteristics of a true mineral,

cannot be classified with *mineral phosphates*. They may be treated as *amorphous nodular phosphates*, *phosphatic limestone beds*, *guanos*, and *bone beds*.

#### AMORPHOUS NODULAR PHOSPHATES.

This subdivision comprises the phosphate deposits of South Carolina, North Carolina, Alabama, Martha's Vineyard, some of the Florida deposits, the deposits of North Wales, England, Belgium, northern central and eastern France, and Russia. They generally consist of calcareous matter, more or less completely phosphatized, and occur either as loose nodules in a matrix of variable composition, or as a conglomerate in which the pebbles are phosphate of lime and the matrix is of a calcareous, phosphatic, siliceous, or ferruginous nature. They are the most important, commercially, of all the phosphate deposits. About 600,000 to 700,000 tons are yearly mined, of which, in 1884, 437,000 tons came from South Carolina and the rest mostly from England, France, and Belgium. On the other hand, the total output of all the apatite mines in America and Europe in the best years has not exceeded 50,000 tons.

#### AMORPHOUS NODULAR PHOSPHATES OF SOUTH CAROLINA.

The nature of the phosphate beds of South Carolina was recognized by Prof. C. U. Shepard, sr., before 1860, but the nodules were not put to any practical use until, in 1867-'68, Prof. F. S. Holmes and Drs. Pratt and St. Julien Ravenel, after showing by numerous analyses their richness in phosphate of lime, urged the formation of a company for mining these valuable deposits. Through the energy of Professor Holmes and Mr. G. T. Lewis, of Philadelphia, the first company for mining phosphate in South Carolina was organized in 1868. It was known as the Charleston Phosphate Mining and Manufacturing Company. Since that year no less than fifteen large mining establishments have been started in South Carolina, of which some of the more important are the Bradley, Pinckney, and Bolton, in Berkeley County, and the Coosaw and Oak Point properties, in Beaufort County.

Nodular phosphatic deposits are found at intervals all along the Atlantic Coast of the United States, from North Carolina down to the southern extremity of Florida, but the richest beds occur in South Carolina, in a strip of country running from Broad River 60 miles along the coast in a northeast direction. The belt has a width of from ten to twenty miles. The phosphate does not occur continuously over this region, but in patches, sometimes having an area of many square miles and again only covering a few acres. In this whole area of more than nine hundred square miles, the hills rarely rise to a height of over ten to fifteen feet above high-water level, and the country is cut up into islands and peninsulas by the numerous tide-water inlets and creeks. The Tertiary deposits form a fringe along the Atlantic Coast and the Gulf of Mexico from New Jersey to Texas, but are best developed in the



central portion of this extensive belt. The Claiborne marls, the Santee buhrstones and limestones, and the shell sands of Alabama are the lowest beds of this series. Beneath them lie the Pedee marls, which belong to the secondary formation and contain fossils resembling those from the Chalk of Europe. Immediately over this formation in South Carolina are the Eocene marls. These beds are very extensively developed in that State and are called by Mr. Ruffin "The Great Carolina marl bed," which is divided into three divisions, known, in an ascending order, as the Santee River, Cooper River, and Ashley River beds. The whole formation is about seven hundred feet deep and contains 55 to 95 per cent. of carbonate of lime. It is one of the most important marl beds in the world, on account of both its extent and its agricultural value. The upper part of the Ashley marl contains a great number of fossil shark teeth and cetacean bones, and has been called by Professor Tuomey "the fish bed of the Charleston basin." Overlying this "fish bed" is a deposit of sands and clays of very irregular thickness and containing many shells. The bed sometimes runs out altogether and at other times is several feet in thickness.<sup>1</sup> It is directly overlaid by a bed containing many shark teeth and cetacean bones, as well as the remains of the mastodon, megatherium, elephant, deer, horse, cow, hog, muskrat, and other land animals. Besides these animal remains, the bed contains very numerous irregularly shaped nodules containing 25 to 70 per cent. of phosphate of lime. This is the bed that is worked for phosphates (see Figs. 27, 28, and 29). Sometimes the underlying stratum has not existed or has been eroded and the nodule bed rests directly on the Eocene marls. It is composed mostly of nodules, associated with a much smaller and very variable quantity of bones of land and sea animals, buried in a matrix of a variable character. Sometimes they are in a bed of highly siliceous sand, containing many flat pebbles of white quartz; at other times the matrix consists of ordinary clay or of sand and clay mixed. A light blue or green clay is also often seen.

The nodules are of very irregular shape and vary from the size of a pea to that of a mass weighing a ton or more. The larger masses, however, are often composed of a number of small nodules cemented together. With the nodules and the bones are associated numerous phosphatic casts of the interiors of shells, as well as masses, of rare occurrence, which have the appearance of fossil dung (coprolites). The nodules, like those of England and of France, are all more or less waterworn and rounded and are much bored by marine animals. It is generally the harder varieties that are most bored and most irregular in shape. This may be due to the fact that, being hard, they preserve their original irregular shape and the marks of the boring animals better than the softer varieties. The nodules vary in hardness from 2 to 4 and have a specific gravity of 2.2 to 2.5.<sup>2</sup> When a fragment is rubbed,

<sup>1</sup> F. S. Holmes: The Phosphate Rocks of South Carolina.

<sup>2</sup> Dr. C. U. Shepard, jr.: South Carolina Phosphates,

or, better, when two fragments are rubbed together, they give off an odor of decayed organic matter. They are marked by a complete absence of crystalline structures, though in some rare cases, as in the Bull River phosphate, a distinct concretionary structure is observable. The nodules generally contain casts of Eocene shells and, in some cases, marine bones and shark teeth. The bones of land animals, though mixed with the nodules, are never found embedded in them, showing that these bones were probably deposited after the formation of the nodules.

The nodules are found on the bottoms of most of the rivers running through the phosphate district, having been washed out of their original beds. These river deposits in many cases have proved to be of great commercial value. The nodules are, as a rule, of a much darker color than those of the land and are often black. They are sometimes very siliceous, the separate grains of sand being plainly visible to the naked eye. These grains are due to the sand in the marl before it was phosphatized. Such seems to have been the case with much of the Beaufort River phosphate. In some cases, however, the siliceous matter is probably due to the replacement of some of the carbonate or phosphate of lime in the original nodule by silica, and the result has been to make the nodule much harder. Such a silicifying action was probably due to the presence of soluble silicates in the river waters. In some places, as at the Bolton mine, the land nodules are also very siliceous, and possibly became so by having once formed the bottom of a river or a bay.

At least eleven varieties of nodules, differing much in their physical character, and often in their chemical composition, may be distinguished among the phosphates taken out of the South Carolina beds. These are:

(1) A jet-black variety with a bright, shining, glossy enamel of the same color. It is very rare and generally occurs in small patches. It contains numerous fossils and shells. It is found in Parrot Creek (see map, Pl. I).

(2) A brown variety with a bright enamel of the same color. It is very rich and is found in considerable quantities at the Bradley mine and on the land of the Charleston Mining and Manufacturing Company.

(3) A light-brown variety with little or no enamel. It bleaches white when exposed to the sun and is found on the land of the Bradley Company, of the Charleston Mining and Manufacturing Company, and in many other localities.

(4) A light, chalky variety containing many shells and generally poorer in quality than the varieties mentioned above. It is very widely distributed over the South Carolina phosphate region, and is simply marl which has not been so highly phosphatized as the harder and darker varieties.

(5) A dark grayish-black variety with little or no enamel. It is very siliceous and contains many shells. It is generally found in rivers, and is especially characteristic of the Stono River district.

(6) A gray variety composed of a mass of shells and transparent siliceous sand, cemented together by a phosphatic cement. Sometimes shark teeth are included in the mass. At times it is hard and compact, and at others it is loose, soft, and porous. Such varieties are found in large quantities in the Beaufort River. They are often mixed with a much better quality of nodule which raises the average phosphatic contents.

(7) A dark-gray, phosphatic conglomerate, in which the pebbles are quartz and feldspar, varying from the size of a mustard seed to that of a buckshot. The matrix is a dark-gray, phosphatic marl. This variety is very rare in South Carolina, but is found in small quantities in the Bull River district.

(8) Nodules having a black enamel and a light or dark gray interior. They contain many shell casts and are found in the Coosaw River and on the Edisto River at Fishburne's mine.

(9) A variety consisting of a mass of concentrically laminated nodules cemented together with a matrix of marl containing many shells. This variety is rare and was found only in the Bull River. It is generally rich in phosphatic matter.

(10) A ferruginous, rusty-brown variety, very siliceous and of poor quality.

(11) Brown or black masses having the general appearance of fossil dung (coprolites) and probably of that nature. They are hard and very rich in phosphate of lime. Real coprolites are of rare occurrence.

Occasionally large, flat, non-concretionary masses are found, which are highly phosphatized on the upper side, while toward the lower side the mass grows poorer and poorer in phosphates, until it differs but little in composition from the underlying marl. In such cases the phosphatized part of the rock is of a darker color than the other part. The upper side is also much smoother and harder than the lower side, which is often very jagged and is sometimes almost as soft as the underlying marl. This formation shows that in some cases at least the phosphatization has gone from above downward. Such a process is also proved by the fact that the marl immediately underlying the phosphate bed contains sometimes 20 to 30 per cent. of phosphate of lime,<sup>1</sup> while this quantity decreases with the depth until, at a few inches below the nodule bed, it contains only 10 to 20 per cent. According to Professor Holmes, the marl is much richer in phosphate of lime in those places where it is overlaid by nodules than where no nodules are found.

Some of the varieties of nodules have been found to grow poorer in phosphoric acid as the center of the mass is approached. This is espe-

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<sup>1</sup>Dr. C. U. Shepard, jr.: South Carolina Phosphates,

cially true of those nodules which are coated with an enamel, it being invariably the case that the hard, enamel-like crust is much richer than the soft and less compact interior. In this peculiarity the South Carolina nodules resemble many of those of England and the other phosphate localities in Europe. The phenomenon is dwelt on as one of the strongest arguments for the theory originated by Professor Holmes, that the nodules have been formed by the phosphatization of lumps of

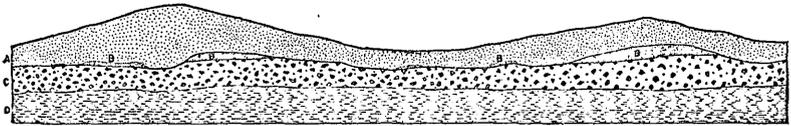


FIG. 27. Section ENE. and WSW. through Pinckney's phosphate field, South Carolina. A, sand; B, ferruginous sand; C, phosphate rock; D, Ashley marl. Scale: 1 inch = 60 feet.

marl. It may, however, be mentioned that a similar condition of the nodule could be produced by the action of waters containing carbonic acid, which would tend to leach out the carbonate and leave the less soluble phosphate of lime. Of course this action would be more pronounced on the exterior than in the interior of the nodule, and consequently the result would be a mass much richer in phosphate of lime on the outside than in the inside.

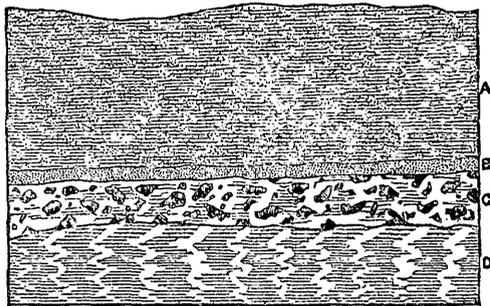


FIG. 28. Average section in Pinckney's phosphate mine, Berkeley County, South Carolina. A, clay sand; B, ferruginous sand; C, phosphate rock; D, Ashley marl. Scale: 1 inch = 6 feet.

The nodule bed varies in thickness from a few inches to about two feet and a half, the average being about seven to nine inches. It is only when the nodules are found in a pocket or depression in the underlying marl that the thickness reaches much over two feet, and even under such circumstances such a thickness is of very rare occurrence. The yield of phosphate per acre varies, not only with the thickness, but also with the compactness of the nodular stratum, as sometimes the nodules are packed as close as cobblestones in a road, while at others they are scattered loosely in the sand or clay matrix. The average yield of clean, dry phosphate is three hundred to twelve hundred tons per acre. The phosphate bed is thought by professor Holmes to be of Post-Pliocene age. In

some places it crops out on the surface and at others is found at a much greater depth. Under the city of Charleston it is found at a depth of over sixty feet.<sup>1</sup> Where the bed does not appear on the surface it is covered by alluvial deposits, consisting of clay, sand, or marl, or of strata of all three. Occasionally there is a stratum of highly ferruginous sand or gravel, sometimes indurated into a regular "hard-pan," directly overlying the phosphate bed and from one to ten inches thick (Figs. 27, 28, and 29). Sometimes this ferruginous substance has penetrated the whole bed to a depth of several inches and cemented the upper nodules into a solid mass; while the lower part of the bed is much looser and more easily mined. Again the sand overlying and intermixed with the nodules has sometimes been cemented together, especially in river bottoms, by the action of soluble silicates. Such has been the case with the phosphate in parts of the Stono River. Here the nodules have in some places been completely permeated by silica and form a solid floor on the river bottom.

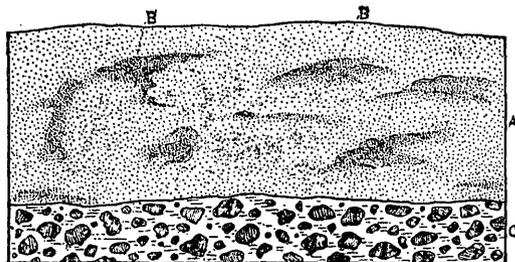


FIG. 29. Section in one of Fishburne's pits, South Carolina. A, sand; B, ferruginous sand; C, phosphate nodules in clay matrix. Scale: 1 inch = 7 feet.

The following sections by Dr. C. U. Shepard, jr., show the general mode of occurrence of the superficial beds of phosphate:

A. Land deposits:

- I. *Soil and subsoil.* A few inches to a foot in depth.
- II. *A light-colored, siliceous clay,* iron stained in places, and containing much fine, transparent sand, and minute scales of silvery mica, with little calcareous matter, one foot or more in thickness.
- III. (Wanting in the more superficial beds.) *A blue, argillaceous marl,* probably altered marsh mud. It does not adhere to the tongue or give an argillaceous odor. Fragments of recent shells occur in this deposit. Its depth is about two feet.
- IV. *A thin layer of coarse sand,* one to three inches in depth.
- V. *The phosphate nodules* in either a loose, siliceous or a tenaceous, bluish or rich buff-colored, argillaceous marl, frequently accompanied with abundant fossil bones and teeth. The upper nodules are often harder, the lower softer, and at some land localities exhibit a gradual transition, by loss of cohesion and decrease of phosphatic contents into
- VI. *A marl,* highly phosphatic toward the rock-bed, and containing occasionally 20 to 30 per cent. of phosphates, but at the depth of a few inches containing only 10 to 20 per cent. of those constituents.

<sup>1</sup> Dr. C. U. Shepard, jr.: South Carolina Phosphates.

VII. *Argillaceous or arenaceous marls*, containing 7 to 10 per cent. of phosphates.

## B. River deposits:

Beneath the river deposits occur either—

- I. *A gray marl*, sometimes in nodules resembling phosphate, with 5 per cent. of phosphates, underlaid by
- II. *A white, hard marl* inclosing phosphate grains and containing 3 to 5 per cent. of phosphates (Wando River); or
- I. *A green sand* with some clay and rich in black phosphatic grains, occurring with the phosphatic rock and beneath it, containing 15 per cent. of phosphates.
- II. *Soft and hard marls* several feet in thickness, and containing 10 to 15 per cent. of phosphates (Stono River); or
- I. *Hard marls*. Poor in phosphates ( $\frac{1}{2}$  to 1 per cent.) unless their tops be coated with phosphate rock (Coosaw River).<sup>1</sup>

It is difficult to calculate the yield of river nodules per acre, as the currents have heaped them up in some places and carried them away from others.

As will be seen from the accompanying map by Dr. C. U. Shepard, jr. (Pl. I), there are three principal localities in the phosphate region where active mining operations are now carried on. It is not, however, all over these areas, but only in certain parts of them, that the nodules are found. Nor are they the only places in South Carolina where phosphates occur, but they are the districts where they are found at a depth beneath the superficial deposits not too great to permit profitable mining.<sup>1</sup> The first of these regions lies north and east of Charleston and stretches from the Wando River and the eastern branch of the Cooper River on the northeast to Rantowles Creek and Stono River on the southwest. In this area are some of the largest phosphate diggings in South Carolina, including as it does the Bradley, Charleston Mining and Manufacturing, the Magnolia, Bolton, and Black and Williams's mines. There also are the river deposits in the Wando, Stono, and Cooper Rivers. Large quantities of small nodules of excellent quality have been obtained from the bed of the upper part of the Wando River. Phosphate of good quality has also been gotten from the bed of Stono River, but the deposit forms in some places such a solid floor on the river bottom that mining operations at the present low price of phosphate would be unprofitable. Mainly on account of their inaccessibility the deposits in the eastern branch of the Cooper have not been much worked.

The second of the three principal phosphate districts is due west of the locality last described and extends from the Edisto River on the east to Horseshoe Creek on the west, including the river deposits in these two streams. The phosphate found in this region is of excellent quality, but does not occur in a continuous bed or at a constant depth. Consequently it can be profitably mined in few places. It occurs largely in pockets and patches on the underlying bed.

The third locality where phosphate exists at a conveniently accessible depth extends with intervals from the Bull to the Broad Rivers, and

<sup>1</sup>Dr. C. U. Shepard, jr.: South Carolina Phosphates.

includes not only the deposits in these rivers, but also the deposits in the Coosaw and Beaufort Rivers and those on Chisholm's Island. This area is essentially a river mining district, though phosphate of good quality is mined on parts of Chisholm's Island by the Pacific Guano Company and by Messrs. Wiley and Gordon. Nodules of excellent quality are obtained from the bottoms of the Bull and Coosaw Rivers, but those of Beaufort River are generally very siliceous, the separate grains of sand being plainly visible to the naked eye.

Outside of the localities mentioned above, phosphatic nodules have also been obtained from the upper part of Hospa Creek and from the Coosawhatchie River (see map, Pl. I). Besides the bed of phosphatic nodules already described, other beds have been found in boring artesian wells in Charleston and the neighborhood which are at a much greater depth and are of a similar nature. Dr. C. U. Shepard, jr., in speaking of these borings, says:

The samples thus collected have been carefully examined and analyzed, the most important contribution to our knowledge being the discovery of the existence of several deeper layers of phosphate rock, occurring at the depth of 300 feet from the surface, and, in the form of isolated pebbles, to a much greater distance. These lower deposits are probably not thicker than a few inches, and consequently they lack all but scientific interest.

The phosphate of South Carolina is obtained from the land and from the river bottoms. The mining on the land is done in open trenches. The area to be mined has to be ditched in order to drain it before mining operations can be begun. Sometimes it is necessary to build embankments, to prevent the diggings from being flooded in stormy weather. At the Bolton mine, on Stono River, high tides sometimes rise two feet above the level of the land. Drainage is, in some mines, hastened by the use of steam pumps. It does not usually pay, unless the phosphate is of extraordinary quality, to remove more than eight or nine feet of overlying earth. The Pacific Guano Company, however, has lately introduced the use of a steam excavator to dig the nodules, and it is supposed that work can be profitably carried on at a greater depth with this machine than with pick and shovel.

The phosphate is carried on cars, generally drawn by an engine, from the mines to the washers. Here it is broken by machinery into coarse fragments not larger than about five inches in diameter, and then passed into the washers, where it is freed from the adhering sand and clay. Several different kinds of washers are used. The most common one is a long trough, in which revolves a shaft armed with a projection in the form of a broken helix. The trough is inclined at a small angle. The nodules are passed from the breakers to the lower end of the trough and are forced up the inclined plane by the revolving shaft against a strong stream of water. Sometimes the phosphate is washed in a revolving cylinder perforated with holes and supplied on the inside with spiral flanges of steel. A stream of water is thrown into the cylinder

through an iron pipe. After passing through the washers the nodules fall on an iron screen, which separates the large masses from the smaller pieces. Sometimes two or three screens having different-sized meshes are used. The small-sized product is of lower grade than the large, as it is mixed with numerous siliceous pebbles which have gone through the screen with it.

The next step is to dry the nodules. This is done either by burning them with wood in large sheds, which sometimes hold several thousand tons, or by passing hot air through the mass. Sometimes the nodules are treated with fire and hot air combined. In this way they are freed from the 12 to 18 per cent. of moisture which they contained after being washed and are ready for shipment. On cooling, the nodules absorb about 1 per cent. of moisture, and such is their porosity that they can be made to absorb 5 to 15 per cent. of water.<sup>1</sup> The drying of the nodules takes 35 to 40 cords of wood for 1,000 tons of nodules, and the process lasts thirty-six to forty hours. The drying and burning of the phosphate not only save the freight on the water which it originally contained, but also make it better fitted for manufacturing purposes.

The nodules in the river bottoms are now obtained by dredging boats, though, a few years ago, large quantities were obtained by negro divers and with oyster tongs. The dredging scoops have to be very strongly built in order to break through the nodular stratum. The boats are held in position at the four corners by what are called "spuds." These are strong square poles with iron points. They are dropped into the water before dredging is begun, and go through the nodule stratum and down into the bed below, thus affording a firm support to the boat. The nodules are thrown from the scoop into the washer, which is on a lighter alongside the dredging boat. The washer, in some cases, is the same as those used by the land-mining companies; but often it consists of a truncated cone, with perforated sides, revolving on a horizontal axis. It is supplied on the inside with steel spirals, arranged around the side like the grooves in a rifle. Into both ends of the cone heavy streams of water flow. The nodules are dumped by the dredge into the small end of the cone and come out at the large end. They are then removed by a derrick to another lighter and towed to shore.

Besides the ordinary dredging machine, several other contrivances are used for raising phosphate from river bottoms. The owners of the Sea Island Chemical Works, instead of using the ordinary dredging scoop, have a contrivance consisting of six large claws which open when they descend, and close, forming a kind of bucket, when they rise. It is said that one of the machines which this company owns can dredge in 50 to 60 feet of water, while the ordinary dredging boat cannot raise the phosphate in over 20 feet of water. Another dredge has been lately introduced by Mr. Brotherhood and is known as the Broth-

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<sup>1</sup> Dr. C. U. Shepard, jr.: South Carolina Phosphates, 1880.

erhood dredge. It consists of a revolving chain of thirty-two buckets, and is very similar to the dredge used to deepen the channel of the St. Lawrence River some years ago.

The deposits of South Carolina, though of low grade compared with some others, are now more generally used than any other known phosphate. The output of the mines, which is yearly increasing, is shipped to the North, South, and East by sea and to the West by rail. This popularity is due, not only to the cheapness of the phosphate (\$5 to \$6 per ton in 1886), but to the many good qualities of the low-grade acid phosphate made from it. The fact that the nodule bed extends, at an accessible depth, over many miles of country, the easy approach for large vessels up to the very mines, the abundance of water, fuel, and labor, and a climate that permits mining operations to be carried on throughout the whole year, all combine to make the South Carolina phosphates the cheapest and consequently the most productive source of supply of this material.

The mode of formation of the South Carolina nodules has been a matter of considerable dispute. Professor Holmes thinks that the surface of the Eocene marl was worn, by the action of boring animals and of erosion, into numerous lumps and balls. These, with bones of sea animals, were washed upon the seashore and, as the coastline began to rise, were collected into salt-water lagoons and swamps. Numerous quadrupeds came to lick the salt, and deposited their fæces and often died here. Hence the presence of bones of land and sea animals in the phosphate beds. The phosphoric acid in the fæces and carcasses of these animals phosphatized the lumps of marl and thus formed the phosphatic nodules.

Prof. N. S. Shaler thinks that the nodules, in some cases, have been formed by concretionary and segregating action at the bottom of swamps. Many facts, such as the frequent occurrence of phosphatic nodules in patches, and often in concave basins, as in Russia, as well as their association with peaty beds, as in North Carolina, seem, in many cases, to strongly favor this theory. Phosphatic nodules have also been found at the bottom of beds of limonite in the Ohio Valley. Professor Shaler thinks that the nodules were scattered sparingly in the deposit in which they were formed and that they were concentrated in their present position by the erosion of the original bed.<sup>1</sup>

*Analyses of South Carolina rock phosphates, by Dr. C. U. Shepard, jr., in South Carolina Phosphates, Charleston, 1880.*

An average of several hundred analyses gave :

	Per cent.
Phosphoric acid.....	25 to 28
Equivalent to bone phosphate of lime.....	55 to 61
Carbonic acid.....	2.5 to 5
Equivalent to carbonate of lime.....	5 to 11

<sup>1</sup> Proc. Boston Soc. Nat. Hist., vol. 13, 1869-'70, p. 222.

	Per cent.
Sulphuric acid .....	0.5 to 2
Lime .....	35.0 to 42
Magnesia .....	Trace to 2
Alumina .....	Trace to 2
Sesquioxide of iron .....	1.0 to 4
Fluorine .....	1.0 to 2
Sand and silica .....	4.0 to 12
Organic matter and combined water .....	2.0 to 6
Moisture .....	0.5 to 4

*Table of analyses of South Carolina rock phosphates by Dr. C. U. Shepard, jr.*

	Stono River light-colored nodule.	Stono River dark-colored nodule.	Stono River nodule.	Ashley River land nodule, dried.	Cooper River land deposit.	Chisholm's Island nodule, dried.	Bull River nodule, dried.	Coosaw River nodule, dried.	Coosaw River nodule, dried.
Moisture .....	3.68	.....	1.50	0.00	.10	0.84	0.79	0.57	0.66
Organic matter and combined water .....	4.78	.....	5.59	5.26	.07	4.22	5.80	4.31	3.75
Carbonic acid .....	4.68	4.28	3.89	4.47	3.55	3.54	3.61	3.79	4.34
Equal in carbonate of lime to .....	10.69	9.73	8.84	10.04	8.06	8.04	8.19	8.61	9.84
Phosphoric acid .....	25.61	26.68	25.75	27.01	27.11	27.26	25.14	27.26	26.78
Equivalent in bone phosphate to .....	55.91	58.24	56.21	58.95	59.18	59.50	54.88	59.51	58.46
Sand .....	11.55	12.41	11.77	11.37	15.39	9.06	13.30	9.06	11.77

*Analysis of South Carolina rock phosphate from Oak Point Mine, by Dr. C. U. Shepard, jr.*

Bone phosphate of lime .....	58.66
Carbonate of lime .....	6.90

*Analysis of phosphatic nodules from Bulow mine, property of William L. Bradley, by R. A. F. Penrose, jr.*

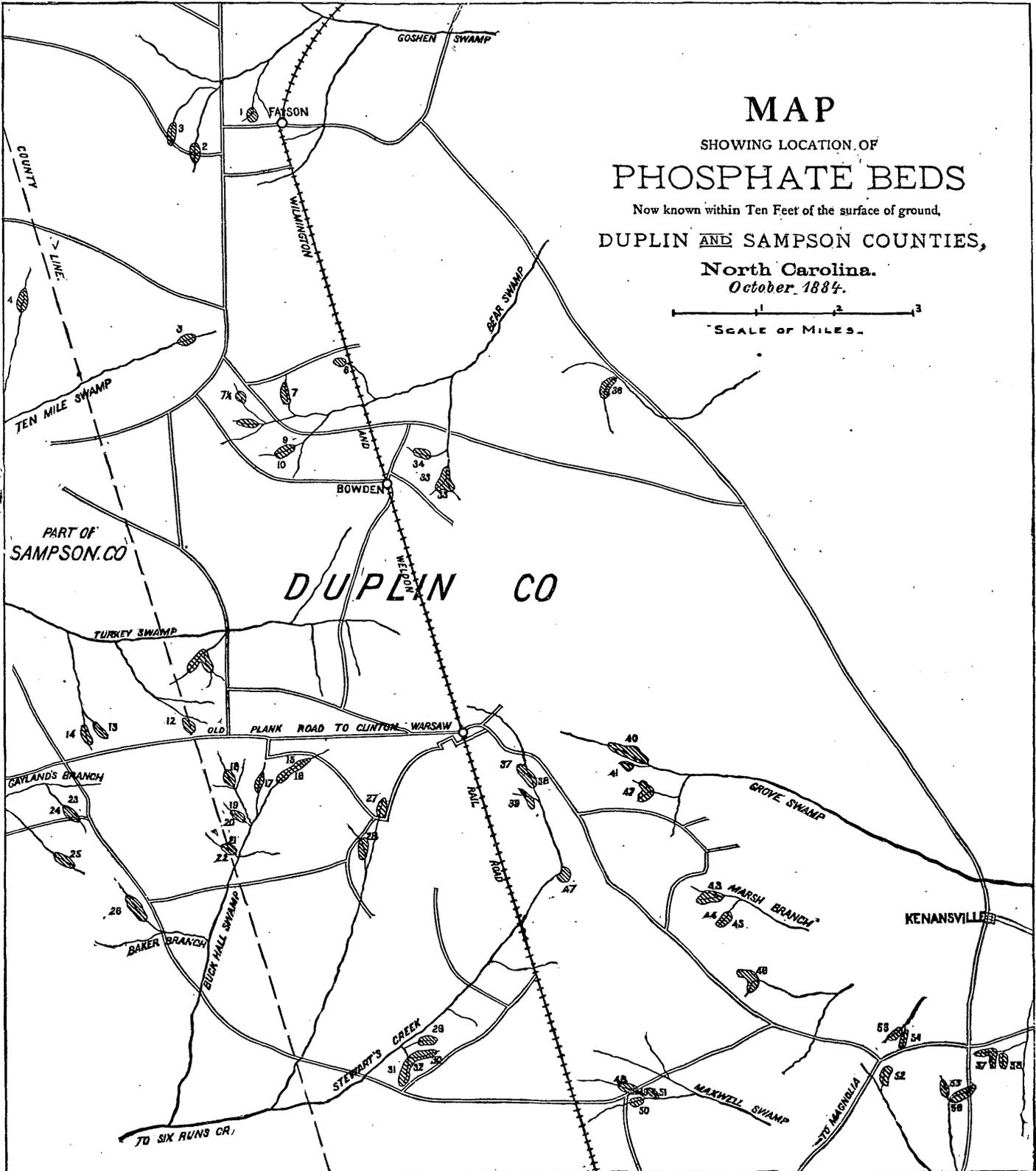
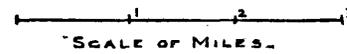
Bone phosphate of lime .....	62.039
Carbonate of lime .....	6.914
Organic matter and moisture .....	5.106

#### AMORPHOUS NODULAR PHOSPHATES OF NORTH CAROLINA.

Deposits of phosphate of lime have been known to exist in the flat country near the coast of North Carolina for several years, but not much attention was paid to them until 1884, when, under the direction of Dr. Dabney, of the agricultural station of that State, they were thoroughly examined. The result seemed to show that the phosphates were either too scanty in quantity or too poor in quality to be of much commercial importance. They are found in the southeastern part of North Carolina, and principally in the counties of Sampson, Duplin, Pender, Onslow, Columbus, and New Hanover.

# MAP SHOWING LOCATION OF PHOSPHATE BEDS

Now known within Ten Feet of the surface of ground,  
DUPLIN AND SAMPSON COUNTIES,  
North Carolina.  
October, 1884.



The deposits are of two kinds: (1) Beds of nodules, resembling very much the South Carolina beds and (2) a conglomerate in which the pebbles are phosphate and the matrix a white calcareous rock.

(1) The beds of nodules overlie the Eocene marl and consist of numerous phosphatic nodules, shark teeth and bones, associated in a sandy matrix or in a shell marl. Generally, the bed immediately overlies a stratum of shell marl and is occasionally overlaid by a similar stratum. Sometimes the underlying bed is replaced by a deposit of a pale-green, indurated sand, containing shark teeth and other bones. The two following sections will show the mode of occurrence of these phosphates:

1. Soil, sand or clay, 5 to 10 feet.
2. Shell marl, 5 to 10 feet.
3. Bed bearing phosphate nodules, 1 to 3 feet.
4. Sea-green, sandy marl, 2 to 4 feet.
5. Ferruginous hard pan, 6 to 12 inches.
6. Interstratified lignites and same sands as in 4.

The above section was obtained in a canal on the land of Mr. N. Daniel, Sampson County. Fragments of lignite are sometimes associated with the nodules.

Section 2, from the beds on J. W. Best's farm, Duplin County.

1. Sandy soil, 1 to 10 feet.
2. Nodule bed, 1 to 2 feet.
3. Shell marl.

The nodules are of a lead-gray color and vary from lumps the size of a man's fist to masses weighing several hundred pounds. The average size is larger than that of the South Carolina nodules. They vary in composition from the close, compact, and homogeneous masses found in some places in Onslow County, to the coarse-grained and highly siliceous rock of Sampson and Duplin Counties. The latter variety contains considerable quantities of sand, which can be distinguished with the naked eye, and occasionally siliceous pebbles the size of a chestnut. In fact, the nodules are often a phosphatic sandstone, in which the grains of sand are cemented by phosphatic matter. Occasionally they are found containing numerous Tertiary shells. Many shells are also found mixed with the nodules in the sandy matrix, and they preserve their most delicate outlines in a state of great perfection, while the nodules are much rolled and rounded. These facts would seem to show that the shells were brought into their present position by the animals that once inhabited them after the bed of nodules had been formed. A similar condition has been observed in the English beds of phosphate nodules. The North Carolina nodules are much bored by mollusks and in every respect resemble those from the Russian Cretaceous formation.

The nodules all tend toward flat shapes, in which they differ from those of South Carolina, which have no definite form. One specimen found measured 18 inches long 12 wide and 2 thick. This flat character would seem to favor the idea that the nodules were formed by the phos-

phatization of the surface of a bed of sandy marl. The phosphate, having a tendency to segregate, formed in some places richer than in others. Then, when the bed was exposed to erosion, only the parts which were strongly enough cemented together survived. Often, around the siliceous pebbles in a nodule, concentric bands of phosphate of lime may be observed, showing its strong tendency to form in segregations.

These deposits have not as yet been put to any commercial use. They are of a low grade, averaging only about 45 per cent. phosphate of lime, and occur only in small patches of from one to twelve acres.

(2) The second variety of phosphate deposits found in North Carolina belongs to the class of phosphatic conglomerates. They are found in New Hanover and Pender Counties and consist of a mass of Tertiary shark teeth, bones, nodules, and quartz pebbles, all well rolled and rounded and cemented together, along with grains of greensand, in a calcareous matrix. At Castle Hayne, New Hanover County, they occur in a bed sometimes over six feet deep. The largest pebbles and nodules are nearest the top of the formation and never exceed the size of a horse-chestnut. They grow smaller with the depth, and at six feet they are not larger than an apple seed. The character of the whole mass of the deposit also varies very much with the depth. The top of the bed is a hard and solid rock, but at two feet it begins to get softer, and at three to four feet the conglomerate bed is simply a mass of loose, calcareous marl containing pebbles. The section below, from near Castle Hayne, N. C., will show the nature of this bed.

1. White sand 0 to 3 feet.
2. Brown to red, ferruginous, sandy clay or clayey sand, 1 to 3 feet.
3. Green clay, 6 to 12 inches.
4. Dark-brown, indurated peat, 3 to 12 inches.
5. White, calcareous marl, 0 to 2 feet.
6. White shell rock, 0 to 14 inches.
7. Phosphatic conglomerate rock, 1 to 3 feet.
8. Gray marl containing smaller nodules than the overlying bed, 2½ to 4½ feet.
9. Light-colored, calcareous marl, containing nodules which are smaller than those in the overlying beds and which grow fewer and smaller at a depth. Many shells.

The line between the shell rock (6) and the conglomerate bed (7) is very sharply drawn. There are occasionally a few nodules found in the shell rock near the line of contact, which may have been derived from the conglomerate. The surfaces of all the beds are very uneven, especially that of the calcareous marl in the above section, which occurs only in patches on top of the shell rock (Fig. 30).

Near Wilmington, N. C., the following section was obtained :

1. Sandy soil, 2 feet.
2. Greensand bearing a few phosphatic nodules about the size of a pea, 4 feet.
3. Gray marl, 6 feet.
4. Limestone rock bearing a variable amount of nodules, of the same size as near Castle Hayne.

The nodules in 4 sometimes make up as much as three-fourths of the contents of the bed; at others they occur scatteringly through the

rock, and occasionally are not found at all. They are kidney and egg shaped and generally much less bored and irregular than the South Carolina nodules. They vary from gray to greenish black in color and have a specific gravity of 2.6 to 2.7.

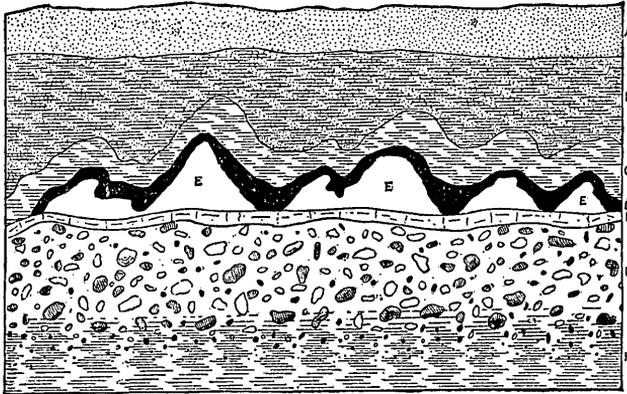


FIG. 30. Strata overlying the phosphate bed at Castle Hayne, New Hanover County, North Carolina. A, sand; B, ferruginous, sandy clay; C, green clay; D, indurated peat; E, calcareous marl; F, white shell rock; G, phosphate conglomerate; H, marl containing smaller nodules. Scale: 1 inch = 5 feet.

Two companies have been formed to grind this conglomerate rock and sell it for local use. The whole mass does not contain more than 10 to 20 per cent. phosphate of lime, but it is said to have been successfully used as a fertilizer. The separate nodules are very variable in composition.

Table of analyses of North Carolina rock phosphates made at the North Carolina experiment station.

[I to XI. From neighborhood of Warsaw, Duplin County.]

	I.	II.	III.	IV.	V.	VI.	VII.
Moisture .....	0.02	1.57	1.08	1.79	1.73	1.06	0.63
Samples dried at 212 degrees F. contain sand and insoluble matter.....	38.09	28.92	42.96	5.17	59.47	29.46	37.36
Carbonate of lime .....	3.81	2.43	4.18	5.91	3.12	54.83	4.96
Phosphate of lime.....	45.16	57.18	42.46	37.28	28.19	3.90	44.51
Equivalent to phosphoric acid.....	20.10	26.19	19.45	17.07	12.91	25.15	20.39
				VIII.	IX.	X.	XI.
Moisture .....				0.66	0.39		
Sand and insoluble matter .....				30.44	36.59	45.62	44.73
Carbonate of lime.....				6.30	6.30	4.59	2.30
Phosphate of lime .....				53.03	45.78	39.86	39.33
Equivalent to phosphoric acid .....				24.29	20.97	18.26	18.01

Table of analyses of North Carolina rock phosphates etc.—Continued.

[XII to XVI. From neighborhood of N. A. Faison's, Duplin County.]

	XII. White compact.	XIII. Gray compact.	XIV. White gritty.	XV. Gray.	XVI. Common black.
Moisture .....	2.07	2.50	0.77	2.70	0.81
Sand and insoluble matter.....	1.49	0.05	32.79	0.64	45.91
Carbonate of lime.....	12.00	8.98	1.45	7.07	5.84
Bone phosphate.....	71.82	76.82	7.42	76.54	36.02
Equivalent to phosphoric acid.	32.90	35.19	3.40	35.06	16.50

[I to XV. Nodules from Sampson County, N. C.]

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Sand and insoluble .....	47.18	47.41	70.78	54.96	1.58	51.75	32.16	44.99
Carbonate of lime.....	5.91	5.27	4.20	3.91	9.55	4.52	3.91	5.25
Bone phosphate.....	28.09	38.31	20.24	32.05	69.55	32.53	50.73	37.70
	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	
Sand and insoluble.....	36.04	52.53	49.34	29.41	51.93	50.42	53.43	
Carbonate of lime.....	4.71	5.68	4.66	5.63	6.43	1.86	6.43	
Bone phosphate.....	44.82	32.22	33.62	38.09	29.93	35.52	29.47	

[I to II. Nodules from Pender County, N. C.]

	I.	II.
Sand and insoluble matter .....	61.96	24.77
Carbonate of lime.....	4.32	15.55
Bone phosphate.....	21.02	47.50

[I. Nodules from phosphatic conglomerate from New Hanover County, N. C.]

Sand.....	I.	43.66
Carbonate of lime .....		34.56
Magnesia .....		0.86
Potash .....		0.39
Oxide of iron and alumina.....		0.56
Phosphate of lime .....		19.99
Sulphuric acid.....		Trace
Chlorine.....		Trace
		100.02

[II to VIII. Nodules from phosphatic conglomerate from New Hanover County, N. C.]

	II.	III.	IV.	V.	VI.	VII.	VIII.
Sand and insoluble matter .....	22.07	33.52	.....	18.50	20.02	3.25	31.66
Carbonate of lime .....	42.12	20.45	.....	39.04	42.12	51.34	15.94
Phosphate of lime .....	20.50	33.97	30.90	25.34	22.68	31.59	42.09
Equivalent to phosphoric acid.	9.39	15.57	14.16	11.61	10.39	14.57	19.28

*Table of analyses of North Carolina rock phosphates etc.—Continued.*

[I to IV. Phosphatic conglomerate of New Hanover County, N. C.]

	I.	II.	III.	IV.
Sand and insoluble matter.....	20.28	24.96	42.08	35.48
Carbonate of lime.....	57.29	54.71	10.12	51.81
Phosphate of lime.....	11.81	16.42	26.64	6.40
Equivalent to phosphoric acid.....	5.41	.....	12.57	2.83

[I. Phosphate conglomerate from New Hanover County, N. C.]

Carbonate of lime.....	64.26
Phosphate of lime.....	11.16
Equivalent to phosphoric acid, 5.11.	
Magnesia.....	0.81
Potash.....	0.40
Sulphates and chlorides.....	Trace
Sand, soluble silica, oxide of iron, alumina, etc., undetermined.....	23.37
	100.00

## AMORPHOUS NODULAR PHOSPHATES OF ALABAMA.

The phosphate deposits of Alabama belong to the Cretaceous formation and are found in two parallel belts running across the State. The following very general section, in an ascending order, will show their positions:

- (1) Eutaw group.
- (2) Phosphate stratum.
- (3) Rotten limestone formation.
- (4) Phosphate stratum.
- (5) Ripley group.

The Cretaceous formation of Alabama probably corresponds to the Upper Chalk of Europe, which also, in some places, contains beds of phosphatic nodules. It runs from the western part of Georgia in a WNW. direction through Alabama into Mississippi, where it takes an abrupt curve to the north. After passing through the western and northern part of Mississippi it enters Tennessee and runs through that State almost to the Kentucky boundary line. The phosphate deposits, it is said, can be traced along a considerable length of this formation, but, as far as has yet been discovered, it is only in Alabama, and there only in a few places, that the deposits are of considerable extent. In that State the Cretaceous strata dip gently to the south, and as a result of this dip the nodule bed, at the base of the Rotten Limestone, is found at ten to twenty miles north of the one at the summit of that formation.

The general character of the two deposits is very much the same. They are composed of shells, phosphatic nodules, shell casts, and fossils, all much worn, broken, and rounded, and buried in a matrix of a soft, white or gray limestone. The nodules are generally flat in their general shape and chestnut brown in color, and average, in size, from one-

half an inch to three inches in diameter. They are very irregular in form and occasionally show one side which is completely phosphatized and another which is composed largely of carbonate of lime. This is strong evidence for the theory of their formation by the phosphatization of the surface of a calcareous bed, as mentioned in the case of the North Carolina deposits. The fossils of the two beds differ considerably. Ammonites are very plentiful in both, but *Hippurites* and *Baculites* were found in much larger quantities in the lower bed than in the upper one. The following two sections will show the different relations of the two beds:

(a) Upper bed (at Coatopa):

1. Greensand containing nodules and shell casts, but numerous only at the base, 4 feet.
2. Soft, calcareous rock containing nodules, 1 foot to 1½ feet.
3. Rotten limestone.

(b) Lower bed (at Hamburg):

1. Greensand bearing some casts and nodules, 0 to 5 feet.
2. Gray limestone containing many nodules, 5 feet.
3. Hard, indurated sand ledge, containing shells, 8 to 12 inches.
4. Yellow sand containing shells, 2 feet.
5. Ferruginous sand containing specks of mica, about 30 feet.
6. Indurated sand ledge containing shells 8 to 12 inches.
7. Yellow sand containing shells, 2 feet.
8. Greensand.

The section of the upper bed is well seen at the town of Coatopa, in Sumter County. The Greensand here is often oxidized and has a rusty-red appearance; it composes a large part of the surface soil in the neighborhood and forms part of the so-called "Black Belt," famous for its fertility. It contains many phosphatic shell casts, but is generally richest in them near the line of contact with the underlying bed, where they sometimes make up 50 per cent. of the whole mass. Occasionally they cover the whole surface of the ground and must be carted away in order to permit agricultural operations. The underlying bed contains many more nodules and shell casts than the Greensand. Sometimes it is almost a solid mass of them with a soft, gray, calcareous matrix. The bed is from 1 foot to 1½ feet thick and seems to underlie a large extent of country. In some places the nodules and fossils are more scattered in the bed than in others, and in still other places the bed has been entirely eroded away and the Greensand comes into direct contact with the Rotten Limestone. Very few bones were found in this upper bed.

Outcrops of this same nodule bed can be seen near the Tombigbee River, at Moscow, and also at Livingston, on the Sucarnochee River. In the underlying Rotten Limestone there are no phosphatic nodules.

The section of the lower nodule bed is seen at numerous places all across the State. Thus it is found at Eutaw, Selma, Greenborough, Prattville, Wetumpka, and especially well at Hamburg, near Marion.

In this last place the surface is largely composed of greensand, though, in some places, this is washed off, exposing the phosphate-bearing bed. Where the ground has been much eroded and cut into gullies, it is covered by a solid sheet of nodules, phosphatized shell casts, fossils, ferruginous concretions, and unaltered shells. There is a much larger per cent. of the brown nodules here than in the upper nodule bed; but as in that bed, so here, the nodules are very few compared with the fossils and shell casts. The indurated ledge represented in the section seems to have the same general composition as the sand that underlies it, but to be in a hardened condition.

The phosphate deposits of Alabama are more difficult to mine than the South Carolina phosphates and cannot be shipped as cheaply. Consequently they have not as yet been put to any practical use. But they have been found in sufficient quantities in several places to become of considerable local importance. Among other places, they are found in considerable quantities on the land of Mr. J. F. Wiatt, near Coatopa, and of Mr. Spencer and Messrs. Davis, near Hamburg.

*Table of analyses of amorphous nodular phosphates of Alabama.*

[Northern belt. (a) The nodules and phosphatic casts of fossils from Spencer's field, Hamburg, Ala.]

	Phosphoric acid.	Bone phosphate.	Analyst.
Nodule .....	22.00	48.00	W. I. Hetzberg, University of Alabama.
Phosphatized shell .....	19.80	43.16	Do.
Surface nodules .....	38.00	82.84	John Daniel, University of Alabama.
Surface nodules .....	35.5	77.39	Do.
Surface nodules, sample 1 pound .....	25.66	55.88	Charles Gibson, Chicago.
Nodules from near Selma ..	26.1	56.90	John Daniel, University of Alabama.
Nodules from near Selma ..	25.8	56.24	Do.
Nodules from near Selma ..	36.0	78.48	Do.
Nodules from near Selma ..	38.0	82.84	Do.

[(b) Matrix of the nodules from Spencer's field, Hamburg, Ala.]

	Phosphoric acid.	Bone phosphate.	Analyst.
Matrix of nodules .....	5.12	11.16	E. M. Harris, University of Alabama.
Matrix of nodules .....	1.2	9.16	John Daniel, University of Alabama.
Matrix of nodules .....	4.65	10.14	L. L. Dean, University of Alabama.
Matrix of nodules .....	8.00	17.44	Do.
Blue matrix of nodules .....	2.2	4.80	Charles Gibson, Chicago.
White matrix of nodules ..	3.6	7.85	Do.

*Table of analyses of amorphous nodular phosphates of Alabama—Continued.*

[II. Southern belt. (Bulletin No. 5 of the department of agriculture of Alabama.)]

	Insoluble matter.	Phosphoric acid.	Bone phosphate.
Nodules from near Livingstone.....	8.48	1.10	2.40
Nodules from near Livingstone.....	15.02	.64	1.39
Shell casts and nodules from near Coatopa.....	9.38	14.56	31.78
Shell casts from Moscow.....	25.52	1.55	3.36

## AMORPHOUS NODULAR PHOSPHATES OF MARTHA'S VINEYARD.

The phosphates of Martha's Vineyard occur as black or dark-gray nodules, varying from one-fourth of an inch to four inches in diameter, in two beds of Greensand. The beds are of Tertiary age and are well seen in the cliffs at Gay Head. They are each 18 to 24 inches thick and dip at an almost vertical angle. They are associated with beds of lignite, clay, and sand. The nodules are mixed with numerous bones of cetaceans, crustacean remains, and other fossils. The more southerly of the two beds contains 5 to 15 per cent. of nodules and bones, while the bed to the north contains in some places almost no nodules, and in others as much as 25 per cent. of them. The nodules have a water-worn appearance and have been much bored by marine mollusks. They give off a smell of decayed organic matter when two fragments are rubbed together, and have a hardness of about 3.

This deposit has not yet been put to any practical use. The nodules are probably too scattered in the bed and too expensive to mine to allow them to be of any commercial value.<sup>1</sup>

## AMORPHOUS NODULAR PHOSPHATES OF FLORIDA.

Phosphate deposits have been found in various places in Florida, but as far as is yet known they are either of too small extent or of too poor quality to pay for mining. The only deposit which covers more than a few acres is found in Alachua County, near the central part of the State. The phosphate found here belongs to the subdivision of phosphatic conglomerates. The rock consists of small pebbles, from the size of a mustard seed to that of a pea, closely packed in a matrix of indurated calcareous marl. The pebbles are very compact, have a small conchoidal fracture and sometimes an enamel-like luster. They are creamy white to chestnut brown in color and are associated with

<sup>1</sup> It seems to me certain that these beds containing nodules were deposited in the delta of a large river and that the nodules, together with the greater part of the fossils with which they are intermingled, were derived from pre-existing strata in essentially the same manner as those which occur in the estuaries of the rivers near Charleston, S. C.

For a further description of these deposits see a report on the island of Martha's Vineyard, now in press, to appear in the Seventh Annual Report of the U. S. Geological Survey.—N. S. S.

worn and rounded bones and shells. Prof. C. U. Shepard, sr., thinks that many of the pebbles may be the worn casts of marine shells, while some of them seem to be fragments of coral. This conglomerate occurs in masses weighing from one to twenty pounds. The largest mass yet found was 18 inches long, 14 wide, and 4 thick. The pebbles occur in a bed covering about ten acres and are associated with pieces of a porous limestone rock, very common in the region. The bed varies from a fraction of a foot to five feet in thickness. Sometimes it crops out at the surface, and at others it is found at a depth of four or more feet. At Gainesville, a town 19 miles west of this bed, a similar rock is said to have been found, in boring an artesian well, at a depth of 248 feet.

The masses of rock are not nodules, but seem to be simply broken fragments. They are much weathered and rounded and are buried in sand.

In some places the pebbles, rounded bones, and coral fragments occur loose in a calcareous matrix, as if weathered out of the original conglomerate. Samples of pebbles from this loose material are said by one of the owners of this place (Dr. Simmons) to average 85 per cent. phosphate of lime, while the whole mass of the rock, as analyzed by C. U. Shepard, jr., averages about 48 per cent.

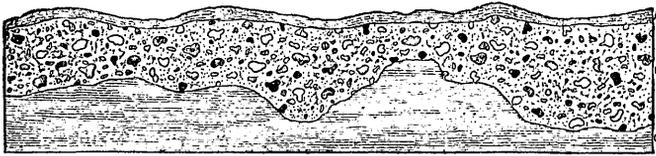


FIG. 31. Section in quarry at Rocky Hill, on Lochloosa Creek, near Magnesia Springs, Alachua County, Fla. A, sandy soil; B, calcareous nodules, white, brown, and purple, embedded in sand; C, spongy, calcareous rock, blending at a depth of 3 to 4 feet into a phosphatic rock. Scale: 1 inch=8 feet.

On the northwest side of this bed runs a stream known as Lochloosa Creek, beyond which is a ridge rising sixty to seventy-five feet above the creek, and called Rocky Hill. The hill is overlaid almost entirely by a deposit of calcareous stones and pebbles, embedded in sand, which sometimes entirely runs out, and again reaches a depth of over six feet. Below is a soft, porous, calcareous rock, which is of a spongy consistency and hardens on exposure to air. It is quarried for building the chimneys and foundations of houses. In one of the quarries examined this formation gradually blended, at a depth of three to four feet, into a massive and compact phosphate rock, which is similar in appearance to the phosphatic fragments in the bed described above, except that it is in a solid mass, and is probably the ledge whence the fragments were derived. The surface of the spongy, calcareous rock is very uneven and has been much eroded (Fig. 31). It seems as if Rocky Hill, when submerged, was much worn before the pebbles and the sand were deposited on top of it.

## AMORPHOUS NODULAR PHOSPHATE DEPOSITS OF NORTH WALES.

The rock phosphate deposits of North Wales belong to the Caradoc and Bala group of the Cambro Silurian or Lower Silurian formation. They immediately overlie the Bala limestone beds and are overlaid by fossiliferous shales, sometimes more or less calcareous. They belong to the class of rock phosphates, or phosphates having no definite chemical composition, and are remarkable as being, geologically, the oldest of the commercially important phosphate beds which still preserve the remains of organic life.

The phosphate bed has been traced by Mr. D. C. Davies from the town of Llanfyllin to the hills north and west of Dinas Mowddwy.<sup>1</sup> Mr. Davies has calculated that the area already known to contain this bed amounts to almost 140 square miles, and he thinks it will probably be found wherever the Bala limestone occurs.

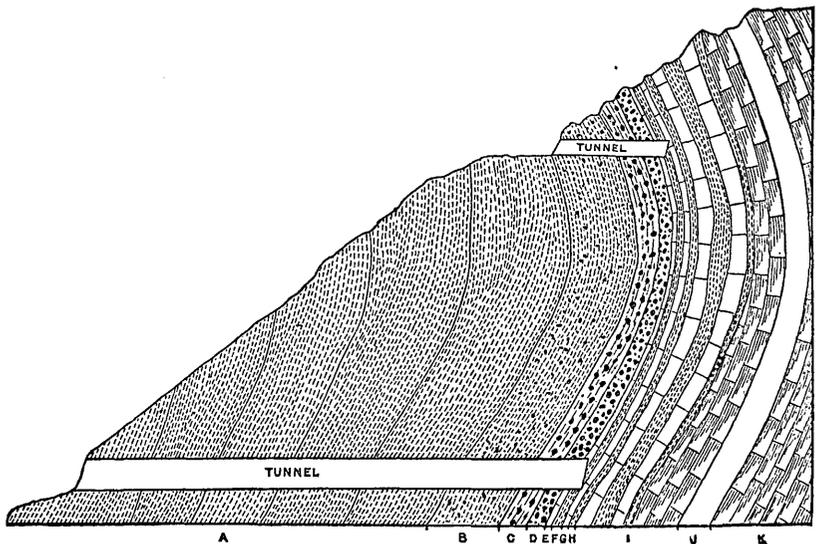


FIG. 32. Section of strata at Cwmngwynen phosphate mine, southwest of Llangynog, North Wales; after D. C. Davies, Quarterly Journal Geological Society of London, 1875. Scale: 1 inch = 80 feet.

As will be seen from the sections (Figs. 32 and 33), the formation in which the phosphate bed occurs has been much twisted and contorted. In fact, the phosphate bed, wherever found, is in an almost vertical position. It varies from ten to fifteen inches in thickness and consists of a mass of black nodules, varying from the size of an egg to that of a coconut, "closely packed together and even running into each other." The nodules are cemented into a solid mass by a black matrix, and the whole mass gives an average of 46 per cent. phosphate of lime, while the separate nodules sometimes contain 64 per cent. The bed contains considerable graphite, which gives the black color to both the nodules and the matrix and often gives the former a polished and glossy ap-

<sup>1</sup> Geol. Mag., vol. 2, London, 1875, p. 183.

pearance. There are numerous remains of animal life in the bed, but the whole deposit has been so affected by chemical action that, though the traces of organic forms are left, it is often very difficult to distinguish them. Still Davies<sup>1</sup> has recognized the remains of *Modiola*, *Aviculopecten*, *Orthoceras*, *Orthis*, *Lingula*, and trilobites, besides traces of many other species.

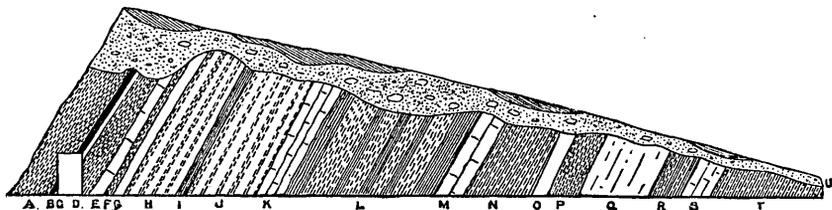


FIG. 33. Section of strata at Berwyn phosphorite mine, west of Llangynog, North Wales; after D. C. Davies, *Geological Magazine*, London, 1875. Scale: 1 inch=32 feet.

M. H. Johnson,<sup>2</sup> who has made numerous sections of the North Wales nodules, has found that many of them contain a species of sponge. He has also found in the nodules fragments of mollusk and crustacean shells, with bodies looking like *Coscinopora*. From these observations he concludes that the nodules are of organic structure. It seems more likely, however, that the nodules resulted from the phosphatization of a calcareous bed, which may have contained the organic remains discovered by Mr. Johnson in the nodules. Davies thinks the bed represents the remains of an old Laminarian zone and that it originated by the phosphatization of calcareous matter by the phosphates from animal matter and seaweed.

The nodules have been so affected by heat and chemical action that they often are found blending and running into each other. They sometimes blend gradually with the matrix, the whole bed assuming a shaly structure, so that it is often impossible to draw a distinct line of division. The mass of the stratum is sometimes found to have a very similar composition over large areas; but where the underlying bed becomes more arenaceous the nodules become much poorer in phosphate and richer in siliceous matter.<sup>3</sup> Thus, at Green Park, the bed averages only 20 per cent. phosphate of lime. The phosphate stratum, in some places, contains numerous concretions and crystals of sulphide of iron, which rust on exposure to the atmosphere, thus changing the color of the bed from black to brown. The phosphate of lime is itself often replaced by these sulphides. Such is the case in many parts of the western outcrop of the bed, especially on the flanks of Mount Aran

<sup>1</sup> *Geol. Mag.*, vol. 4, London, 1867, pp. 251-253.

<sup>2</sup> *Ibid.*, vol. 2, n. s., 1875, p. 238.

<sup>3</sup> This is a strong argument for the theory of the formation of the nodules by the phosphatization of the underlying bed.

Mowddwy. Such large quantities of sulphides and graphite as are found in this phosphate bed, according to Davies, seem to show the former presence of vegetable life.

An examination of the analyses given farther on will show that there is little or no carbonate of lime in these phosphates. Davies, in speaking of this fact, says:<sup>1</sup>

Schmidt found in the inner side of the mouth of *Unio* and *Anodonta* no less than 15 per cent. of phosphate of lime, 3 per cent. of carbonate of lime, and 82 per cent. of organic matter, from which the inference was drawn that the phosphate was separated from the blood by this organ for the purpose of cell formation.<sup>2</sup> The doctor adds: "It seems probable that the carbonate is converted, in the animal, into phosphate by the phosphorus it contains." Here, perhaps, we have a clue to the missing carbonate. The great preponderance of phosphatic organisms, with which the period covered by the deposit commenced, gradually absorbed and secreted all carbonate of lime, whether held in solution in the water or redissolved from the shells of dead mollusks; and so, turning it into phosphate, grew and multiplied exceedingly, and became at last almost sole masters of the position by this appropriation, until the supply of carbonate of lime became insufficient for their sustenance, as the mineral conditions came on under which the overlying shales were deposited.

It seems possible, however, that the absence of carbonate of lime in the Wales phosphate is due to its having been leached out during the process of partial metamorphosis to which the bed has been exposed, as the effect of metamorphosis is often to segregate from the rock which is being acted on the minerals of which it is composed.

The phosphate bed is often separated into two or three smaller beds by thin bands of the underlying limestone. It is always found, however, that when the upper one or two beds, as the case may be, run into the overlying shale they always run out and the lowest bed is always the continuous one.

The bed immediately underlying the phosphate bed is a pure limestone, often covered on the surface with small brachiopods and other fossils. It has an average thickness of 6 inches and contains 15 to 20 per cent. phosphate of lime. Like the phosphate bed, it is very continuous and the two are always found together. It is underlaid by a large series of interstratified shales and more or less fossiliferous limestones. This formation, known as the Bala limestone, gradually runs into the underlying ash beds.

The phosphate bed is overlaid by a series of fossiliferous shales. Those immediately over it have all been phosphatized to a greater or less extent, and the more the phosphatization has gone on the more completely have all traces of organic life been obliterated. In the overlying shale at Cwmgwynen, Davies found remains of *Echinosphearites balticus*, *Caryocystites*, and other echinoderms, *Lingula*, *Modiola*, *Theca*

<sup>1</sup> Quart. Jour. Geol. Soc. London, 1875, vol. 31, pp. 364.

<sup>2</sup> *Unio* and *Anodonta*, as well as all other species of the suborder to which they belong, are fresh-water forms, while the beds under consideration are certainly of marine origin. It is most likely that the phosphate matter came from brachiopods and trilobites.—N. S. S.

*Forbesii*, *Cycloceras arcuatum*, *C. Sonax*, *Orthocerata*, *Illænus Davisii*, and other forms.

The phosphate bed of North Wales was discovered by a miner in 1863, in a ravine near Cwmgwynen, 5 miles from the town of Llanfyllin. At first the nature and value of the bed were unknown, but finally a specimen was sent to Dr. A. Völcker, who analyzed it and made known its importance. Several mines have since been started at Cwmgwynen, Penygarnedd, Berwyn, Llanfyllin, and other places, but none of them has been successful and at present no Welsh phosphate is mined. The reasons for this want of success were the distance of the mines from any railroad or navigable river, the low percentage of phosphoric acid (see analyses), and the depressed state of the phosphate market. Moreover, the bed is expensive to work, as regular mining operations are necessary to win the phosphate; it also often contains considerable iron, which causes superphosphate made from it to have a sticky consistency.

*Analyses of North Wales rock phosphates.*

[I and II. Analyses of two specimens from Cwmgwynen, by Völcker (Quart. Jour. Geol. Soc. London, 1875).]

	I.	II.
Phosphate of lime.....	64.16	48.50

“There was no carbonate of lime, some fluoride of calcium, alumina, and oxide of iron.

“The darker-colored contained more graphite and were richer in phosphate of lime than the lighter-colored specimens.”

[III. Analyses of nodule from Berwyn mine, North Wales, by D. H. Richards (ibid., vol. 31, pp 364, 365).]

Moisture and organic matter .....	4.200
Sand .....	22.600
Tribasic phosphate of lime.....	64.165
Oxide of iron and alumina.....	6.890
Other constituents not determined.....	2.145
	100.000

Another analysis of a similar nodule gave 61.44 per cent. phosphate of lime.

[IV and V. Analyses of Berwyn mine phosphate, North Wales, by F. C. Hills and Co. (ibid., p. 365).]

	IV.	V.
Loss on burning.....	6.77	3.06
Phosphoric acid (1).....	22.54	20.92
Lime.....	31.08	30.13
Oxide of iron and carbonic acid.....	19.12	22.88
Insoluble matters.....	20.49	23.01
Total.....	100.00	100.00
(1) Equal to tribasic phosphate of lime.....	49.207	45.67

Five other analyses of the bulk of the deposit, made by Messrs. Hills, gave an average of 46.85 per cent. phosphate of lime. There was also in all the samples about one-half per cent. of copper. Analyses of phosphate from near Llanfyllin, North Wales, gave Messrs. Hills “a range of from 20 to 30 per cent. of phosphate of lime,” (Quart. Jour. Geol. Soc. London, 1875, vol. 31, p. 365.)

[VI and VII. Analyses of two samples from northwest of Dinas Mowddwy and Llan-y-Mowddwy, North Wales, by Hills (Quart. Jour. Geol. Soc. London, 1875).]

	VI.	VII.
Phosphate of lime.....	2.90	1.72
Sulphur .....	34.38	34.20

The rest was made up of sand, iron, and alumina.

[VIII. Analysis of North Wales phosphatic limestone, by Völcker (Rep. Brit. Assoc. Advanc. Sci., 1865, p. 38).]

Tribasic phosphate of lime.....	34.92
Oxide of iron .....	2.34
Alumina .....	6.52
Carbonate of lime.....	20.75
Carbonate of magnesia .....	5.92
Magnesia, in a state of silicate.....	2.07
Iron pyrites.....	2.79
Sulphuric acid .....	0.16
Insoluble siliceous matter .....	20.95
Organic matter and loss.....	3.58
	100.00

[IX. Analysis of phosphatic black shale, by Völcker (ibid., p. 38).]

Organic matter and loss .....	3.98
Lime .....	37.16
Phosphoric acid .....	29.67
Equal to tribasic phosphate of lime, 64.16.	
Magnesia .....	0.14
Oxide of iron .....	1.07
Alumina.....	5.84
Matter insoluble in dilute hydrochloric acid .....	22.14
	100.00

[X. Analysis of phosphatic black shale, by Völcker (ibid., p. 39).]

Tribasic phosphate of lime.....	52.15
Lime, present as fluoride of calcium and as silicate.....	4.23
Magnesia.....	0.32
Alumina .....	7.71
Oxide of iron .....	2.01
Sulphuric acid.....	0.26
Iron pyrites.....	7.52
Insoluble siliceous matter.....	22.44
Organic matter and loss .....	3.36
	100.00

#### AMORPHOUS NODULAR PHOSPHATE DEPOSITS OF ENGLAND.

Phosphates are found in England, both in the Cretaceous and Tertiary formations. The Cretaceous phosphates are the most important, in both quantity and quality. They occur in two different parts of the Lower Cretaceous, namely, in the Upper and in the Lower Greensand.

*Phosphatic beds of Cretaceous Upper Greensand.*—The outcrop of the Upper Greensand formation in England begins in the north at Flamborough Head, in Yorkshire, and runs west and southwest for about twenty miles, when it turns abruptly to the southeast and extends continuously in that direction to within three miles of the north coast of the Wash, where it becomes covered with alluvium. It appears again on

the south shore of the Wash at St. Edmunds and runs south by southwest to Downham Market. Here it becomes covered with alluvium and does not appear again for about twenty-three miles, when it crops out three miles below Cambridge, on the Cam. From Cambridge it runs in a southwesterly direction through the counties of Cambridge, Bedford, Buckingham, Oxford, Berks, Wilts, and Dorset, and reaches the southern coast at Lyme Regis and Sidmouth. On the southern coast of Dorsetshire there are numerous outcrops of Upper Greensand, as well as on the Isle of Wight. In the southeast of England there is also a very considerable Greensand outcrop. It commences near Beachy Head, in Sussex, and runs west by a little north to Petersfield, in the east of Hampshire. Here it turns abruptly to the north and runs in this direction to Alton and Farnham, in Hampshire and Surrey, respectively. Thence it takes another abrupt turn to the east, and runs in a general easterly direction until it comes to the coast again, at Folkestone in Kent.

The Lower Greensand is not so continuous as the upper, but it occurs at intervals along most of the outcrops mentioned above, and in Sussex and Kent it is the uninterrupted accompaniment of the Upper Greensand. In Yorkshire it runs from Flamborough Head west for about fifteen miles. It crops out again with the Upper Greensand about three miles south of Barton and runs continuously to Burgh. Again it crops out near Cambridge, and extends thence to Buzzard in Bedford. From there on, in a southwest direction, it occurs in small outcrops along the line of the Upper Greensand. In the Isle of Wight there are large outcrops of it. This same Greensand belt can be traced across the English Channel to the Continent. In the Brunswick and Hartz districts, at Goslar, Schoeppenstedt, and Salzgitter, the same nodules and shell casts are found as in the Lower Greensand in Cambridgeshire and Bedfordshire. But, though the belt is thus seen to have a very wide extent, the conditions which are necessary for the profitable working of a phosphate deposit are so many and so rarely satisfied that the phosphatic beds have been mined in very few places throughout this many hundred miles of outcrop. On the Continent the bed has been worked to no considerable extent.

The relative positions of the Upper and Lower Greensand formations is best shown by a section. The following one is given by Messrs. Paine and Way.<sup>1</sup>

The Cretaceous formation of England is divided into the Chalk and the Greensand. These again are subdivided as follows :

Chalk.....	}	1. Soft, white chalk with flints.
		2. Hard, white chalk with few or no flints.
		3. Chalk marl.
Greensand.....	}	1. Upper Greensand and firestone rock.
		2. Gault, or blue marl.
		3. Lower Greensand, made of iron sand and occasional limestone beds.

<sup>1</sup> Jour. Royal Agric. Soc., vol. 9, 1848.

The first two beds of the chalk are very poor in phosphoric acid, rarely containing over twelve-one-hundredths of 1 per cent., but the underlying marl is much richer and sometimes contains almost 2 per cent. of phosphoric acid. The marl is of a grayish color and contains specks of Greensand, which become more and more numerous until the marl gradually merges into the underlying Greensand bed containing the phosphatic nodules. The passage from the Upper Greensand to the Gault is often very abrupt, especially in Cambridgeshire and Bedfordshire, where the nodule bed often lies on the eroded surface of the Gault. The Lower Cretaceous deposits of Cambridgeshire and Bedfordshire differ from those of the south and west of England in the fact that the former lack that great thickness of Upper Greensand which exists in the southern counties. At the same time the lower beds of the Chalk are the same in both areas. In Hampshire and Dorsetshire there is a thin stratum, similar to the Cambridge nodule beds, which, like it, passes up gradually into the Chalk marl. But the difference is that in the case of the southern counties the arenaceous deposit, which sometimes reaches the thickness of many feet, comes between the phosphate bed and the Gault, while in the case of the Cambridge and Bedford deposits the nodule bed, which rarely exceeds one foot in thickness, rests immediately on the Gault. Concerning the absence of this arenaceous deposit in Cambridgeshire, Mr. O. Fisher<sup>1</sup> says: "It is probably due to the ridge of old rocks beneath the London area, which shut off the early Cretaceous sea, to the north of it, from those southwestern lands which yielded the sandy spoils." He also suspects a similar cause to have "produced the marked change between the Lower Cretaceous rocks in Cambridgeshire and the corresponding beds in Norfolk and Lincolnshire." Mr. Seeley<sup>2</sup> thinks that this increased thickness of Greensand to the south and southwest is due partly to the shelving of the sea bottom towards the south and partly to a current piling it up in the hollow, but principally because the southern area was nearer to the old plutonic rocks, whence, he thinks, the necessary ingredients of the Greensand came.

The principal phosphate diggings have been in the Upper Greensand of Cambridgeshire and Bedfordshire. The nodules in this deposit are buried in the Greensand, which varies from one inch to a foot in thickness and which is all that is left in these districts to represent the immense thickness of Greensand in the southern counties. In fact, it is a matter of serious doubt with some geologists whether the two deposits really represent one and the same geologic horizon.

The matrix of the nodules is not pure Greensand, but is composed partly of siliceous and calcareous matter and partly of glauconitic and phosphatic grains. The siliceous matter consists mostly of colored

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<sup>1</sup> Quart. Jour. Geol. Soc. London, vol. 29, 1873, p. 62.

<sup>2</sup> Geol. Mag., vol. 3, London, 1866.

quartz, obsidian, and grit. The calcareous matter is composed mostly of sponge-spicules, spines and plates of echinoderms, minute shells, polyzoa, bivalve entomostraca, microscopic corals, foraminifers, and calcareous concretions.<sup>1</sup> There are also in the bed "lumps of Chalk marl<sup>2</sup> which have fewer green grains in them than the matrix in which they are embedded." From this and other facts Mr. Fisher concludes that these phosphate beds seem to have been washed out of a calcareous marl, similar in character to the marl which lies above it. In short, he continues, the nodule bed is a condensation of the "Chalk marl with glauconite grains." On the other hand, Mr. Sollas thinks that the nodule bed has been derived from the destruction of the underlying Gault. The Gault contains nodules and fossils, but not nearly so many as the overlying bed. Mr. Fisher urges against this hypothesis that the nodules of the Gault are smaller and of a lighter color than those of the nodule bed proper. Though the nodules are of a lighter color on the surface, the interior is of a color very similar to that of the Greensand nodules. Mr. Sollas shows that by the action of hydrochloric acid the Greensand nodules assume this same color on the surface, and consequently it is possible that the Gault nodules may have been acted on by water, acidulated by some acid or acid salt, percolating through the bed, and thus had their surfaces bleached.

The phosphatic part of the nodule bed consists of shell casts, fossils, and nodules. There are numerous species of *Rhabdospongia*, *Bonneyia*, *Acanthophora*, *Polycantha*, *Retis*, and *Hylospongia*, besides many other Cretaceous forms. The nodules and casts are of a black or dark-brown color and have a very variable specific gravity and hardness.

Many of them are worn, broken, and rounded, showing them to be clearly derivative masses, while others are perfect in shape and show no signs of having been removed from their original bed.<sup>3</sup> The derivative fossils and nodules are covered with *Plicatulae*, and the smooth, broken surfaces of many of them, which are coated in this way, show, as Mr. Fisher thinks, that they must have been phosphatized before being deposited in their present bed, and he thinks that the phosphate was concentrated from a carbonic acid solution by animal matter. Besides the shell casts and fossils, there are two distinct varieties of nodules proper. The first is a reddish-brown and utterly shapeless variety. It is very soft when freshly dug, never becoming harder than ordinary chalk.<sup>4</sup> It has a very light specific gravity and is invariably rich in phosphoric acid.<sup>5</sup> A second variety is much more plentiful than the last. It consists of a dark-brown mass of a very variable shape. It is hard and heavy. It varies from pieces of micro-

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<sup>1</sup> W. J. Sollas: Quart. Jour. Geol. Soc. London, vol. 28, 1872, p. 398.

<sup>2</sup> O. Fisher: *ibid.*, vol. 29, 1873, p. 53.

<sup>3</sup> O. Fisher: *ibid.*

<sup>4</sup> Paine and Way: Jour. Royal Agric. Soc., 1848.

<sup>5</sup> See analyses.

scopic smallness to masses weighing four pounds. It occurs adhering to the surfaces of *Syphona*, corals, and shells, and appears to have once been in a plastic state. This substance has been called by Dr. G. A. Mantell<sup>1</sup> "molluskite," and he considers it the remains of the soft parts of mollusks. In describing it he says:

This substance is of a dark-brown or black color, and occurs either in shapeless masses, which are irregularly distributed among the shells and other organic remains, in sandstone, limestone, etc., or as casts of shells, or occupying their cavities. \* \* \* Upon analysis this substance is found to contain a large proportion of animal carbon. The rocks of firestone at Southbourne, on the Sussex coast, are mottled with brown molluskite and hard amorphous concretions, consisting of carbon and phosphate of lime, mixed with sand and other extraneous matter. Casts of shells of the genera *Venus* and *Arca*, etc., entirely composed of the same kind of materials, are also abundant in those rocks. \* \* \* The gelatinous bodies of the *Trigonia*, *Ostrea*, *Rostellaria*, *Terebratula*, etc., detached from their shells, may have been intermingled with the drifted wood in a sand-bank; while in some instances the animal matter would remain in the shells, be converted into molluskite, and retain the form of the original.

Both Mr. Fisher<sup>2</sup> and Mr. Sollas,<sup>2</sup> who have spent considerable time in studying the nodule bed of the Upper Greensand, concur in the belief that the nodules are not of either concretionary or coprolitic origin, but are composed of phosphatized animal matter. In this belief they agree with the theory of Dr. Mantell in its most important point.

Many of the nodules are traversed by shrinkage cracks and wrinkles and have a peculiar granulated surface like that of leather. Mr. O. Fisher says:

On the whole a microscopical examination of these bodies rather recalls me, so far, to my original opinion that they were sponges, while at the same time it must be admitted that in their external appearance they much resemble *Alcyonaria*.

It is often found that the nodules are richer in their exterior part than in the interior. Thus Professor Way found the following results in analyzing different parts of a spongoid body:<sup>3</sup>

Exterior.....	{ 32.27 per cent. phosphate of lime.
	{ 61.71 per cent. carbonate of lime.
Intermediate.....	{ 13.87 per cent. phosphate of lime.
	{ 67.14 per cent. carbonate of lime.
Interior.....	{ 10.26 per cent. phosphate of lime.
	{ 67.17 per cent. carbonate of lime.

Such results have been found to hold true with many other phosphates and show, beyond a doubt, that the phosphatization went on from the outside towards the interior. As regards the internal structure of some of these nodules, Mr. Sollas says:<sup>4</sup>

Thin sections examined under the microscope vary from colorless to yellowish brown when transparent, but sometimes they are almost opaque from included earthy

<sup>1</sup> Medals of Creation, vol. 1, p. 432.

<sup>2</sup> Quart. Jour. Geol. Soc., vol. 29, London, 1873.

<sup>3</sup> Jour. Roy. Agric. Soc., 1848.

<sup>4</sup> Quart. Jour. Geol. Soc., vol. 29, London, 1873.

matter. Granular patches of a deep-red color are sometimes scattered throughout the lighter-colored portions. Spicules occur in many sections, presenting some of the most characteristic forms of sponge-spicules; as, for example, hexaradiate, triradiate, hamate, sinuate, and connecting forms. These spicules are frequently grouped together in a manner which seems to indicate that they cannot have been washed in from the sea bed during fossilization. Globular bodies  $\frac{1}{400}$  inch in diameter are numerous; they seem to be gemmules. *Polycistina* and *Xanthidia* occur in some sections. With polarized light the sections appear distinctly cryptocrystalline, presenting an appearance very nearly resembling that of chalk flints when examined in the same way. A very curious phenomenon may be alluded to here. A number of small circles may be seen in some sections, each of which is marked by a black cross, the arms of which radiate from the center to the circumference. On turning the analyzer the cross revolves and, when the analyzer has been turned round 90°, is replaced by a complementarily illuminated cross. The explanation of these appearances seems to be as follows: Small *Globigerina* shells and other similar spaces occur in the nodules, into which the crystalline apatite, which was diffused throughout the fossil, has penetrated and crystallized inwards from their walls to their centers, thus forming a radiating mass of crystals. It is well known that crystals arranged in this way will produce the phenomena described.

Mr. Sollas<sup>1</sup> thinks that many of the nodules of the Upper Greensand are phosphatized sponges. Others he considers to be "phosphatized animal matter decomposed so far as to have lost all traces of its original structure before mineralization." He found fish scales and bones in many of these nodules, and therefore concludes that the animal matter was sometimes derived from small fish. He does not seem to take into consideration that the scales and bones may have been buried in a matrix of calcareous matter, and that this substance, whether it was marl or limestone, may have been phosphatized, thus forming phosphatic masses, which, of course, would contain the same fossils as the original calcareous substance from which they were formed.

The phosphate bed of the Upper Greensand varies considerably, not only in the quantity of phosphatic nodules, but also in the chemical composition of the individual nodules. It is often found that two places may be equally rich in the quantity of nodules, while the content of phosphoric acid in them may be widely different.

All through the counties of Dorset, Somerset, Wilts, and Devon the nodules are very much more siliceous and less abundant than the nodules of Cambridgeshire and Bedfordshire.<sup>2</sup> Besides the variability in the phosphatic richness of the bed, it is also sometimes very variable in its mode of occurrence. At times it will cover many square miles continuously, while at others it occurs in pockets in the surface of the Gault. At other times, according to Mr. Fisher, the bed shows signs of contortion, as indicated in Fig. 34. It will be seen, by examining the analyses given beyond, that the Greensand matrix of the phosphatic nodules varies also very much in its content of phosphoric acid. The

<sup>1</sup> Quart. Jour. Geol. Soc., vol. 28, 1872, p. 398.

<sup>2</sup> L. Jenyns: Geol. Mag., London, 1866.

amount varies from 2 to 10 per cent., and is probably due to small grains of phosphatic matter in it.

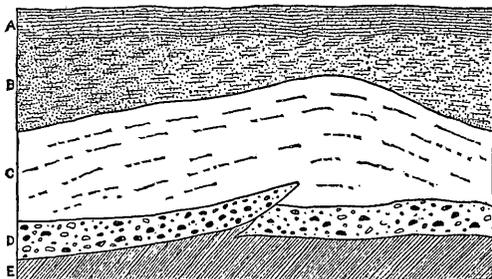


FIG. 34. Distorted bed in Cambridgeshire, England; after O. Fisher: *Geological Magazine*, London, 1871. A, shelly soil; B, clay or clayey gravel; C, white clay; D, phosphate nodule bed; E, Gault.

*Phosphatic beds of Cretaceous Lower Greensand.*—These beds occur between the Coral Rag formation at the base and the Gault on the top. Their position with regard to these formations will be best seen in Fig. 35, section at Upware, Cambridgeshire.<sup>1</sup> The Coral Rag is a coralline rock varying much in texture, sometimes loose and porous, and at others compact and oölitic or arenaceous. Upon this the Kimmeridge Clays rest, probably conformably.<sup>2</sup> But at some places, as at Upware, the Kimmeridge Clay has been washed off the Coral Rag, which, in such cases, often comes into direct contact with the overlying nodule bed. Sometimes, as a result of this destruction, there is a deposit of fragments of Coral Rag and Kimmeridge Clay immediately overlying the Coral Rag formation.

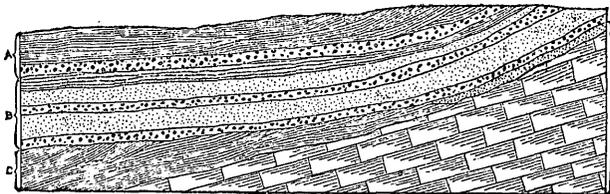


FIG. 35. Section at Upware, Cambridgeshire; after W. Keeping. A, Gault and phosphatic nodule beds; B, clay, sand, and nodule beds; C, Kimmeridge Clay and Coral Rag; D, junction bed.

Next in an ascending series comes the "lower phosphate bed." Mr. Keeping considers this as the first definite bed of the Upware Neocomian. It consists of a mass, indiscriminately mixed together, of phosphatic nodules and shell casts, fossils, pebbles of quartz, flint, Lydian stone, and jasper, besides occasionally a fragment of Coral Rag. They are all more or less rounded and worn, though some of them still preserve their angular shape. The stones and nodules vary from one-

<sup>1</sup>The Fossils and Palæontological Affinities of the Neocomian Deposits of Upware and Brickhill, by Walter Keeping, p. 4.

<sup>2</sup>Ibid., p. 3.

sixteenth to an inch in diameter and are embedded in a sandy matrix. Very often the mass has been cemented together by calcareous matter, forming irregular patches of conglomerate. There also occur in this bed many delicate and beautiful shells of mollusca, which are not at all worn, but preserve their most delicate parts intact. Lamelli-branches and gasteropods are numerous.

Above this bed comes a bed of sand composed largely of grains of ironstone, quartz, chert, and Lydian stone. Near the overlying and underlying beds there are irregular masses of slightly phosphatic sandstone.

Next above this sand bed comes the "upper phosphate bed." It resembles the "lower phosphate bed" in most respects, except that its nodules are of a lighter color, and the bed is not cemented by carbonate of lime, so that it has nowhere been indurated into a conglomerate. The siliceous pebbles are the same.

Overlying this is another bed of sand very similar to the lower sand bed.

Above this comes a clay bed. It has been referred to the Gault, but Messrs. Keeping and Bonney think that it is probably the representative of a bed of sandy clay belonging to the Lower Greensand. This is thought more likely, because phosphatic nodule beds, especially in the Cretaceous formation, usually occupy the lines of chronological breaks.

The overlying bed is another bed of phosphatic nodules. It contains many fossils and is very similar to the two nodule beds already described. This bed is overlaid by the Gault formation.

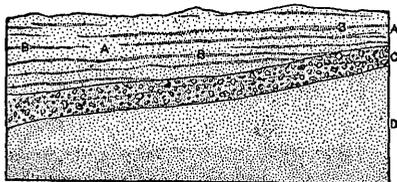


FIG. 36. Section at Sandy, Bedfordshire, England, after J. F. Walker. A, sand; B, oxide of iron; C, conglomerate; D, sand.

Sometimes the three phosphate beds mentioned above seem to combine into one (Fig 36). Sometimes, also, the lower bed is not cemented, but is loose and sandy, just like the upper beds. The following sections will show the variations in the upper Neocomian deposits:

*Section by W. Keeping and E. B. Tawney, at Spinney Abbey.*

		Ft. In.
A {	1. Brown surface earth .....	1 6
	2. Head of blue clay .....	0 9
	3. Irregular gravelly zone, the pebbles being mostly flints and coprolites, about .....	0 3

	Ft. In.
4. Blue, yellow, and coarsely mottled plastic clay, with scattered coarse quartz and other sand grains and numerous sandy concretions.....	2 0
5. The "silt bed," a chocolate-brown and yellowish sand, passing into a sandy clay, which is rather coarse, loose, and like an ordinary shore sand. It consists principally of quartz and iron grains. This bed passes gradually into bed 4 .....	2 0
B { 6. The "upper coprolite seam," a pebble bed of phosphatic nodules, Lydian stone, chert, quartz, and other pebbles as big as beans packed in loose, iron-colored sand. Some iron concretions occur in its upper part, where it passes into bed 3.....	2 0
7. The "lower coprolite seam," a thin band where the coprolites are darker and better than in the upper seam. The sandy matrix is hardened almost to a rock by carbonate of lime, which was probably derived from the underlying bed (a).....	0 3
C { A calcareous grit of coralline age. It is a hard, gritty, bedded limestone, gray colored, with scattered large oölitic grains; no fossils seen.....	

In the last section the nodules are darkest near the base. The phosphatic and siliceous pebbles are in about equal quantities. Silicified wood, ferruginous concretions, and hard lumps of clay are numerous. The nodules contain more alumina than those of the Upper Greensand (Walker).

The nodules proper of the phosphate beds are of a very variable character, in which respect they resemble the nodules of North and South Carolina. They vary in size from pieces no larger than a grain of sand to masses weighing 3 or 4 pounds. They give off an organic smell when rubbed, have a cubic fracture, and vary from yellow to chocolate brown in color. Their hardness is 3 to 4. The darker nodules are near the bottom of the bed; though, in most cases, the color depends on the substance originally phosphatized (Keeping). The nodules sometimes are of a perfectly homogeneous and opal-like nature. From this they go through all stages of sandiness, till they are simply nodules of phosphatic sandstone. Keeping, in describing them, says:

There are certain curious branching, interlacing, undulating, or simply straight-crossing structures forming little gutters over the surface of the nodule, and canals penetrating into its substance. \* \* \* Some of these are mere shrinkage cracks and others are the marks of where "episites," such as *Serpula* and *Polyzoa*, have been attached to the inner surface of the original shell; others again are probably the work of boring creatures, especially sponges, but the great variety and many peculiarities of type that occur and their constant association with phosphatic nodules are facts not sufficiently explained by the accumulated work of all the above-mentioned agents.<sup>1</sup>

These nodules are not so rich in phosphate of lime as those of the Upper Greensand; they average 40 to 50 per cent. (Völcker), while those above the Gault average 50 to 60 per cent., phosphate of lime (Way). (See analyses.)

<sup>1</sup> This exactly describes the surface of many of the phosphatic nodules of the Alabama Cretaceous formation.

Most of the fossils in these Lower Greensand phosphate beds have been derived from older formations. They are rolled and worn to such an extent that it is frequently impossible to identify them. Keeping, in speaking of the piles of phosphatic material at the mines, says, that "the coprolite heap looks like one mass of *Ammonites biplex*, mostly worn and fragmentary." The fossils are mostly worn species of mollusca of Oxfordian, Kimmeridgean, or Portlandian species of the Upper Jurassic (W. Keeping). Many of the derived species are of the Neocomian age, such as *Ammonites Deshayesi*, *Ancyloceras* sp., *Hamites* sp., *Thetis minor* Sowerby, *Terebratula ovooides* Sowerby, and other forms.

Thus it will be seen that these latter fossils have been derived from a bed but very little older than the nodule bed, as this latter deposit belongs, according to J. F. Walker,<sup>1</sup> to the Upper Neocomian formation. Mr. Walker<sup>2</sup> also thinks that a large number of the derived fossils came from the underlying Kimmeridge Clay. Many of the fossils of the Upware nodule bed are preserved in amorphous or crystalline calcite, others in ferruginous sandstone and phosphate of lime. The fossil wood is silicified. According to W. Keeping, all the shell casts and fossils that have been mineralized by phosphate or limonite are derived fossils and belong mostly to Jurassic species. They are easily recognized by their rolled and water-worn condition. Walker divides the fossils into (a) indigenous fauna, preserved in oxide of iron, and (b) derived fossils, preserved in phosphate of lime. H. G. Seeley, on the other hand, thinks that all these fossils are natives of the beds in which they are found.

As regards the mode of phosphatization of these beds, Walker, Keeping, Teall, and others agree in the theory that it is the result of the soaking of calcareous substances in decomposed animal and vegetable matter. The Coral Rag fragments in the bed are not at all phosphatized. In this particular the deposit resembles those of Alabama and the Carolinas, where shells perfectly free from phosphatic matter are associated with beds of highly phosphatic nodules and fossils. This would seem to show that the non-phosphatic substances were deposited after the nodules had been phosphatized. But Dr. C. U. Shepard, jr.,<sup>3</sup> and W. Keeping explain the phenomenon by supposing that the purer forms of carbonate of lime are not so susceptible to phosphatization as the impure forms.

A very distinctive feature between the Upper and Lower Greensand phosphate deposits is the nature of the matrix of the nodules in the two formations. As has been already said, the matrix of the Upper Greensand is a calcareous Greensand containing 2 to 10 per cent. of phosphoric acid, while the matrix of the Lower Greensand nodule beds

<sup>1</sup> Mon. Fossil Trigonias, Pubs. Palæontographical Soc., vol. 29, 1875, p. 145.

<sup>2</sup> Annals Mag. Nat. Hist., 1866.

<sup>3</sup> South Carolina Phosphates.

is a highly siliceous sand, containing no phosphate, except where the nodules have been decomposed. The siliceous pebbles of these lower beds are of very general distribution. They are found all along the Lower Greensand outcrop in England at Upware, Sutton, Brickhill, Farrington, and other places, also in the Neocomian strata at Schöpenstedt, in Brunswick. Many of these pebbles are fossiliferous.

Mr. Keeping<sup>1</sup> found in some chert pebbles many shells and crinoids of the Carboniferous age. In others he found many Jurassic shells and echinoderms. He thinks most of the pebbles were derived from an ancient barrier axis, which, in the Lower Neocomian period, separated the north from the south Neocomian seas in Europe, but "which was in the time of the deposition of the iron sand series suffering rapid denudation and destruction."

The Lower Greensand phosphate beds have numerous outcrops in Surrey, Sussex, and Kent. They are, however, thought by W. Keeping not to be of the same age as the beds of Cambridge and Bedford, but to belong to the Sandgate and Hythe series.

*Tertiary phosphate beds.*—The Tertiary phosphate deposits occur in or directly under the various Crag formations of Norfolk, Suffolk, and Essex, but are richest and most extensive in the county of Suffolk. The Crag of Suffolk and Norfolk runs along the coast from about 5 miles northwest of Kromer, in Norfolk, for a distance of 70 to 80 miles to Hardwick, in the northern part of Essex. This belt is from 7 to 22 miles wide, being widest in the neighborhood of Norwich and narrowest at Halesworth, in Suffolk. Beyond these limits the Crag often occurs in patches in the county of Essex. The Suffolk and Norfolk Crag does not extend all over the above mentioned area, but in many places it is covered by alluvium, and in others, especially in Essex and in the south of Suffolk, it has been removed by erosion, and the London clay crops out.

It is in the county of Suffolk, and especially in the district between the rivers Orwell, Deben, and Alde, and in the country surrounding the central mass of Coralline Crag at Sutton, that the Tertiary phosphate beds have been most successfully and profitably worked. The Crag formation of this country is composed largely of the Coralline and Red Crag. These formations are each separable into two divisions. Prof. J. Prestwich<sup>2</sup> has divided the Coralline Crag into the upper part, consisting mostly of remains of Bryozoa, and the lower part, consisting of light-colored sand with many shells mixed in with it. The two beds together are rarely over 20 feet thick, and rest on the London Clay (Eocene). The Red Crag consists of irregularly stratified sands stained with oxide of iron. It comes above the Coralline Crag, though in most

<sup>1</sup> The Fossils and Palæontological Affinities of the Neocomian Deposits of Upware and Brickhill, 1883.

Quart. Jour. Geol. Soc. London, vol. 27, 1871.

cases it rests directly on the London Clay, the Coralline Crag having been eroded. The two divisions of the Red Crag are often very difficult to distinguish. The only difference is that the lower division usually has more shells scattered through it. According to Professor Prestwich, the lower division includes all the beds going under the name of red and Norwich Crag, while the upper division includes the Chillesford sands and clays. Both the Coralline and the Red Crags belong to the Upper Pliocene period and are of the same age as the Upper Antwerp Crag.<sup>1</sup>

The phosphate beds occur at the base of the Coralline and Red Crags and immediately over the London Clay. The bed sometimes thins out, and at other times it separates into two seams, divided only by a few feet of shelly crag. Occasionally, also, nodules, and seams of nodules, are found running through all parts of the Red Crag, though the bed at its base is generally the largest and most continuous. The phosphate bed consists of a mass of phosphatic nodules and shell casts, siliceous pebbles, teeth of cetacea and sharks, and many mammal bones, besides occasional fragments of Lower Greensand chert, granite, and chalk flints. There are numerous fossils and shells, *Cardium edule*, *Pectunculus glycymeris*, *Cyprina islandica*, and other forms. The bed varies from 2 to 18 inches in thickness. The nodules vary considerably in both quality and quantity. They are at times of a compact and brittle nature, while at others they are tough and siliceous. They average about 53 per cent. phosphate of lime and 13 per cent. phosphate of iron. The quantity of bones in the beds also varies very much. Sometimes there are few and at other times there are great quantities of mastodon and rhinoceros teeth and bones of other mammals, similar in some respects to those at Eppelsheim in Germany.<sup>2</sup> Large cetacean bones and teeth of *Charcharodon* and *Oxychina* are also found. There is considerable dispute concerning the origin of the fossils and nodules in the phosphate beds of the Crag. That most of them are derived masses is shown by their worn and rounded condition. Mr. Jenyns<sup>3</sup> believes that they have come from the London Clay, and in support of this view he calls attention to the similarity of the nodules of the two formations. Professor Prestwich<sup>4</sup> thinks that most, if not all, of the nodules of the Red Crag came from the Coralline Crag.

The phosphate deposits of Norfolk are few and scattered. Most of the phosphatic material from this county is in the form of mastodon, elephant, and rhinoceros bones from the forest and elephant beds. None of the Crag phosphate beds have proved so valuable as the Cretaceous beds. The nodules are harder and more siliceous, making them more difficult to grind and less valuable as a soil stimulant when in the un-

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<sup>1</sup> Geol. Mag., London, 1865.

<sup>2</sup> E. Ray Lankester: *ibid.*

<sup>3</sup> *Ibid.*, vol. 3, 1866.

<sup>4</sup> Quart. Jour. Geol. Soc. London, vol. 27, 1871,

acidulated state. Besides this, they contain considerable phosphate of iron, which causes a superphosphate, made from such nodules, to have a sticky consistency and to be very liable to "revert" to an insoluble condition.

The Crag nodules resemble those of the Cretaceous formation, as well as some of those of South Carolina, in the fact that the exterior part often contains more phosphoric acid than the interior. The following analyses by T. J. Herapath<sup>1</sup> illustrate this fact :

	Exterior.	Interior.
1	{ 1.105 per cent. fluoride of lime. 40.019 per cent. phosphoric acid.	{ 0.611 per cent. fluoride of lime. 34.015 per cent. phosphoric acid.
2	{ 3.996 per cent. fluoride of lime. 32.043 per cent. phosphoric acid.	{ 1.961 per cent. fluoride of lime. 21.046 per cent. phosphoric acid.

*History of the rock phosphates of England.*—The Greensand of England has been used as a fertilizer for many generations. As early as 1790 it was considered so valuable as a soil stimulant that it was carried in carts, sometimes for many miles, all over the counties of Essex and Kent. Immense pits, dug in the Greensand marl, concerning which there is no historic record and which are now overgrown by large oaks and other forest trees, bear witness to the great value placed on this marl in by-gone times. A remarkable example is seen at Worldham, where there is a large excavation 15 feet deep, from which, once, thousands of tons of greensand were removed. But the heaps of phosphatic nodules which are often found near these pits, and which seem to have been thrown away as worthless, show that the value of this part of the bed was not known.

It was not until nearly the middle of this century that the agricultural value of these nodules was appreciated. Doctors Mantel, Buckland, and Fitton, in the early part of the century, pointed out the existence of beds of nodules and fossils in the Cretaceous and Tertiary formations of England, but simply spoke of them as remarkable beds of fossils and nodules. Mr. Berthier, in 1820, also made analyses of similar nodules found in France. But their use as a plant food was not recognized until Professor Henslow made a study of the Red Crag nodules at Felixtow in 1842, and suggested their use in agriculture before the British Association in 1845. It was at this time that the name coprolite, or fossil dung, was first given to these nodules by Professor Henslow. At a later date he saw his mistake in believing the phosphatic masses to be of coprolitic origin, and considerably modified his views. It was certainly a most unfortunate name, as it has since been shown that real fossil dung is a thing of very rare occurrence, and hence the name coprolite, as applied to beds of nodular phosphates, is misleading.

Among the most active of the early advocates of English phosphates

<sup>1</sup>Jour. Royal Agric. Soc., 1851,

were J. M. Paine and J. T. Way,<sup>1</sup> who analyzed many specimens of the material and made many practical experiments, which went far to open up the phosphate mining industry in England. From that time on the use of the English phosphatic nodules became more and more extensive, until within the last few years the immense exports of phosphate of lime from South Carolina, the West Indies, and other localities have thrown so much of that material on the market that the English deposits have become a source of minor importance.

The principal mining operations are carried on in the counties of Cambridge, Bedford, and Suffolk. According to O. Fisher,<sup>2</sup> writing in 1873, the miners in Cambridge had to pay \$700 per acre for the right to dig phosphate and had to return the land to its original level condition and re-soil it. With all this expense the average yield was only 300 tons per acre, which sold at \$12 a ton; while in the South Carolina diggings the yield is 300 to 1,500 tons per acre and it sold, at that time, for \$9 a ton. The nodules in England were dug to the depth of 20 feet, but it did not pay to go any deeper.

Dr. C. U. Shepard, jr., informs me that he visited the diggings at Whaddon, near Rowsley, in 1875. They were then working at the depth of 8 to 18 feet, all the surface beds having been exhausted. Sums from \$500 to \$1,250 per acre were paid for the right to take the rock, and the yields per acre were from 150 to 400 tons. The mining was done in open trenches. The phosphate rock was washed in circular horizontal tubes and was kept moving by rakes worked by steam. The capacity was about 5 tons daily, and the cost of washing about 85 cents a ton. Wages were \$6 a week. The nodules were sun-dried and then carted to the railroad for 50 cents per ton.

The production for the three counties of Bedford, Cambridge, and Suffolk from 1875 to 1881 is given as follows:<sup>3</sup>

	Tons.
1875 .....	250,000
1876 .....	258,000
1877 .....	69,000
1878 .....	54,000
1879 .....	34,000
1880 .....	30,000
1881 .....	31,500

*Analyses of the amorphous nodular phosphates of England.*

[I. "Molluskite," from the Upper Greensand, by M. Berthier.]

Phosphate of lime .....	57.00
Carbonate of lime .....	7.00
Carbonate of Magnesia .....	2.00
Silicate of iron and alumina .....	25.00
Water and bituminous matter .....	7.00
	98.00

<sup>1</sup> Jour. Royal Agric. Soc., 1848.

<sup>2</sup> Quart. Jour. Geol. Soc. London, vol. 29, 1873.

<sup>3</sup> Mineral Statistics of the United Kingdom, by Robert Hunt, F. R. S. (From D. C. Davies, Earthy and Mineral Mining, London, 1884.)

## [II. Phosphate from the Upper Greensand, at Dippen Hall (Way).]

Insoluble siliceous matter .....	9.84
Soluble silica .....	2.36
Phosphoric acid .....	27.60
Equal to bone earth phosphate, 59.60.	
Carbonic acid .....	6.96
Lime .....	44.56
Magnesia and loss .....	0.81
Oxide of iron and alumina .....	4.61
Organic matter .....	3.26
	<hr/>
	100.00

## [III. Fossil sponge, a branching Alcyonite from the Upper Greensand (Way).]

Insoluble siliceous matter and soluble silica .....	7.68
Phosphoric acid .....	29.87
Equal to bone earth phosphate, 61.30.	
Carbonic acid .....	8.77
Lime .....	42.29
Oxide of iron and alumina .....	6.87
Water, organic matter, fluorine and loss .....	4.52
	<hr/>
	100.00

## [IV. Red nodule from the Upper Greensand, at Dippen Hall (Way).]

Insoluble siliceous matter, with a little clay .....	7.18
Soluble silica .....	3.28
Organic matter .....	2.49
Phosphoric acid .....	27.13
Equal to bone earth phosphate, 55.96.	
Carbonic acid .....	8.77
Lime .....	39.85
Magnesia .....	0.96
Oxide of iron and alumina .....	10.60
Fluorine .....	Trace
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	100.26

## [V. Phosphatic nodules from the Upper Greensand (Völcker).]

Moisture and organic matter .....	4.68
Lime .....	43.21
Magnesia .....	1.12
Oxide of iron .....	2.46
Alumina .....	1.36
Phosphoric acid .....	25.29
Carbonic acid .....	6.66
Sulphuric acid .....	0.76
Chloride of sodium .....	0.09
Potash .....	0.32
Soda .....	0.50
Insoluble siliceous matter .....	8.64
Fluoride and loss .....	4.96
	<hr/>
	100.05

## [VI. Upper Greensand from Dippen Hall (Way).]

	Coarse part.	Fine part.
Insoluble siliceous matter .....	21.85	26.25
Soluble silica .....	20.18	13.11
Organic matter .....	6.25	5.95
Phosphoric acid .....	7.80	10.38
Carbonic acid .....	10.91	10.34
Lime .....	20.58	19.87
Magnesia .....	1.59	0.87
Oxide of iron and alumina .....	8.18	6.18
Potash and soda, not estimated.....		
	<hr/>	<hr/>
	97.34	97.95

## [VII. Upper Greensand from Dippen Hall (Way).]

	Coarse part.	Fine part.
Insoluble siliceous matter .....	26.83	32.81
Soluble silica .....	26.30	29.14
Organic matter .....	2.64	3.02
Phosphoric acid (1) .....	9.31	6.61
Carbonic acid .....	2.35	2.30
Lime .....	15.24	9.53
Magnesia .....	1.43	1.97
Oxide of iron and alumina .....	13.11	11.46
Potash .....	Not est.	3.10
Soda .....	Not est.	0.00
	<hr/>	<hr/>
		99.94
(1) Equal to bone earth phosphate.....	19.22	.....
(1) Equivalent of earthy bone.....		13.63

## [VIII. Cambridgeshire glauconite (Professor Liveing).]

Water .....	10.80
Silica .....	51.09
Alumina.....	9.00
Iron (protoxide) .....	19.54
Magnesia.....	3.37
Lime .....	0.30
Soda .....	3.56
Potash .....	2.47
	<hr/>
	100.13

## [IX. Phosphate nodules from Lower Greensand (Way).]

Insoluble siliceous matter .....	43.87
Soluble silica .....	3.25
Organic matter, water, and fluorine .....	3.44
Phosphoric acid.....	20.80
Equal to bone earth phosphate, 42.48.	
Carbonate of lime.....	1.06
Lime in combination with phosphoric acid.....	23.86
Oxide of iron and alumina .....	3.35
Magnesia and loss.....	0.37
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	100.00

## [X. Phosphatic nodule from Lower Greensand (Way).]

Silica and sand .....	13.64
Sulphate of lime .....	50.16
Water in combination .....	14.97
Water (accidental) .....	7.47
Phosphoric acid .....	4.80
Lime, additional .....	0.27
Oxide of iron and alumina .....	8.82
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	100.13

From the above analysis it will be seen that most of the phosphoric acid must have been in combination with iron and alumina.

## [XI. Large green grains from a Lower Greensand phosphatic conglomerate (Way).]

Soluble and insoluble siliceous matter .....	18.53
Water .....	2.28
Phosphoric acid .....	20.65
Carbonic acid .....	4.01
Sulphuric acid .....	5.13
Lime .....	34.61
Oxide of iron .....	7.24
Alumina .....	0.98
Potash .....	1.79
Soda .....	1.87
	<hr/>
	97.09

## [XII. Lower Greensand nodules (Völcker).]

	Average samples of siftings from layers at 1 and 2 feet.	Washed rock from another place.
Water of combination .....	5.17	5.67
Phosphoric acid .....	<sup>1</sup> 22.39	<sup>2</sup> 15.12
Lime .....	32.73	26.69
Magnesia, alumina, and fluorine (by difference) .....	6.64	4.51
Carbonic acid .....	3.06	<sup>2</sup> 2.18
Oxide of iron .....	<sup>1</sup> 18.08	20.61
Siliceous matter .....	21.93	25.22
	<hr/>	<hr/>
	100.00	100.00

## [XIII. Partial analysis of phosphatic conglomerate, Lower Greensand, from Folkstone, by Way].

Insoluble siliceous matter .....	30.60
Phosphoric acid .....	7.23
Potash .....	3.31
Soda .....	1.02

## [XIV. Lower Greensand mass, from which the principal fossils and nodules were picked, by Way.]

Insoluble siliceous matter .....	75.46
Soluble silica .....	8.12
Organic matter .....	2.30
Phosphoric acid .....	0.64

<sup>1</sup> Phosphate of lime, 48.51; carbonate of lime, 6.95.

<sup>2</sup> Phosphate of lime, 32.76; carbonate of lime, 4.95.

Carbonic acid.....	5.64
Lime.....	2.01
Magnesia.....	0.18
Oxide of iron and alumina.....	5.59
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	99.94

*Analyses of crag phosphates.*

These average 50 to 60 per cent. phosphate of lime (Way).

## [I. Phosphate from the crag at Surrey, by Herapath.]

Water.....	3.400
Organic matter.....	Trace
Silica with some silicate of alumina and silica of iron.....	13.240
Chloride of sodium.....	Trace
Sulphate of soda.....	Trace
Carbonate of lime.....	28.400
Carbonate of magnesia.....	Trace
Sulphate of lime.....	0.736
Phosphate of lime (tribasic).....	21.850
Phosphate of magnesia.....	Trace
Perphosphate of iron.....	24.760
Phosphate of alumina.....	6.998
Phosphate of manganese.....	Trace
Fluoride of calcium.....	Some
Loss.....	0.586
	<hr/>
	100.000

## [II. Partial analysis of three Suffolk nodules, by Herapath.]

Earthy and other phosphates.....	64.056	79.545	67.176
Fluoride of calcium.....	0.311	2.554	2.768
Nitrogen.....	Traces	0.0314	Undet.

## [III. Crag nodules from coast of Suffolk (Herapath).]

Water with a little organic matter.....	4.000	3.560
Salts soluble in water (chloride of lime and sulphate of soda).....	Trace	Trace
Silicic acid, colored red by a little undecomposed silicate of iron.....	5.792	6.309
Carbonate of lime.....	10.280	8.959
Sulphate of lime.....	Distinct trace	0.611
Phosphate of lime (tribasic).....	70.920	69.099
Phosphate of magnesia.....	Trace only	Trace
Perphosphate of iron.....	6.850	8.616
Phosphate of alumina.....	1.550	2.026
Oxide of manganese.....	Trace	0.016
Fluoride of calcium.....	0.608	0.804
	<hr/>	<hr/>
	100.000	100.000
	<hr/>	<hr/>
Nitrogen.....	.0254	Undet.

## [IV. Suffolk crag phosphate (Herapath).]

Water driven off at from 300°-350° F.....	2.600
Water and organic matter, expelled at a red heat.....	9.000
Chloride of sodium, etc.....	Evident trace

Carbonate of lime.....		39.500
Carbonate of magnesia.....		0.520
Sulphate of lime.....	Distinct trace	
Phosphate of lime.....		15.860
Phosphate of magnesia.....	Trace	
Perphosphate of iron.....		9.200
Phosphate of alumina.....		4.708
Peroxide of iron.....	None	
Alumina.....		6.212
Fluoride of calcium.....		1.698
Silicic acid.....		10.601
		99.899

## [V. Suffolk phosphate nodules, by Herapath.]

Water and organic matter.....	7.200	9.210
Chloride of sodium and sulphate of sodium.....	Trace	Trace
Carbonate of lime.....	18.514	5.176
Carbonate of magnesia.....	0.855	2.016
Sulphate of lime.....	Some	1.161
Phosphate of lime.....	51.018	45.815
Phosphate of magnesia.....	Trace	Trace
Perphosphate of iron.....	8.902	12.476
Phosphate of alumina.....	2.700	6.387
Oxide of manganese.....	0.057	0.267
Peroxide of iron.....		
Alumina.....		
Fluoride of calcium.....	3.161	2.688
Silicic acid and loss.....	7.593	14.804
	100.000	100.000
Nitrogen.....	0.0289	0.0198

## PHOSPHATES OF BELGIUM.

The phosphate deposits of Belgium belong to the upper part of the Cretaceous formation. They are mined almost exclusively in the province of Hainaut, which is the southern part of the kingdom, and borders on the French province of Aisne. The following section will show the general geologic relations of the phosphate beds of this region:

Tufeau de Ciply (Ciply Marl) <sup>1</sup>	}	Craie de
Poudingue de Ciply (Ciply Conglomerate)		Maëstricht
Craie Grise ou Brune (Brown or Gray Chalk)		(in part).
Craie Blanche (White Chalk).		

The top bed, Tufeau de Ciply, is a soft, coarse-grained, calcareous rock of a white or light yellow color. It crops out in numerous places in the communes of Cuesmes, Hyon, Ciply, and Mesvin, and rests unconformably on the underlying beds. In Cuesmes it comes in direct contact with the White Chalk (Craie Blanche), but in Ciply and Mesvin it is separated from it by a considerable thickness of intervening strata,

<sup>1</sup> In his recent memoir (Quart. Jour. Geol. Soc. London, pp. 325-340, 1886) Mr. Cornet expresses the opinion "that the Brown Phosphatic Chalk of Ciply and the Chalk of Spiennes should be regarded as forming together one geological whole, a peculiar stage of the Belgian Cretaceous series."—N. S. S.

as shown in the section above. Immediately under the Tufeau comes the Cibly Conglomerate. This is a denudation deposit, and is known as the Poudingue de Cibly, or Poudingue de la Malogne.<sup>1</sup> In some places it immediately overlies the White Chalk, as in the neighborhood of Cibly, and at others it is separated from it by a very variable thickness of Gray or Brown Chalk. The Conglomerate consists of a mass of phosphatic nodules, shell casts, and fossils, cemented by a calcareous matrix. Sometimes the bed is cemented into a solid mass, and again it is loose, and easily worked with pick and shovel. There are numerous shells and remains of gasteropods, lamellibranchs, brachiopods, sea-urchins, and sponges. There are, also, many teeth and vertebrate bones of fish and sharks, all much worn and rounded, showing clearly that they have been changed from the bed in which they were originally deposited. *Belemnitella mucronata* and *Ostrea vesicularis* are among the common forms found in the bed.<sup>2</sup> The nodules vary from a quarter of an inch to 5 inches in diameter, and are generally of a brown color. They contain a small quantity of phosphate of lime (25 to 50 per cent.) compared with that of American and English phosphates, which rarely run under 55 per cent. and 50 per cent. of phosphate, respectively. When ground and heated in a dark room the Cibly phosphate shows the same phosphorescence as the Spanish phosphorite, but in a less degree. The nodule bed is very continuous at the base of the Tufeau de Cibly,<sup>3</sup> but is generally in such a thin sheet that it does not pay to work it. Occasionally, however, it has been collected in pockets on the surface of the underlying bed, to such an extent that it has been mined with profit. Such is the case in Cuesmes and Cibly, where openings have been made and large quantities of phosphate taken out. The thickness of the bed is very variable, ranging generally from a few inches to 3 feet. The underlying bed is much worn and eroded on the top.<sup>4</sup>

It is from the bed immediately underlying the Cibly Conglomerate that over nine-tenths of the phosphate now mined in Belgium is obtained. This bed is known as the Craie Grise or Craie Brune, and comes between the Cibly nodule bed and the White Chalk (Craie Blanche). It is of a very variable thickness, being in some places entirely eroded, so that the Cibly Conglomerate comes in direct contact with the White Chalk. At other localities it reaches a very considerable thickness, as near the town of Cibly, where it is 30 meters deep. The bed consists of a coarse-grained rock, easily crumbled in the fingers, softer at the top than at the bottom, and of a gray or brown color. It is formed of a mixture of grains of carbonate of lime and small pebbles of phosphate of lime, about the size of a pin head. The proportions of the two constituents

<sup>1</sup> Cornet and Briart: Bull. Acad. roy. Belgique, 2d series, vol. 37, 1844, pp. 338, 844.

<sup>2</sup> F. L. Cornet: Bull. Soc. géologique France, 3d series, vol. 2, 1874, p. 570.

<sup>3</sup> Mr. Melsens: Bull. Acad. roy. Belgique, 2d series, vol. 38, 1874, pp. 25-52.

<sup>4</sup> F. L. Cornet: Bull. Soc. géologique France, 3d series, vol. 2, 1874, pp. 567-577.

are about 25 to 30 per cent. of grains of carbonate of lime, and 70 to 75 per cent. of phosphatic pebbles. The phosphate grains are equally plentiful all through the upper 10 feet of the bed, but below this they begin to grow scarcer and scarcer, until the bed gradually runs into the White Chalk (Craie Blanche). In this lower bed no phosphatic nodules are found, but in their place there occur beds of brown, siliceous nodules lying between the strata. The overlying phosphate bed (Craie Grise or Craie Brune) is a regularly stratified deposit and dips gently to the northwest.

The phosphate grains were at first thought to be glauconite which had been turned brown by weathering. They are of a brown color and are very porous. When exposed to the action of heat for some time they become crumbly and very easy to grind. This is explained by Mr. Nivoit<sup>1</sup> as being caused by the decomposition of the animal matter in the nodules. The specific gravity is 1.80 to 2.90. The phosphatic bed runs in a band of several hundred meters' breadth, through Cuesmes, Hyon, Cibly, Mesvin, Nouvelles, and Spiennes, all in the province of Hainaut. Estimating the surface of the belt as 180 hectares (444.78 acres), and supposing that mining can be carried on to a depth of 8 meters, there would be 14,500,000 cubic meters of workable rock in the place.<sup>2</sup>

The upper part of the phosphate bed averages 11.50 per cent. of phosphoric acid (see analyses p. 107). A large part (50 to 55 per cent.) is composed of carbonate of lime. Numerous methods have been tried to separate the phosphate from the matrix. Treating the mass with hydrochloric acid<sup>3</sup> has been tried, in the hope of dissolving out the carbonate and leaving the phosphate untouched, but it was found that the acid attacked the phosphate at the same time as it did the carbonate. Another method is to expose the mass of nodules and matrix to the air for some time in order to allow it to disintegrate. It is then separated from a part of the associated carbonate of lime by shaking on a screen, or washing in a stream of running water, which carries off the more finely divided part of the carbonate. Sometimes the rock is ground, and a considerable part of the limestone removed by a fan. This method is, however, not as efficient as the washing process, and is only used where water is scarce. By none of these processes has the quality risen above 40 to 50 per cent. phosphate of lime.<sup>4</sup>

An examination of the analyses given will show that the freer the phosphatic grains are from the calcareous matrix, the nearer they approach in composition to the nodules of the Cibly Conglomerate.<sup>5</sup> They

<sup>1</sup> Mr. Nivoit: *Comptes rendus Acad. sci.*, Paris, vol. 79, 1874.

<sup>2</sup> Cornet and Briart: *Bull. Acad. roy. Belgique*, 2d series, vol. 37, 1874, p. 841.

<sup>3</sup> A. Petermann: *Bull. Acad. Sci. Roy. Belgique*, vol. 39, 1875, p. 31.

<sup>4</sup> According to Cornet experiments are now in progress which indicate that the proportion of phosphate may be raised to 65 per cent. See *Quart. Jour. Geol. Soc. London*, vol. 42, 1886, p. 334.—N. S. S.

<sup>5</sup> Mr. Nivoit: *Compt. Rendus Acad. sci.*, vol. 79, Paris, 1874.

resemble very much in composition the nodules of the Marnes Crayeuses in France. The Poudingue de Cibly and the underlying Craie Grise or Craie Brune combine to make a formation very similar to the phosphate conglomerate of New Hanover County, the Poudingue resembling the upper part of the New Hanover bed and the Craie Grise or Craie Brune resembling the lower part. As will be seen by referring to the description of the North Carolina bed, the upper part contains much larger nodules and is more compact than the lower part, which is of a loose texture and has nodules of more uniform composition than the upper part. The nodules of the lower part of the New Hanover bed resemble those of the Craie Grise or Craie Brune both in decreasing in quantity at a depth and in their brown color. The principal differences are that the American beds are of Tertiary age, while the Belgium beds belong to the Cretaceous period. The nodules are smaller in the Chalk beds than in the lower part of the New Hanover beds, while the nodules of the Cibly Conglomerate are apt to be larger than those of the upper New Hanover bed. Also, the nodules of the upper part of the New Hanover beds are of more variable physical and chemical character than those of the Cibly Conglomerate.

The phosphates of the Cibly Conglomerate bed were discovered as early as 1858 by Mr. Lehardy de Beaulieu,<sup>1</sup> and were described again in 1866 by Messrs. Cornet and Briart.<sup>2</sup> But it was not until 1873 when Messrs. De Cuyper and Gendebien and Mr. Desailly opened mines, that the phosphates of Belgium were worked.

The phosphates of the Craie Grise were discovered in 1873 by Messrs. Cornet and Briart,<sup>3</sup> and since that time they have been almost the only beds worked, as they have proved more profitable than the Conglomerate bed. The mining is generally done in open trenches, though shallow shafts are sometimes sunk, and horizontal galleries are run in from the sides for a distance of 10 to 12 meters.

<sup>1</sup> Mémoires et Pub. Soc. sci. Hainaut, 2d series, vol. 7, 1860.

<sup>2</sup> Bull. Acad. Roy. Belgique, vol. 22, 1866.

<sup>3</sup> Bull. Acad. Roy. Belgique, vol. 37, 1874.

NOTE.—As this report is going to press I have received a memoir of Mr. F. L. Cornet, published in the Quarterly Journal of the Geological Society of London, August 2, 1886, pp. 325-340, entitled "On the Upper Cretaceous series and the Phosphatic beds in the neighborhood of Mons (Belgium)." This valuable memoir contains some important information concerning the geological and economic history of the region about Mons. The most important points are summarized below:

*Production of the Mons district in English tons.*

Year.	Tons.	Year.	Tons.
1877 .....	3,850	1881 .....	29,528
1878 .....	5,630	1882 .....	40,043
1879 .....	7,578	1883 .....	58,660
1880 .....	15,500	1884 .....	85,000

The most important points set forth in this contribution concern the circumstances which have led to the formation of the phosphates of the Mons district. The author

*Analyses of the amorphous nodular phosphates of Belgium.*

[I. Ciply Conglomerate nodules (A. Petermann, Bull. Acad. roy. Belgique, vol. 39).]

Water and organic matter .....	6.39
Carbonate lime .....	40.55
Phosphate lime (21.82 phosphoric acid) .....	47.63
Sulphate lime.....	3.19
Silica.....	0.31
Magnesia (chlorine and alkalies not determined).....	1.93
	100.00

[II. Nodules (Nivoit, Assoc. franç. avanc. sci., 1875).]

Constituents.	From Perthes, at base of Craie Blanche.	From Ciply Conglomerate.	Craie Grise (whole mass, nodules and matrix).
Loss by calcination (1).....	25.10	25.55	31.00
Sand and clay.....	1.65	1.30	2.10
Oxide of iron .....	1.20	0.90	1.10
Lime .....	50.89	51.60	54.00
Phosphoric acid (2) .....	21.10	20.35	11.13
Sulphuric acid.....	.....	0.12	.....
Chlorine.....	0.14	0.25	.....
Fluorine.....	.....	0.18	.....
	100.08	100.25	99.33
(1) Equal to phosphate of lime.....	46.06	44.42	24.30
(2) Nitrogen <i>a</i> .....	0.25	0.35	.....

*a* Some of the nitrogen is in the form of ammonia salts.

clearly shows that these phosphates have been formed by the concentration of phosphatic matter originally disseminated in lime carbonate, the concentration having been effected by the action of water containing carbonic acid gas derived from decayed vegetation. Even in its somewhat concentrated form the proportion of lime phosphate is too low and that of lime carbonate too high for the material to be used in the manufacture of superphosphates. "But," says the author, "by simple mechanical processes, either by dry or wet methods, a product is obtained which contains from 40 to 50 per cent. of phosphate. Some experiments now being made lead us to hope that a proportion of 65 per cent. may be reached." These experiments in concentration have a great interest to us, for the reason that they may show the way by which the low-grade phosphates of Alabama and other parts of this country can be utilized.

The diagrams accompanying this report are of interest, as they show the relation of the phosphatic deposits to the erosive agents which have served to bring about this concentration in superficial beds.—N. S. S.

[III. Craie Brune (Nivoit, *ibid.*)]

Constituents.	Nodules and matrix mixed.	Washed nodules.
Organic matter .....	2.83	4.40
Lime .....	53.24	52.00
Magnesia .....	0.12	Trace
Alumina and oxide of iron .....	1.01	1.29
Potash and soda .....	0.19	0.28
Carbonic acid .....	23.10	24.32
Sulphuric acid .....	0.89	0.92
Phosphoric acid .....	11.66	15.19
Silica and sand .....	1.96	1.60
Chlorine and fluorine .....	Trace	Trace
	100.00	100.00

[IV. Craie Brune (Petermann, *Bull. Acad. Sci. roy. Belgique*, vol. 39, p. 34).]

	Phosphoric acid.
(a) Mass poor in phosphate grains .....	10.60
(b) Mass poor in phosphate grains .....	9.27
(c) Mass rich in phosphate grains .....	13.90
(d) Incoherent fragments .....	10.87
(e) Incoherent fragments .....	11.62
(f) Incoherent fragments .....	10.87

[V. Craie grise ou brune (Nivoit, *Assoc. française avanc. sci.*, 1875).]

Loss by calcination .....	31.00
Sand and clay .....	2.10
Phosphoric acid .....	11.13
Lime .....	54.00
Oxide of iron .....	1.10
Loss and undetermined matter .....	0.67
	100.00

## PHOSPHATES OF NORTHERN FRANCE.

The phosphates of northern France occur mostly in the provinces of Ardennes and Meuse, though they are also found in smaller quantities in other northern provinces. They are in the Cretaceous, and, like the phosphates of the English Cretaceous, appear both at the summit and base of the Gault (Gault Argileux). But there is also a third bed, which is not found in England, and which occurs immediately under the Craie Blanche, a calcareous bed corresponding to the Upper Chalk of England. The following section will show the relative positions of these beds, in descending order:

- (1) Craie Blanche ("Upper Chalk").
- (2) Marnes Crayeuses ("Chalk Marl").

- (3) Sables Glauconieux (Chloritic Marl of England).
- (4) Gaize (Upper Greensand of England).
- (5) Gault Argileux (Gault of England).
- (6) Sable Vert (Lower Greensand).

The above section can be seen in many places in the western part of the provinces of Ardennes and Meuse.

The nodule beds in the Upper and Lower Greensand resemble, in many respects, the corresponding beds in England. The Lower Greensand has a very variable thickness, sometimes running out almost entirely, and at others attaining a depth of 50 feet. It is at the base of this mass of sandy clay, colored sometimes by grains of glauconite, that the Lower Greensand phosphate bed occurs.<sup>1</sup> The nodules are rounded, worn, and mixed with many fossils and shell casts. They vary from the size of a nut to that of a man's fist. They are of a brown color, and are generally of a lighter hue on the surface than in the center. Sometimes the nodules occur loose in the sand and at others, as at Clermont and Varennes, they are cemented into a conglomerate. There are in the bed numerous shark teeth, shells, remains of crustaceans, and other fossils. The nodules often contain grains of quartz and greensand, veins or crystals of pyrite, gypsum, and sometimes of galena. There are also often associated with them concretions of pyrite, crystals of gypsum, and balls of ferruginous clay.

The French nodules resemble the English in being of a variable consistency, sometimes being very compact and glassy in appearance, and at others being so siliceous that they often, as at Beurey, look like grains of sand cemented by a little phosphate. It has already been shown that the composition of such nodules, at least so far as the relative amounts of silica and carbonate of lime are concerned, depends largely on the character of the water bottom from which the nodules were formed.

The nodule bed of the French Lower Greensand is very continuous and rarely runs out,<sup>1</sup> though it varies considerably in thickness, ranging from two to nine inches, and averaging about seven inches.<sup>2</sup> There are also nodules, more or less phosphatic, scattered through the overlying Lower Greensand, as well as through the Gault, but they are not in sufficient quantities to be of any commercial importance. The nodules and shell casts of the Gault are much more homogeneous and compact in their composition than those of the Lower Greensand.<sup>3</sup>

The next phosphate bed, in an ascending series, comes in the Upper

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<sup>1</sup> Mr. Nivoit: Assoc. franç. avanc. sci., 1875.

<sup>2</sup> The nodules contain 8.80 to 50.54 per cent. phosphate of lime and average 39 per cent.

<sup>3</sup> It will be seen that there is only one regular bed of nodules in the French Lower Greensand, while in the English formation of the same horizon there are three beds, which, however, often run into each other and form one stratum.

Greensand, or "Gaize," which is a lenticular deposit lying between the Gault beneath and the Sables Glauconieux above. It reaches its maximum thickness of 105 meters near the town of d'Antry. It runs out in the north at d'Attigny and in the south near Nettancourt. It is a more or less clayey and siliceous deposit, often containing a large amount of silica in a semi-gelatinous form. The phosphate bed lies about 50 feet from the base of this deposit, and is irregular and undulating. It is of variable thickness, ranging from two to twelve inches and averaging about five inches.<sup>1</sup> The nodules average 55 per cent. phosphate of lime and are of the same general character all through the bed. Their surface is black or dark green, and is richer in phosphate than the interior, which is often simply a mass resembling in every respect the Gaize formation surrounding the nodules. In this respect these resemble some of the English phosphates, which are often found to contain 50 per cent. of phosphate on the exterior part, while towards the interior the quantity of phosphoric acid grows less and less till, in the center of the nodule, there is a mass of marly sand or sandy marl. The fossils are very numerous and are all much rolled and worn. In the Sables Glauconieux, which overlie this bed, there are found very similar nodules. They do not, however, occur in a regular stratum, but are scattered through the formation.

The last bed of phosphate, in an ascending series, which is found in the Ardennes and Meuse Cretaceous, lies at the base of the Craie Blanche (Upper Chalk), and on top of the Marnes Crayeuses (Chalk Marl). These nodules differ considerably from the underlying phosphates. They are of a white or gray color, homogeneous in composition, and consist almost entirely of carbonate and phosphate of lime. The bed is of very little commercial importance, as it is thin, irregular, and apt to run out.

All these French Cretaceous phosphates are very soft and porous, and can absorb a large amount of water. They easily disintegrate on exposure to air, and are readily ground to an impalpable powder. In fact, those of the Marnes Crayeuses are so soft that they go to pieces while being washed, and are, therefore, not much used. The French differ from the Belgium nodules in having more siliceous matter and less carbonate of lime.<sup>2</sup>

The nodules are dug in trenches or in shafts, from which galleries thirty to forty feet long are run. They are washed by throwing them on a screen over which a stream of water is running, thus reducing the mass to from one-half to one-third of its original weight. When water is scarce they are allowed to lie exposed to the air until dry, and then shaken on a screen. Thus cleaned they retain 10 to 15 per cent. of their original matrix. They are then broken and ground.

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<sup>1</sup> Nivoit: Assoc. franç. avanc. sci., 1875.

<sup>2</sup> Mr. Nivoit thinks that the nodules were formed by a phosphatic solution coming in contact with carbonate of lime either already deposited or being deposited.

The principal phosphate mining districts are the canton Grand Pré, in Ardennes, and the cantons Clermont, Louppy-le-Château, and Villotte, in Meuse. The nodules of the Lower Greensand have been more extensively mined than the other beds, having been worked in seventy communes; while the Upper Greensand nodules are worked in twelve, and the Marnes Crayeuses in only one commune (at Sainte Marie, near Vauziers). The nodules at the base of the Craie Blanche have not been profitably worked in either Ardennes or Meuse.

The production of phosphate of lime from the north of France in 1875 was 66,000 tons, of which 41,000 came from Meuse and 25,000 from Ardennes, and 1,500 workmen were employed in washing and mining.

Following is a table<sup>1</sup> showing the cost of mining and shipping one cubic meter of nodules from the Lower Greensand, allowing 1,500 kilograms to the cubic meter. Also a table showing the expense of treating in the same way one cubic meter of Upper Greensand nodules, allowing in this case a weight of 1,600 kilograms to the cubic meter.

*Cost of mining and shipping phosphates of northern France.*

Items of expense.	Lower Green-sand.	Upper Green-sand.
	<i>Francs.</i>	<i>Francs.</i>
Cost for right to dig .....	4.00	10.00
Extraction .....	15.75	31.00
Transportation to washers and from them to mill.....	4.00	4.00
Washing .....	2.50	5.00
Grinding and putting in bags.....	9.00	10.40
Shipping (expédition).....	1.75	2.50
Extra costs (traisgénéraux).....	5.00	5.00
Total for a cubic meter.....	42.00	67.90
Total for a ton.....	28.00	42.45

*Analyses of amorphous nodular rock phosphates of northern France.*

[I. Grand Pré nodules, Upper Greensand, by Nivoit.]

Loss by calcination.....	8
Clay, sand, and greensand .....	42
Phosphoric acid.....	20
Lime .....	27
Oxide of iron.....	3

[II. Nodules from base of Craie Blanche by Nivoit.]

Loss by calcination.....	25.10
Clay and sand .....	1.65
Phosphoric acid.....	21.10
Chlorine.....	0.14
Lime .....	50.89
Oxide of iron .....	1.20

100.08

<sup>1</sup>Nivoit: Assoc. franç. avanc. sci., 1875.

## [III. Similar nodules, analyzed at the École des Mines, Paris.]

Silica.....	4.80
Alumina and oxide of iron.....	3.20
Carbonate of lime.....	45.82
Phosphate of lime.....	46.13
	100.00

## [IV. Sables Verts nodules, by Nivoit (Assoc. franç. avanc. sci., 1875.)]

	I. From Islettes.	II. From Louppy le Château.	III. From d'Ander- nay.	IV. From Beurey.
Loss by calcination.....	15.00	9.60	10.50	8.00
Sand and clay.....	27.98	23.80	31.03	39.80
Phosphoric acid.....	18.72	22.03	18.78	16.30
Sulphuric acid.....		2.12	0.89	0.92
Oxide of iron.....	4.30	11.30	15.65	10.60
Lime.....	21.00	29.33	20.80	22.00
Magnesia.....	2.10	Trace.	Trace.	0.89
Loss and matter not determined..	0.90	1.82	2.35	1.49
Total.....	100.00	100.00	100.00	100.00

## [V. Gaize nodules from Grand Pré, by Nivoit.]

Loss by calcination.....	7.20
Sand and clay.....	13.50
Phosphoric acid.....	31.00
Sulphuric acid.....	1.00
Oxide of iron.....	7.50
Lime.....	38.50
Loss and matter not determined.....	1.30
Total.....	100.00

## [VI. Nodules from the Marnes Crayèuses, Sainte-Marie, by Nivoit.]

Loss by calcination.....	16.20
Sand and clay.....	26.30
Phosphoric acid.....	18.00
Oxide of iron.....	12.15
Lime.....	27.35
Total.....	100.00

## PHOSPHATES OF CENTRAL FRANCE.

The phosphates of the center of France, in the department of Côte-d'Or, and in the southeast, near the source of the Rhone, around Bellegarde, are of the Lower Gault and Lower Greensand formations. They differ in no material way from the corresponding beds in Ardennes and Meuse. The same formations are worked farther south along the Rhone, at Seyssel, near Grenoble, and elsewhere. In Isère and Drome there is a bed not represented in the north; it is a thin, glauconitic stratum, lying between the Valenginien and the Marnes d'Hauterive. It contains *Belemnites dilatatus* and *Belemnites pestilliformis*. The same

bed also crops out near Castellane and Nice. It is of very little commercial importance.

The phosphate bed of Côte-d'Or consists of a bed of yellow sand of fine texture, mixed with shells, fossils, and phosphatic nodules, which often form a separate bed in the sand. The bed immediately underlies the gray and red clays of the Gault.

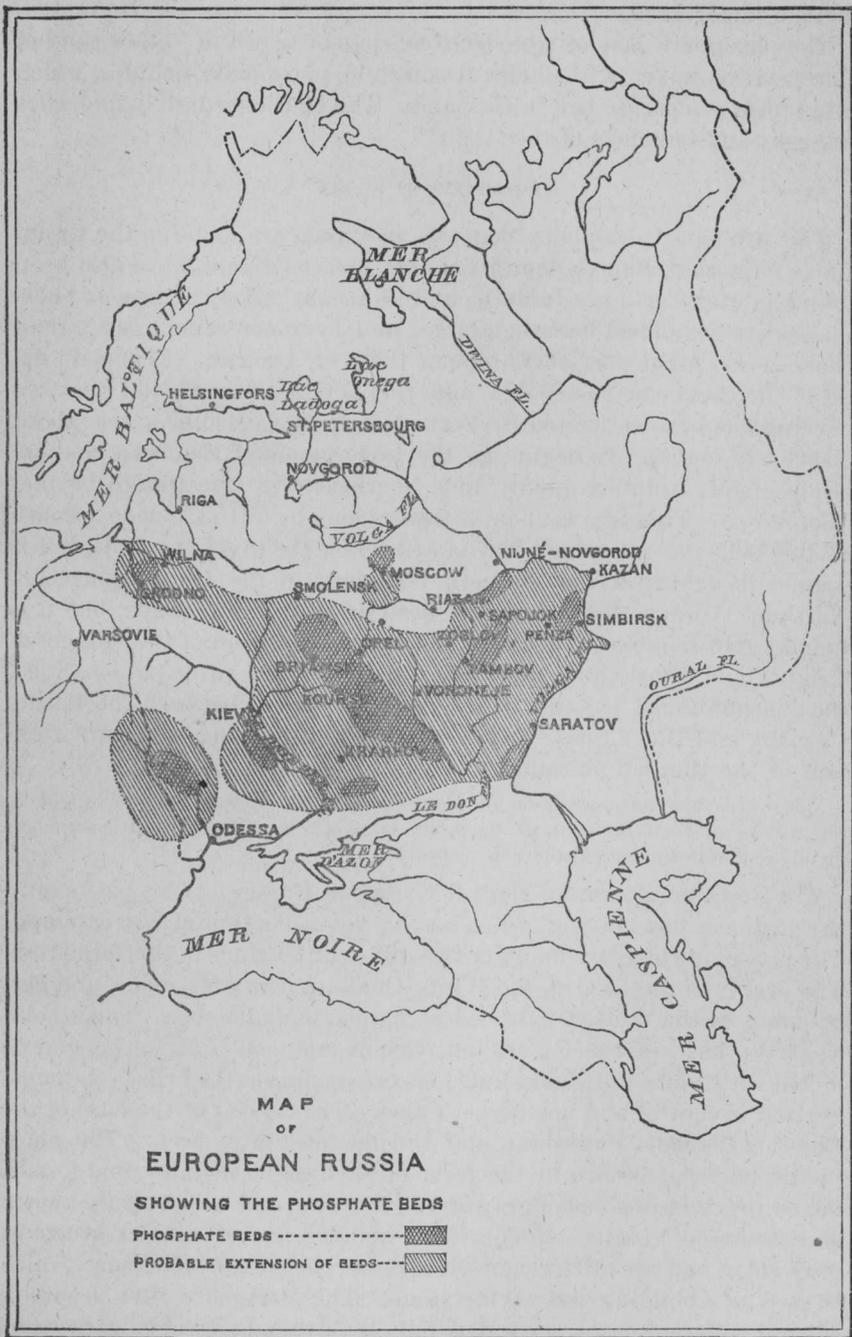
#### PHOSPHATES OF RUSSIA.

The principal phosphate deposits in Russia are found in the Cretaceous formation, though deposits of very limited extent have also been found in the Tertiary, Jurassic, and Silurian. The Cretaceous phosphates are developed here on a larger and more continuous scale than those of any other part of Europe or those of America. The main deposit lies between the Volga and the Dnieper Rivers, and the area covered has been estimated by Yermoloff at 20,000,000 hectares (about 50,000,000 acres). It begins in the government of Smolensk and extends almost uninterruptedly in a southeasterly direction to beyond Woronesch. This area is about 370 miles long by 60 to 125 wide. South of this belt the phosphate bed is lost under the overlying beds, but it reappears again on the southern boundary of the Cretaceous basin. North of Woronesch the bed has been destroyed by erosion, but it is found again 125 miles northwest, in the neighborhood of the villages of Tambof and Spask and Simbirsk. Besides these principal localities, the phosphate bed is found in several other places between the Baltic, Caspian, and Black Seas. Mr. Yermoloff,<sup>1</sup> in speaking of the great extent of the Russian phosphates, says :

*Nous ne croyons pas exagérer en affirmant que la Russie centrale repose sur du phosphate de chaux, qu'elle pourrait en paver la moitié de l'Europe, tant les couches qu'elle renferme sont inépuisables de richesses.*

The Cretaceous series in central European Russia forms a basin, only the northern boundary of which has as yet been thoroughly explored. The phosphate beds are found at two different horizons in this formation. The first is at the base of the White Chalk or Craie Blanche, and corresponds to the White Chalk bed of Ardennes and Meuse. The second is at the base of the Greensand (Cenomanian, or Grès Verts) and is mixed with glauconite and sand. It corresponds to the beds of the same horizon in central and northern France. The deposit at the base of the Chalk is the most important, and the one most often seen. The phosphatic material occurs in the form of shell-casts, nodules, and fossils, mixed together in a bed of gray or yellow sand, and is commonly known as "ssamorod" (native stone). The nodules are of a black-brown or gray color, and are often cemented together, forming a solid mass, which is used as a building and paving stone. The phosphate often occurs in several different beds, separated only by a thin layer of calcareous or

<sup>1</sup> Alex. Yermoloff: Jour. agric. pratique, 1872.



MAP  
OF  
EUROPEAN RUSSIA

SHOWING THE PHOSPHATE BEDS

PHOSPHATE BEDS ----- [Cross-hatched box]

PROBABLE EXTENSION OF BEDS ----- [Dotted box]

siliceous matter. There are usually from one to three of these separate beds and sometimes as many as seven. Their thickness varies from 6 to 20 inches.

The following sections by Dr. C. U. Shepard, jr., will show the position of the phosphate beds :

Section 1. In the township of Briansk, government of Orel, on the banks of the Desna, the ssamorod occurs in large flat pieces, 3 to 4 feet square and 10 inches thick.

The order of occurrence is as follows :

- (1) Argillaceous marl.
- (2) White chalk.
- (3) Siliceous marl, with thin layers of chalk and small nodules of phosphate of lime 1½ feet thick.
- (4) Ssamorod occurring (as above described) in flat slabs.
- (5) White sand 2 feet thick.
- (6) Second deposit of ssamorod, in nodules; 8 inches thick.
- (7) Brown sand over 5 feet thick.

The upper deposit of phosphate slabs consists of hard brown nodules, cemented together by siliceous and calcareous matter. The lower layers are dark green and soft when first dug.

Section 2. The same slabs also occur in the neighborhood of Kursk and towards Orel. At Dmitrovsk the occurrence is as follows :

- (1) Red clay, 7 feet thick.
- (2) White, calcareous marl, containing many small, phosphatic nodules, 4 feet thick.
- (3) Very small nodules of phosphate cemented by calcareous matter, 14 inches thick.
- (4) Thin layer of brown quartz sand with small nodules.
- (5) Phosphatic slabs, 10 inches thick.

These slabs are not flat on the upper side, but irregular and kidney-formed. The size of the slabs varies considerably; some are as large as 3 feet long by 2 wide.

Section 3. The occurrence at Jablovsk is as follows :

- (1) Soil and earth.
- (2) Marl, a few feet in thickness.
- (3) Chalk, a few feet in thickness.
- (4) Siliceous marl, with fine grains and pebbles of phosphate, 1 to 2 feet thick.
- (5) Sand a few inches thick.
- (6) Phosphate rock.

Here the rock comes to sight on the sides of water-worn gullies in the rolling country.<sup>1</sup>

The phosphate stratum underlies an immense extent of country, but it is often at such an inaccessible depth, that most of it is of but little practical value, and it can only be profitably mined where it crops out in the ravines. Besides their inaccessibility, the nodules are of poor quality, varying, as they do, in their content of phosphoric acid from 12 to 35 per cent., and averaging only 20 per cent.<sup>2</sup> The nodules are very siliceous, the grains of sand being plainly visible in them. In this respect they very much resemble the North Carolina Tertiary phosphates.

<sup>1</sup>Dr. C. U. Shepard, jr., MSS.

<sup>2</sup>Alex. Yermoloff, Jour. agric. pratique vol. 1, 1872.

When the nodules are cemented together in slabs, the masses are generally 1 to 2 feet square and 8 to 12 inches thick. Their upper surface is smooth, shiny, and mammillated; the lower one, which is irregular and uneven, shows plainly that the slabs are composed of nodules held together by a siliceous and calcareous cement.

According to Yermoloff the beds of Smolensk, Orel, Kursk, and Woronesch contain not less than 6,000 tons per acre, while those of Tambov, which are said to be the richest in Russia, contain 20,000 to 30,000 tons per acre.

As regards the origin of these phosphates, Count Keyserling thinks that they were formed by carbonated waters dissolving the phosphate of lime of the bones and other phosphatic matter of dead animals and re-depositing it in a bed of siliceous and calcareous marl.

The existence of ssamorod in central Russia has been known ever since the early part of this century, but its value was not appreciated. In the geological survey of Russia, by Sir R. Murchison, the phosphate rock is simply spoken of as "a shelly agglomerate and concretionary iron-stone," and several deposits of it are spoken of as "ferruginous, siliceous, and concretionary banks." The discovery that ssamorod is a phosphatic rock is due to Professor Chodneff, of St. Petersburg, in 1845. Count A. Keyserling and Professor Claus, of Dorpat, first made known the existence of phosphate in the departments of Kursk and Woronesch a few years later. In 1866, Professor Engelhardt, in his geological survey of Russia, afforded valuable information concerning the extent, value, and accessibility of the phosphatic beds.

Several factories have been started to make use of these deposits, but generally with little success. Large works were started at Ukolowa, Riga, and in Kursk, but were soon closed. The phosphate is of too low grade to pay for the expense of mining it.

Besides the beds already described, phosphatic deposits of much more limited extent have been found elsewhere in Russia. Thus Professor Schwackhofer,<sup>1</sup> of Vienna, has discovered a deposit of phosphatic nodules in the Silurian schists of Poland, on the Dniester. The average of twenty-five analyses gave 74.23 per cent. bone phosphate, which is much higher than the average of Russian Cretaceous phosphates. The amount of phosphatic material in the bed is, however, very limited, and consequently it is of no commercial importance. A phosphatic limestone containing 12 per cent. of phosphoric acid had also been discovered in the government of Novgorod.<sup>2</sup>

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<sup>1</sup> Ueber das Vorkommen und die Bildung von Phosphoriten an den Ufern des Dniesters in Russisch-Podolien, Galizien und der Bukowina, by Professor Schwackhofer.

<sup>2</sup> A. Yermoloff, Jour. agric. pratique, vol. 1, 1872.

*Analyses of the amorphous nodular phosphates of Russia.*

[Analyses given Dr. C. U. Shepard, jr., by T. Lahusen, of the Imperial School of Mines, St. Petersburg.]

[With the exception mentioned under the head of notes all the samples analyzed were nodular.]

Locality.	Government.	Chemist.	Bone phosphate of lime.	Sand.	Notes.
Belskaga in Roslavl.	Smolensk.	Engelhardt ...	31.15	43.69 to 50.13	Siliceous.
Do .....	do .....	Kostytscheff..	60.42 to 63.39	5.51 to 7.61	Argillaceous.
Seshti in Roslavl.	do .....	Schmidt .....	36.18	44.57	Siliceous.
Briansk.....	Orel .....	Engelhardt ...	{ 35.25 39.26	39.77 37.43	Green and soft. Brown and hard.
Do .....	do .....	Latschinoff ...	33.37	48.25	Prepared phosphate meal.
Voronova .....	do .....	Malyschaff ...	45.36	28.79	
Linbachina in Briansk.	do .....	Morkjraff .....	31.92	47.47	Gray.
Do .....	do .....	Latschinoff ...	62.65	9.15	Black.
Kotovetz in Schtyrovosk.	Kursk .....	Malyschaff ...	59.01	11.97	Cemented in siliceous chalk.
Kursk .....	do .....	Latschinoff ...	{ 28.92 to 30.89	57.10 to 53.70	Upper side of flat cakes. Lower side.
Turoff .....	Woronesch	Malyschaff ...	36.87	44.92	
Jendovischti .....	do .....	do .....	29.92 to 40.47	43.29 to 50.45	
Bondary .....	Tambov ..	Yermoloff .....	36.18 to 41.24	45.26 to 35.50	
Bytschkoff .....	do .....	do .....	15.98 to 60.76	13.03 to 54.16	
Spask .....	do .....	do .....	60.00	9.50	
Do .....	do .....	do .....	40.32	41.28	
Do .....	do .....	do .....	58.64	12.25	Argillaceous.
Do .....	do .....	do .....	27.57	59.70	Do.

[Analysis by Dr. C. U. Shepard, jr., of phosphate rock ground at the mill at Ukolowa, Central Russia.¹]

Quartz .....	34.05
Organic matter .....	0.90
Sulphate of lime .....	1.60
Bone phosphate of lime .....	42.05
Carbonate of lime .....	12.23
Fluoride of lime .....	6.98
Phosphate of magnesia .....	1.30
Alumina and oxide of iron .....	1.16
	100.27

[By Dr. C. U. Shepard, jr., Jablovsky phosphate rock.²]

Phosphoric acid .....	13.35
Equivalent bone phosphate of lime .....	29.14
Sand and insoluble siliceous matter .....	54.40

¹ Ground phosphate rock partially freed from sand.

² A superphosphate made from 12 parts (by weight) of this phosphate and 9 parts of sulphuric acid (specific gravity 1.50) gave a product which was wet, sticky, and acid.

[Analysis of Russian phosphate rock, by Yermoloff.]

Phosphoric acid.....	20.26
Lime.....	29.07
Magnesia.....	0.00

[Russian rock phosphates, by Yermoloff.]

	Clay and sand.	Phosphoric acid.	Carbonic acid.	Sulphuric acid.	Lime.	Magnesia.	Alumina and oxide of iron.
Block phosphate from near Kursk, by Claus.....	50.00	13.60	3.45	.86	21.00	0.65	2.20
Nodules from near Spask, by Yermoloff.....	9.50	27.48	3.95	1.08	42.00	0.40	3.19
Nodules from near Spask, by Yermoloff.....	59.70	12.63	1.98	0.44	18.54	.....	.....
Block of nodules from one of the richest beds of the government of Tambov, by Yermoloff.....	35.50	20.26	.....	0.85	29.07	.....	3.47
Fossil bone from same locality as last, analyzed at Agricultural Institute of St. Petersburg.....	1.45	31.76	.....	.....	48.53	1.48	0.32
Fossil wood from phosphate bed near Spask, by Engelhardt.....	.....	35.23	3.44	.....	51.90	.....	1.15
Phosphate from government of Orel, analyzed at the Agricultural Institute of St. Petersburg.....	7.10	29.84	6.06	1.39	47.99	0.47	0.89

[Analysis of Silurian phosphate rock from the Dniester, by Professor Schwackhofer.]

Phosphate of lime.....	74.23
Sand and insoluble matter.....	5.61
Fluoride of lime.....	6.00
Oxide of iron.....	0.50-5.0

## PHOSPHATIC LIMESTONE BEDS.

Under this heading are included those sedimentary limestones which contain considerable quantities of phosphate of lime. Such deposits have been found in Kentucky; and Yermoloff mentions that a limestone containing 12 per cent. phosphate of lime exists in the government of Novgorod, Russia.

Most limestones contain a small per cent. of phosphate, but as yet very few have been found which contain large amounts, and none are known which have become of commercial importance.

## PHOSPHATIC LIMESTONES OF KENTUCKY.

Several beds of phosphatic limestone have been discovered by Prof. N. S. Shaler in Kentucky, but the one richest in phosphate of lime was found in Fayette County.<sup>1</sup> It belongs to the lower part of the Cincinnati group and consists of a thin stratum, never reaching a greater thickness than from 6 to 12 inches. It is a "somewhat friable rock of a bluish gray color; brownish gray on the weathered surfaces; containing many microscopic marine univalve shells. Adheres strongly to the tongue." It is much more brittle than the associated limestones, and contains 31.815 per cent. of phosphoric acid. It is probable that beds of

<sup>1</sup> Geol. Survey Kentucky, N. S. Shaler, Director, 1878, New Series, vol. 4, p. 65.

this kind derived their phosphate of lime from the numerous animals, having phosphatic shells, which inhabited the Silurian sea.

Phosphatic limestone beds, like those just described, supply the soil of the surrounding country with large quantities of phosphate of lime, and it is very likely that the wonderful fertility of some districts in the limestone regions of Kentucky and Virginia is due to the decomposition of such beds.

*Analysis of Fayette County phosphatic limestone, by Dr. Peter (Kentucky Geol. Surv., 1878).  
Dried at 212° F.*

Phosphoric acid, lime, magnesia, alumina, iron oxide .....	85.270
Carbonate of lime .....	9.180
Carbonate of magnesia .....	.371
Silica and insoluble silicates .....	4.780
Fluoride of calcium, alkalies, organic matter, etc., not estimated ..	.399
<hr/>	
Total .....	100.000

#### GUANOS.

The class of guanos includes all those deposits which are largely, or entirely, composed of the excrement of birds. Such deposits are subdivided into *soluble guano* and *leached guano*. The former is composed of deposits which have preserved all, or a large part of, their soluble ingredients, while the latter includes such as have lost these soluble constituents by the action of rain or sea-water, and have been converted into a mass, insoluble, or almost insoluble, in water, and varying, in consistency, from a loose powder to a hard compact rock.

The soluble guanos will be treated first, and then the leached guanos will be described.

#### SOLUBLE GUANO.

Most of the soluble guano of commerce has come from the coast of Peru. It has been used in that country for agricultural purposes from very ancient times. Of such value was it esteemed by the natives that the punishment of death was imposed by the early Incas and their Spanish successors on any one who was found killing the birds that made these precious deposits. Peruvian guano was first recommended (1804) to be used in the raw state for agricultural purposes in Europe by Humboldt, who brought a specimen from the islands off the coast of Peru; but it was not exported in any considerable quantities until 1842, when 182 tons were shipped to England. After that time the use of it increased very rapidly until 1870-1875, when the best beds were exhausted, and the use of acidulated phosphates gradually drove the poorer qualities almost entirely out of the market. It is still imported to the United States and Europe as a source of superphosphate. In the raw state very little of it is used compared with the immense quantities of superphosphates now sold.

The following tables will show the imports into Great Britain, Germany, and France :

*Imports into Great Britain (Stockhardt).*

	Cwt.		Cwt.
1844 .....	208,502	1855 .....	6, 101,220
1845 .....	568,600	1856 .....	3, 830,020
1846 .....	1,784,060	1857 .....	5, 767,240
1847 .....	1,647,840	1858 .....	7, 070,820
1848 .....	1, 428,220	1859 .....	1, 682,440
1849 .....	1, 668,760	1860 .....	2, 828,700
1850 .....	2, 338,500	1861 .....	3, 568,460
1851 .....	4, 860,280	1862 .....	2, 832,720
1852 .....	2, 597,780	1863 .....	4, 671,480
1853 .....	2, 463,320	1872 .....	117,089
1854 .....	4, 470,222	1873 .....	184, 921

*Imports into Germany (Meyn).<sup>1</sup>*

	Tons.		Tons.
1861 .....	25,000	1866 .....	55,621
1862 .....	30,000	1867 .....	52,413
1863 .....	48,785	1868 .....	73,922
1864 .....	50,699	1869 .....	85,233
1865 .....	59,940		

*Imports into France (Meyn).<sup>1</sup>*

	Tons.		Tons.
1857 .....	52,000	1862 .....	46,000
1858 .....	38,000	1863 .....	68,000
1859 .....	33,000	1864 .....	69,000
1860 .....	40,000	1865 .....	47,000
1861 .....	38,000	1866 .....	57,000

The deposits of guano are found mostly on the islands on the coast of Peru and Bolivia. They are also found on the mainland, but these are not so large as those on the islands. The deposits consist of the excrements of flamingoes, divers, penguins, and other sea fowls, mixed with the carcasses of these birds, as well as those of seals, sea-lions, and other marine animals, which inhabit these seas in vast numbers. The guano is generally pulverulent on the surface, but becomes compact at a depth. It is in some places over a hundred feet in thickness, and is white to brown in color. There often occur in it small lumps containing ammonia salts, and others containing large quantities of phosphate of lime or silica. Gypsum is also abundant in some of the guano beds. The phosphates in the guano occur largely as tricalcic, dicalcic, ammonio-magnesian, and ammoniac phosphates, so that a large part of it is in a very soluble form, hence its value as plant food. There is also in the guano a soluble base called guanine, with the formula  $C_5H_5N_5O$ . It will thus be seen that, though some of the ingredients of guano are insoluble, others are very soluble, and, for the preservation of such a deposit a very dry climate is necessary. The coast of Peru is peculiarly adapted to the formation of guano beds, not only on account of the absence of rain, but

<sup>1</sup>Die natürlichen Phosphate.

also on account of the large flocks of sea birds which inhabit the islands along the coast and feed on the vast schools of fish swarming in the surrounding seas.

The first beds that were mined were on the Chincha Islands, off the coast of Peru. The guano of this locality was the richest of all the deposits on the South American coast. The islands are small, rarely more than three miles in circumference, and the beds were practically exhausted as early as 1872. Among the other islands which have been worked and stripped of their valuable deposits are those of Macabi and Guañape, north of the Chincha Islands, as well as those of Ballestas, Lobos, Foca, Pabellon de Pica, Tortuga, Huanillos, and many other islands on the same coast. As will be seen from the analyses, the composition of the guano from these localities varies considerably. It depends on the circumstances under which the deposit was formed, such as the amount of rain, the exposure to the spray of the sea-water, and other conditions.

Though the Peruvian coast is the most important locality for guano, yet it has been obtained in considerable quantities in other places also. It is found near the Cape of Good Hope and northwest of it, at Saldanha Bay. It is also found on the island of Ichaboe, as well as at Algoa Bay, which is on the southern coast of Africa. The guano from these African localities has often been leached by the action of rain and sea water, but it is also found containing large quantities of soluble salts of ammonia and phosphorus. The island of Ichaboe contained 200,000 tons of guano, all of which was removed in fifteen months after its discovery in 1844.

Soluble guano has been found on the Kuria Muria Islands, on the coast of Arabia; at Shark's Bay, Australia, and at many other places in small quantities. The variety known as "bat guano" is generally found in caves, and consists of the dung of bats, mixed with the bodies of their dead, as well as with the remains of rats, mice, etc. Such deposits are of very limited extent. They are found in many places in America and Europe. In the United States bat guano is found in Indiana, Kentucky, Alabama, and many other States. Near San Antonio, Tex., there are several caves containing large quantities of it. It is also found in many places along the coast of the Mediterranean, and especially in Italy.

*Analyses of soluble guano.*

[I. Mean of 21 analyses of Macabi Island guano, by Barral.]

Nitrogen.....	10.90
Phosphates.....	27.60
Potash.....	2 to 3

[II. Analysis of Macabi guano, by Bobierre.]

Water.....	30.80
Bone phosphate.....	35.50
Nitrogen.....	8.22

## [III. Analysis of Guañape Island guano, by Dr. C. U. Shepard, jr.]

Nitrogen .....	8.20 to 12.80
Phosphoric acid.....	10.77 to 17.62
Sand and siliceous matter.....	0.75 to 3.75
Water.....	11.83 to 29.96

## [IV. Average of 22 analyses of Guañape guano, by Barral.]

Nitrogen .....	10.95
Phosphates .....	28.00
Potash .....	2 to 3

## [V. Analysis of Guañape guano, by Bobierre.]

Water .....	24.00
Sand .....	1.30
Organic matter and ammoniacal salts (1).....	37.00
Bone phosphate of lime .....	36.00
Undetermined matter .....	1.70

100.00

(1) Nitrogen .....	7.75
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## [VI. Analyses of soluble guanos, by Dehérain.]

	Angamos, coast of Bolivia. White guano.	Bolivian.	Los Patos.	Island of Elide, coast of California.	Îlot de Pedro-Bey, coast of Cuba.
Organic matter.....	70.21 to 52.92	23.00	32.45	27.37 to 34.50	6.16
Containing nitrogen.....	20.09 to 14.38	3.38	5.92	1.34 to 6.98	0.28
Equivalent in ammonia..	24.36 to 17.44	4.10	7.18	1.62 to 8.46	0.34
Total phosphates.....	13.30 to 20.95	48.60	34.81	28.00 to 31.00	48.52
			Mexican coast.	Galapagos, Ecuador.	Falkland Islands.
Organic matter.....			13.05 to 18.00	.....	17.35 to 28.68
Containing nitrogen.....			0.21 to 3.45	0.7	0.56 to 2.26
Equivalent in ammonia .....			0.26 to 4.19	0.85	0.68 to 2.74
Total phosphates .....			8.00 to 25.00	60.30	21.46 to 25.62

<sup>1</sup>Containing sometimes very considerable quantities of phosphates of alumina and the oxide of iron.

## [VII. Analysis of Peruvian guano by Dr. Ure, Am. Jour. Agric., 1845.]

Uric acid .....	10.50
Ammonia .....	19.00
Phosphoric acid.....	14.00
Lime and magnesia.....	16.00
Salts of soda and potash.....	6.00
Oxalic acid, with carbonic and muriatic acids.....	13.00
Water .....	13.00
Sand .....	2.00
Volatile and organic matters .....	6.50

100.00

## [VIII. Analysis of Peruvian guano, by Nesbit, Agricultural Chemistry, London, 1859.]

Moisture.....	15.10
Organic matter, etc. (1).....	51.27
Silica.....	2.20
Phosphate of lime.....	22.13
Phosphoric acid.....	3.23
Equal to phosphate of lime, 7.00.	
Alkaline salts, etc.....	6.07
	100.00
(1) Nitrogen.....	13.54
(1) Ammonia.....	16.42

## [IX. Analysis of Ichaboe guano, Am. Jour. Agric., 1845.]

Ammonia.....	13.50
Humic acid.....	4.00
Phosphates.....	25.00
Oxalic, etc., acids.....	20.00
Salts of soda, etc.....	7.00
Water and volatile matter.....	27.50
Sand.....	3.00
	100.00

## [X. Analyses of soluble guanos, by Nesbit, Agricultural Chemistry.]

	Angamos.		Peruvian.	Chilian.	Bolivian.	Saldanha Bay.	Shark's Bay.
	I.	II.					
Moisture.....	10.90	12.55	9.30	20.46	16.00	17.92	14.47
Organic matter, etc. (1).....	67.36	61.07	57.30	18.50	13.16	14.08	7.85
Sand.....	1.04	5.36	0.75	22.70	3.16	2.80	14.47
Phosphates.....	16.10	13.76	23.05	31.00	60.23	59.40	29.54
Alkaline salts, etc.....	4.60	7.26	9.60	7.54	7.45	5.80	33.67
	100.00	100.00	100.00	100.20	100.00	100.00	100.00
(1) Nitrogen.....	19.95	18.24	15.54	4.50	2.11	0.63	0.35
(1) Equal to ammonia.....	24.19	22.12	18.87	5.47	2.56	0.76	0.47

## [XI. Analyses of Peruvian guano and of Ichaboe guano; from The Cultivator, vol. 1, 1844.]

	Peruvian guano.	Ichaboe guano.
Water and volatile ammonia.....	15.27	3.14
Organic matter and ammoniacal salts.....	51.44	63.52
Chloride and sulphate of soda.....	5.50	5.02
Insoluble siliceous matter.....	0.57	1.16
Phosphate of lime and little phosphate of magnesia.....	21.11	22.20
Carbonates of lime and magnesia.....	6.11	4.96
	100.00	100.00

## [XII. Analyses of soluble guano, by Norton, Elements of Scientific Agriculture, 1860.]

	Bolivian.	Peruvian.	Chilian.	Ichaboe.
Water .....	5 to 7	7 to 10	10 to 13	18 to 26
Organic matter and ammoniacal salts .....	56 to 64	56 to 66	50 to 56	36 to 44
Phosphates .....	25 to 29	16 to 23	22 to 30	21 to 29

## [XIII. Analyses of soluble guanos, Cameron, Chemistry of Agriculture.]

	Upper Peruvian.	Ichaboe.	Bird Island.	Cuban.	Kuria Muria.	Patagonian.
Water .....	10.00	20.00	15.00	26.00	18.10	25.00
Organic matter .....	21.68	24.40	6.50	4.10	12.41	18.30
Yielding ammonia .....	(4.50)	(6.00)	.....	.....	(2.05)	(2.00)
Earthy phosphates .....	51.50	20.40	37.25	43.70	42.67	44.00
Carbonate of lime .....	.....	.....	40.00	24.10	4.19	.....
Alkaline salts .....	14.12	6.20	1.15	.....	4.13	2.10
Sand, clay, and other useless matter .....	2.70	29.00	0.10	2.10	18.50	10.60
	100.00	100.00	100.00	100.00	100.00	100.00

## [XIV. Analysis of soluble guano from "an island in the Pacific," by R. S. Burn, Year-Book of Agricultural Facts.]

Water .....	4.60	4.60
Organic matter and ammoniacal salts .....	16.85	16.38
Phosphates .....	71.40	69.90
Carbonate of lime .....	3.15	7.90
Alkaline salts .....	3.90	1.07
Sand .....	0.10	0.15
	100.00	100.00
Ammonia .....	1.32	1.26

## [XV. Analysis of bat guano, Report Indiana Geological Survey, 1879, p. 163.]

Loss at red heat .....	44.10
Organic matter .....	4.90
Ammonia .....	4.25
Silica .....	6.13
Alumina .....	14.30
Ferric oxide .....	1.20
Lime .....	7.95
Magnesia .....	1.11
Sulphuric acid .....	5.21
Carbonic acid .....	3.77
Phosphoric acid .....	1.21
Chlorides of alkalis and loss .....	5.87
	100.00

## LEACHED GUANOS.

The second subdivision of guano deposits is leached guano. It is either pulverulent, or in a more or less solidified mass, and consists of guano from which all or almost all the soluble constituents have been

dissolved by the action of rain and sea water. It is found most plentifully on some of the small islands in the Pacific Ocean, northeast of Australia, and on many of the West India Islands. It is also found in some places on the coast of Chili, as on the promontory of Mexillones. Here it occurs as a light yellow phosphatic powder, containing lumps of the same substance and averaging 75 to 81 per cent. of bone phosphate of lime.

Leached guano is found in the Pacific principally on the islands lying between longitude 150° to 180° west and latitude 10° N. to 10° S. Most of this area was put by Congress under the protection of the United States in 1856. It contains some forty guano islands. They are all small and low, and are built up by the formation of coral reefs. Often there is a salt-water lagoon in the center of the island. Among the richest localities are Baker, Howland, Jarvis, McKean, Malden, Starbuck, and Phoenix Islands. The guano is generally pulverulent on the top, and more or less solidified below. Occasionally the soluble portions have been washed into the underlying coral, forming a phosphatic limestone. The following is a section on Baker Island:

- (1) Pulverulent leached guano, yellow.
- (2) Denser stratum of same substance as (1).
- (3) Coral rock containing gypsum.

On Jarvis Island a bed of gypsum has been formed by the evaporation of a central lagoon. Overlying this is a deposit of leached guano, from one inch to one foot thick, covered by a phosphatic crust. Under this crust the bed contains both basic and neutral phosphate of lime. This fact is thought by Dr. C. U. Shepard, jr., to be due to the decomposition of the tribasic phosphate by the gypsum. Occasionally concretionary nodules, composed of interstratified layers of phosphate of lime and gypsum, are found. On Malden Island there is a boggy deposit, which gives off sulphureted hydrogen from the mutual decomposition of the guano and the gypsum.

In the West Indies, leached guano has been found on many of the coral islands and reefs, all the way from the Bahamas to the coast of Venezuela. Among the principal localities are Sombrero, Navassa, Turk, St. Martin, Aruba, Curaçoa, Orchillas, Arenas, Roncador, Swan, and Cat, or Guanahani Islands, the Pedro and Morant Keys, and the reefs of Los Monges and Aves in Maracaibo Gulf. The phosphate from the different localities varies very much. That from Maracaibo Gulf occurs in a compact or granular form of a light brown color. Sometimes it is distinctly mammillated, and at other times it has a concentric structure. It often has a white phosphatic enamel like that which covers the basalt of Ascension Island. The deposit contains many fish bones, and is rich in phosphate of lime, which sometimes amounts to over 85 per cent. of the rock. The Sombrero Island phosphate occurs in two forms: (1) As a granular, porous, and friable mass, in color white, pink, green, blue, or yellow; (2) as a dense, massive, and homo-

geneous deposit of a white or yellow color. It contains 75 to 80 per cent. of phosphate of lime. Many bones occur, and at times the deposit takes the form of a real bone breccia. The principal rock of the island is a palagonite tufa, filled with shells and bones.

The Navassa phosphate is found on an uninhabited island, consisting of a terrace encircled by a high plateau. The phosphate is found in pockets in the living coral, and in the numerous depressions and hollows on the island. It is of a dark brown color, and is composed of a hard mass of oölitic grains. It contains 10 to 15 per cent. of alumina and oxide of iron (Meyn), and is therefore not very popular as a source of superphosphate, as it makes a sticky product.

The phosphate of Aruba Island is of a hard, massive variety, and is white to dark brown in color. Occasionally the underlying coral on this island, as well as on many others in both the West Indies and the Pacific Ocean, has been phosphatized by the infiltration of the soluble parts of the original guano deposits. Thus at Aruba large masses of coral, containing 70 to 75 per cent. phosphate of lime, are found.

Several distinct phosphate minerals occur in pockets in the phosphate beds in the West Indies. One of them, known as pyrophosphorite, was described by Dr. C. U. Shepard, jr., in the American Journal of Science, January, 1878. It is snow white, amorphous, opaque, and has a fracture like magnesite. It has a hardness of 3 to 3.5, and a specific gravity of 2.50 to 2.53. It is essentially an ortho-pyrophosphate of lime with pyrophosphate of magnesia, and has the formula  $Mg_2P_2O_7 + 4(Ca_3P_2O_8, Ca_2P_2O_7)$ .

On the islands of Mona and Moneta, in the West Indies, occur the minerals monite and monetite. They were described and named by Prof. C. U. Shepard, sr., in the American Journal of Science, May, 1882. The monetite occurs as a crystalline mineral, of a white or brown color, in association with monite, which is a white, soft, incoherent mass. Monetite is a crystallized dicalcic ortho-phosphate and has the formula  $CaHPO_4$ . Monite has the formula  $Ca_3P_2O_8 + H_2O$ .

Deposits of leached guano have been found on several islands in the Gulf of California. The deposit on Raza Island averaged over 41 per cent. of phosphoric acid, which corresponds to over 85 per cent. of phosphate of lime. (See analyses.) The beds in this island have been exhausted.

The deposits of the West Indies supply most of the leached guano now sold. Curaçoa annually produces 50,000 to 70,000 tons, and Sombrero about 10,000. The other islands produce much less. The Pacific Ocean islands are, at present, little worked. The difficulty with many of the West India deposits is that they contain large quantities of phosphate of iron and alumina, which make them very undesirable as sources of superphosphate. On some of the islands there occur beds of almost pure phosphate of iron and alumina.

Table of analyses of leached guanos.

[I. Analyses of Baker Island guano (constituents, lumps, crust, coral rock, etc.), by Siegert.]

	(1)	(2)	(3)	(4)	(5)
Water .....	1.45	10.25	9.03	0.90	8.20
Combustible matter (1) .....	2.57	5.11	4.02	4.47	8.30
Potash .....	0.10	0.44	0.43	0.46	0.62
Soda .....	0.45	0.73	0.62	1.21	1.13
Lime .....	53.78	43.83	43.44	45.82	40.63
Magnesia .....	0.27	0.42	0.60	1.89	1.75
Phosphoric acid .....	0.00	33.97	33.62	38.98	37.16
Sulphuric acid .....	1.40	2.07	6.81	1.16	1.17
Carbonic acid .....	39.98	3.18	1.43	5.11	1.04
Total .....	100.00	100.00	100.00	100.00	100.00
(1) Nitrogen .....	0.00	0.00	0.00	0.00	0.92

(1) Unchanged coral white rock.

(2) Yellow-brown crust, often several inches thick, with white interior, of coralline structure.

(3) Gray-brown balls, soft to pulverulent, often several inches thick; coralline structure feebly marked.

(4) Porcelain-like cakes, smooth or rough, soft, 1 to 4 inches thick, and in parallel plates.

(5) Whole guano powdered.

[II. Analysis of Howland Island guano, by Drysdale.]

Water .....	7.20
Combustible matter .....	14.18
Phosphates .....	75.32
Sulphate of lime .....	1.60
Carbonate of lime .....	1.27
Chloride of alkalies .....	0.43
Sand .....	Trace
	100.00

[III. Analyses of Jarvis Island guano, dried at 105 C.]

	Powder.	Lumps.
Water of combination and combustible matter .....	20.80	18.50
Anhydrous sulphate of lime .....	30.00	5.00
Phosphates of lime and magnesia .....	43.20	73.00
Siliceous residue .....	2.00	1.00
Undetermined ingredients and loss .....	4.00	2.50
	100.00	100.00

[IV. Analyses of Phoenix Island guano, by Rumpler.]

Water .....	1.19	2.08
Combustible matter .....	2.03	5.22
Phosphate of lime .....	76.00	70.70
Phosphate of magnesia .....	5.19	13.47
Carbonate of lime .....	0.63	10.50
Sulphate of lime .....	0.34	5.10
Nitrogen in the combustible matter .....	0.39	0.77

## [V. Analysis of Aves guano, by Völcker.]

Water.....	2.39
Organic matter and water of combination.....	7.93
Lime.....	39.48
Magnesia.....	1.17
Phosphoric acid.....	41.34
Sulphuric acid.....	4.57
Insoluble siliceous matter.....	2.28
	<hr/>
Containing nitrogen.....	99.16
	0.139

## [VI. Analyses of Navassa phosphate.]

	Gilbert.	Bret- schneider.
Water.....	3.01	3.54
Organic matter and water of combination.....	7.17	4.64
Lime.....	40.19	38.35
Magnesia.....		1.72
Sequioxide of iron.....	} 11.67	3.40
Alumina.....		6.50
Potash.....		0.34
Soda.....		0.32
Phosphoric acid.....	33.28	35.60
Sulphuric acid.....		0.19
Chlorine.....		0.08
Carbonic acid.....	2.15	2.58
		<hr/>
Silica.....		1.34
Sand.....	2.53	1.31
	<hr/>	<hr/>
	100.00	99.91

## [VII. Analysis of Raza Island phosphate, by Dr. H. Gilbert.]

Water.....	1.92
Neutral phosphate of lime.....	58.78
Bone phosphate of lime.....	18.86
Tribasic phosphate of magnesia.....	3.32
Sulphate of lime.....	8.26
Oxide of iron.....	0.99
Silicic acid.....	3.38
Organic matter.....	4.81
	<hr/>
	100.32

## BONE BEDS.

These deposits include beds which are composed largely of bones.<sup>1</sup> They occur principally as *cave* and *lacustrine* deposits.

## CAVE DEPOSITS.

Caverns have always been the places of refuge and the sepulchers of many kinds of animals, and sometimes bones have collected in them in sufficient quantities to form beds many feet thick. Such deposits are

<sup>1</sup>The phosphate beds of South Carolina and other similar deposits do not belong under this heading, for, though many bones occur in them, they are few compared with the accompanying phosphatic nodules.

much larger and more plentiful in Europe than in North America. The reason for this seems to be that in this country there were none of the carnivora, such as the jackals and hyenas, which have the habit of dragging their prey to their lairs. Consequently our caverns, notwithstanding their abundance and the great number of animals which have lived about them, are generally wanting in the extensive osseous breccias which characterize many caves in England, France, Germany, Hungary, Italy, and many other parts of Europe.

Many of the caves of the Southern States have been much resorted to by bats. The excrements of these creatures, together with the bones of those that have died there, have in many cases formed extensive beds of phosphatic and nitrogenous matter.<sup>1</sup> During the early part of this century, and during the civil war, saltpeter was extensively manufactured from them, and some of them have also been worked as a source of phosphate of lime.

#### LACUSTRINE DEPOSITS.

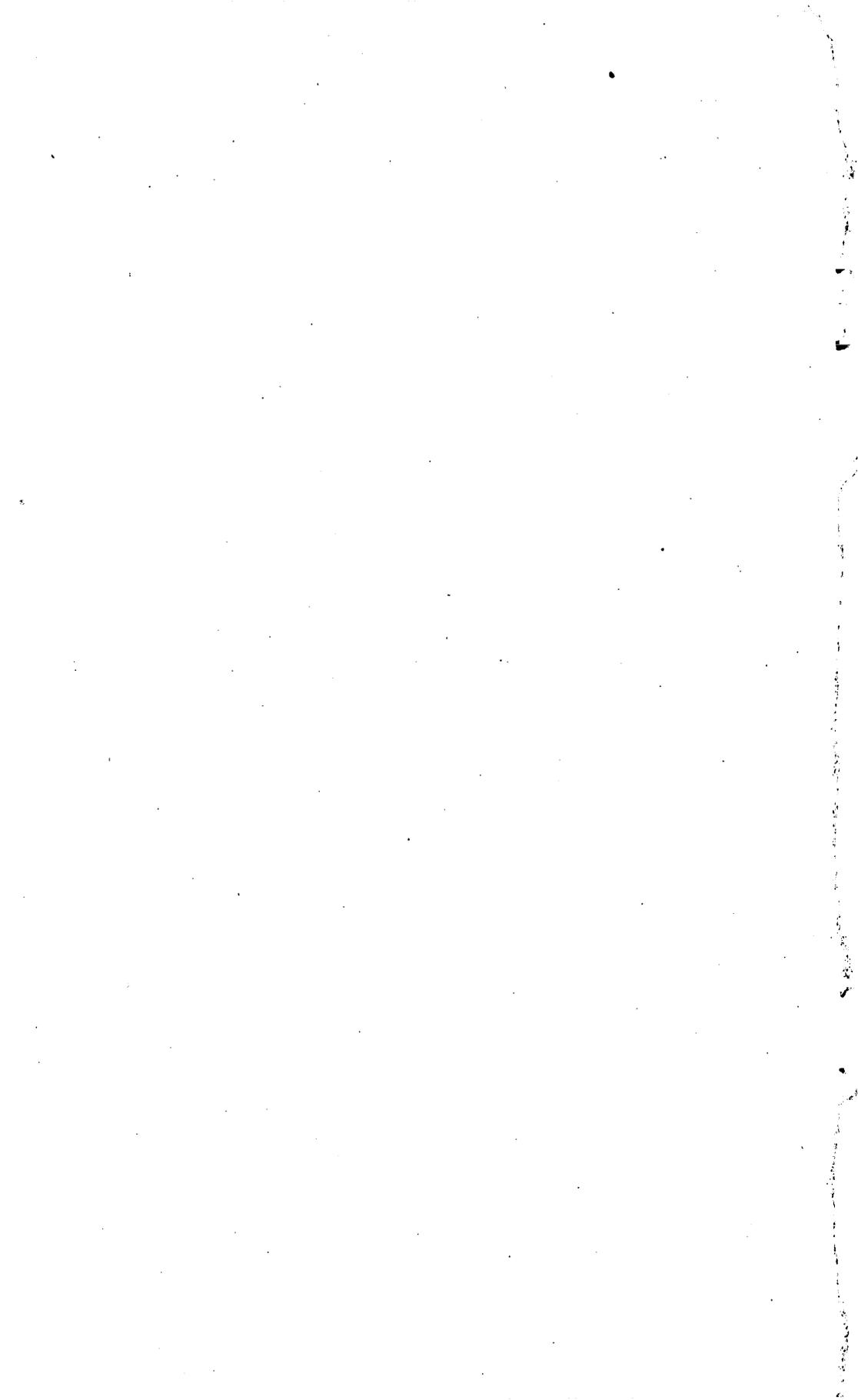
These deposits occur generally about the swampy margins of salt licks, as at Big Bone Lick in Kentucky<sup>2</sup>, and in the ancient lake deposits west of the Mississippi River, as in the Mauvaises Terres of Nebraska. Similar beds are also found in many parts of Europe. The bones found in such localities are the remains of animals which came to the swamps to lick the salt found there, or in search of refuge. Many died natural deaths, while others were mired in the boggy earth, and, being unable to extricate themselves, perished. In this way bones accumulated often in very considerable quantities.

These deposits, as well as those of the cave class, are generally too limited in extent to be of any commercial importance.

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<sup>1</sup> These deposits have been described under the heading of Guanos.

<sup>2</sup> An account of this deposit may be found in an appendix to Mr. J. A. Allen's monograph on The History of the Buffalo, in the memoirs of the Kentucky Geological Survey, Vol. I, 1876.



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