

THE NATURAL HISTORY OF PHOSPHATIC DEPOSITS.

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GREAT interest centres round the element phosphorus in consequence of the part it plays in the organic world, not only as an important constituent of the hard parts of many animals and of the seeds of plants, but also as forming an essential component of living matter. From the earliest appearance of life upon the globe down to the present day, there has been a constant circulation of phosphorus between organic and inorganic nature. From the rocks, in which it is almost always present, though in small quantities, it passes into the soil and into the waters of rivers, lakes, and seas. It is taken up by plants, handed on to animals, and from these it may again pass either directly or indirectly to the solid crust. I ask your attention to the processes involved in this circulation, and to some of the geological consequences which follow from it.

PHOSPHATES OF IGNEOUS ROCKS AND MINERAL VEINS.

Of the various phosphatic minerals apatite is by far the most abundant, and has long been recognised as the principal source of the phosphorus found in the sedimentary rocks and in the organic world. It occurs as definite crystals, less frequently as more or less rounded grains, in all varieties of igneous rocks; but is more common in the basic than in the acid varieties.

Among the British rocks, exceptionally rich in apatite, may be mentioned the mica-traps of the West of England and the Southern Uplands of Scotland; also a peculiar group of hornblende-diabases occurring at Wearde, Ernsettle, and other places in the Plymouth district. The largest apatites I have ever seen in normal igneous rocks occur in hornblende- and mica-andesites from Bail Hill, near Sanquhar. One of these measures $5 \times 2\frac{1}{2}$ mm., and is considerably larger than the porphyritic feldspars occurring in the same rock.

The apatites of igneous rocks have undoubtedly crystallised out of the magma. They occur as inclusions in all the essential minerals, and therefore belong to the earliest phases of consolidation. Under these circumstances it is somewhat surprising that, so far as I am aware, apatite has never been produced synthetically by crystallisation from artificial rock-magmas. It has, however, been observed in lead slags by Mr. Hutchings⁽²⁰⁾ and Professor Vogt.⁽⁴²⁾

But apatite occurs on a much larger scale as a constituent of mineral veins. The most remarkable deposits of this kind are undoubtedly those of Canada, Norway, and Spain. Although the veins of Canada are the most extensive, those of Norway have proved more interesting from a scientific point of view. They have been studied by Brögger, Reusch, Sgogren, Vogt, and others. A general account of their mode of occurrence and a theory as to their origin has been recently published by Vogt,⁽⁴³⁾ from whose writings the following summary is compiled.

The veins in question occur at various points along the south-eastern coast of Norway between Langesundsfjord and Kristiansand. They are intimately associated with intrusive masses of a plutonic rock essentially composed of labradorite, augite and olivine. This rock, locally known as olivine-hyperite, is a variety of olivine-gabbro with ophitic structure; or as some geologists would prefer to call it, an olivine-diabase.

The veins occur in the gabbro itself, and also in the surrounding Archæan schists. In the former case they follow the course of the natural joints; in the latter they usually, but not invariably, lie along the planes of foliation. The individual veins are scarcely ever more than 100 or 150 metres in length; as a rule only 30 to 50 metres. They dip with the joints at angles of from 25 to 50 deg., and wedge out in most cases at distances less than 100 metres. The principal minerals associated with the apatite are magnesian mica, enstatite, hornblende, pyrrhotite, rutile, ilmenite, scapolite, and feldspars.

Veins belonging to the apatite group occur by hundreds and, perhaps, thousands, but they vary considerably in mineralogical composition, and workable apatite is only found in a comparatively small number. It occurs in nests and pockets which are naturally far less persistent than the veins themselves. Masses consisting of nearly pure apatite (95 to 98 per cent.) may occasionally attain a thickness of 3 or 4 metres, but this is very rare. Most of the masses extracted are less than 1 metre in extent.

The minerals show a zonal arrangement with respect to the containing walls, and the nests and lenticles of apatite usually occur in the centre. The mineral is a chlor-apatite, and in this respect differs from the apatites of Canada, Spain, and indeed most other localities.

A point of the greatest possible interest, as throwing light on the genesis of the mineral, is the occurrence of a zone of metamorphism on each side of the apatite-veins wherever they cut the gabbro. The rock in immediate contact with the vein on either side is essentially composed of scapolite and hornblende; and this rock, when followed outwards, passes gradually into the normal gabbro in such a way as to prove beyond all doubt that the metamorphosing process emanated from the vein.

Vogt points out that the relations of the apatite-veins to the gabbro are similar to those of tin-stone-veins to granite; greisen taking the place of the scapolite-hornblende rock. This fact I can fully confirm from my own observations. Thus, at St. Michael's Mount, Cornwall, quartz-veins carrying topaz, apatite, wolfram, and tin-stone, may be seen following exactly the course of the normal joints in the granite. Each vein is bordered by narrow zones of greisen—a rock which differs from granite very much in the same way as the scapolite-hornblende-rock differs from gabbro. Greisen is usually defined as a rock composed of quartz and mica; but, as Professor Judd has pointed out, topaz is almost always present, at least in that variety which is associated with tin-stone-veins.

The evidence that the greisen-type of metamorphism emanated from the tin-stone-veins is, therefore, as clear as that the scapolitisation of the Norwegian gabbros emanated from the apatite-veins. What was the nature of the metamorphosing agent? Scapolite may be formed from labradorite by the addition of chlorine and sodium; topaz from orthoclase by the addition of fluorine and the elimination of alkali. Hence it follows that in both cases the metamorphism must have been due to some halogen compound—a compound of chlorine in the case of the gabbro, and of fluorine in the case of the granite. In this connection it is especially interesting to note that the apatite of the tin-stone-veins is a fluor-apatite, whereas that of the Norwegian apatite-veins is a chlor-apatite. We do not know in what precise form the chemical substances reached the position they now occupy, but that the element chlorine played an important part in the formation of the Norwegian apatite-veins is evident, not only because it occurs in the mineral, but also because it has permeated the surrounding rocks.

Professor Vogt considers that the contents of the apatite and tin-stone veins have been extracted from the gabbro- and granite-magmas by the action, in the one case of hydrochloric and in the other case of hydrofluoric acids. This theory will, to some extent, account for the differences between the two cases. Thus compounds of phosphorus, titanium and magnesium are much more common in basic than in acid rocks, and minerals containing these elements are especially characteristic of the Norwegian apatite-veins.

It must also be remembered that titanium and tin make volatile compounds with chlorine and fluorine, so that the rutile of the apatite-veins is analogous to the cassiterite of the tin-stone-veins. The importance of the halogens as mineralising agents was long ago recognised by Daubrée, and strikingly demonstrated by his classic researches on the synthesis of cassiterite, apatite and rutile.

The "acid extract" once formed must be supposed to have

been forced upwards along the cracks in the already consolidated upper part of the magma, or along the planes of least resistance in the surrounding rocks, either in the form of a solution or, more probably, as a dense gaseous substance at a temperature about its critical point and therefore under great pressure. Professor Vogt's theory of the origin of the apatite-veins by a kind of high pressure solfataric (pneumatolytic) action may at least be regarded as a useful working hypothesis. It is an expansion of the ideas formulated by the illustrious author of "*Études Synthétiques de Géologie Expérimentale*."

MODERN DEPOSITS.

The apatites of igneous rocks and mineral veins are doubtless the principal source of the phosphorus of the sedimentary rocks, and of the organic world, for the other phosphatic minerals of similar origin (monazite, xenotime, etc.) are too rare to have sensibly affected the supply. That they pass into solution is proved by their absence, or extreme rarity in the finer-grained sedimentary rocks which contain zircons in abundance. These two minerals occur together in igneous rocks, but the former is much more common than the latter. If the apatites were not destroyed in the process of denudation they would certainly be found in fine-grained sands, such as those of Hampstead Heath, in much greater abundance than zircon. But as Mr. Dick has pointed out they are extremely rare, and occur only as inclusions in other minerals.

The solution of apatite may be effected by water charged with carbonic acid; more readily by water containing organic acids or ammonium carbonate. Phosphorus is, therefore, present in river and sea waters; but only in small quantities. The water of the Rhine at Cologne contains rather less than one part in 1,000,000 (estimated as P_2O_5); that of the North Sea, off the coast of Norway, about ten times as much.⁽³³⁾ Nevertheless, it is from these very small quantities that organisms living in the water must obtain their supply of phosphorus.

If we leave out of account the very small amount of detrital apatite it is highly probable that the whole of the phosphorus found in the sedimentary rocks has been derived, either directly or indirectly, from the waters of rivers, lakes, and seas by the action of organic life.*

The once celebrated Peruvian guano furnishes an example of the formation of phosphates by the accumulation of animal remains. It was, for little now remains, an unsavoury mass made up of the excrement of sea-birds mixed with their carcasses, and

* Calcium phosphate may be deposited directly from solutions of apatite in regions where this mineral forms an important constituent of mineral veins; e.g., *stieffellite* in association with the Norwegian veins. But this scarcely requires a modification of the above statement.

with those of seals, sea-lions, and other marine animals. It occurred on the islands off the coast, and is said to have attained a thickness of 100 ft.⁽³⁹⁾ Phosphorus was present as tricalcic, dicalcic, ammonio-magnesian, and ammoniac phosphates, many of which are highly soluble compounds. Such a deposit is, therefore, only possible in a comparatively rainless district like Peru. In rainy districts, such as the Central Pacific and Caribbean Sea, where other conditions suitable for the accumulation of guano exist, the soluble salts are leached out and the more insoluble tricalcic phosphate remains behind forming from 75 to 81 per cent. of the deposit. The aqueous solutions containing alkaline, and specially ammonium phosphates thus formed are capable of producing important changes in the underlying rocks. Where, for example, as at Aruba and other islands in tropical seas, guano rests on upraised coral reefs, the underlying limestone has been phosphatised by the substitution of phosphoric for carbonic acid.⁽⁴⁰⁾

The same solutions are also capable of profoundly altering igneous rocks. Thus, I have recently shown that the isolated rock of Clipperton Atoll, in the eastern part of the Pacific, is a trachyte which has been partially and in some cases wholly changed into a hydrated phosphate of alumina with some iron; the silica and alkalis having been almost entirely removed.⁽⁴⁰⁾

Another interesting case of the formation of phosphate of alumina by the action of ammonium phosphate arising from the decomposition of animal matter has been described by M. Armand Gautier.⁽⁴⁰⁾ It occurs in a cave in Herault. In this case the solution probably acted on a clay. M. Gautier proved by direct experiment that aluminium phosphate could be formed by the action of a solution of ammonium phosphate on kaolin.

The above facts clearly show that organic agencies at the earth's surface may produce phosphatic deposits either (*a*) directly, by the accumulation of organic remains, as in the case of guano and bone beds; or (*b*) indirectly, by furnishing phosphatic solutions which may percolate downwards and act as metamorphosing agents on the underlying rocks. Phosphates may also be formed by direct deposition from solution; by the reaction of solutions of different compositions, as when a solution of calcium-bicarbonate comes in contact with one containing ammonium phosphate; or by the removal of a constituent, such as carbonic acid, on which the solvent action of water on tricalcic phosphate depends.

But phosphates may be formed on the floor of the ocean as well as on the surface of the land. Shortly after leaving the Cape of Good Hope the *Challenger* made three soundings of the greatest importance for our present purpose.⁽²⁸⁾ The first of these was in 98 fathoms. The deposit in the course of formation was found to be a green sand, composed of 40 per cent. of foraminifera, 9·4

per cent. of other calcareous organisms, 6 per cent. of siliceous organic remains, including pale green casts of foraminifera, and 40 per cent. of coarse sediment ('35 mm.), including quartz, felspar, garnet, black mica, and hornblende. Small glauconitic concretions containing phosphate of lime were present.

The next sounding, a little further south in 150 fathoms, also brought up green sand. The constituents were generally similar to the last, but there was a large proportion of calcareous organisms, including teeth and fragments of fish bones. The mineral particles were smaller ('2 mm.). The dredge contained glauconitic concretions, from 2 to 6 mms. in diameter, and a good many phosphatic concretions, some over 1 cm. in diameter. There was also much amorphous matter, which gave off an organic odour when heated on platinum foil; the phosphatic nodules were found to consist of grains of quartz and glauconite, precisely similar to those occurring in the deposit, cemented by brown amorphous phosphate of lime.

The two soundings above referred to were on the edge of the Agulhas bank, the next was in deep water (1,900 fathoms) about 100 miles south-east of the bank. The bottom was of globigerina ooze. The mineral particles were much smaller both in size ('12 mm.) and amount (3 per cent.). The dredge contained many small phosphatic concretions (1 to 4 cms.) enclosing glauconite and foraminifera. These facts fully prove that phosphatic concretions are being formed at present on the bed of the sea, and that they are produced in such a way as to cement together the deposits accumulating on the sea-floor at the spot where the nodules are found.

Messrs. Murray and Renard point out, as a general result of their researches, that deposits of phosphate and glauconite are especially characteristic of the continental borders of the great ocean-basins, and that the former occur in greatest abundance where currents of different temperatures or different salinities intermingle. More or less phosphate, generally less than 1 per cent., is always present in globigerina ooze; but it is only in special localities, where a considerable destruction of pelagic organisms may be expected to occur, that important accumulations take place.

Another observation made by the *Challenger* furnishes striking proof that the phosphate of lime separated by fishes and other organisms is dissolved in sea water. At one station in the Pacific, the dredge brought up 1,500 sharks' teeth, besides an immense number of small teeth which were not counted. Although the skeleton of the shark is only partly calcified, it contains a considerable amount of phosphate of lime. The presence of such a large number of teeth, without bones, represents, therefore, the solution of a vast amount of phosphatic matter.

PALÆOZOIC PHOSPHATES.

We pass on now to a review of the distribution of phosphates in the sedimentary rocks.

These phosphates vary greatly in chemical composition, but this variation is mainly due to a varying admixture of sedimentary material, such as quartz, glauconite, tests of foraminifera, etc. When allowance is made for this, there is seen to be great uniformity. The substance is mainly a tricalcic phosphate. The distribution of fluorine in the sedimentary phosphates has been made the subject of a special research by M. Carnot,⁽⁵⁾ with the result that it is usually found to be present in proportions not very different from those of a fluor-apatite. The phosphorite deposits of the south-west of France form a notable exception to this rule, as they contain little or no fluorine. The Florida phosphates, on the other hand, often contain more fluorine than is necessary to make apatite. M. Carnot associates the presence of fluorine with the action of sea-water.

Under the microscope the phosphates are seen to be either amorphous or fibro-crystalline. The latter variety takes on stalagmitic, mammillary, and agate-like forms. The fibres give straight extinction, and are positive.

At one time it was generally held that the lower Palæozoic rocks were deficient in phosphates. This view was successfully combated by our lamented friend, Dr. Hicks,⁽¹⁸⁾ in an important paper, published in the *Quarterly Journal* of the Geological Society for 1875, to which Mr. Hudleston contributed an appendix. These authors prove that phosphate-secreting organisms, such as trilobites, abounded in Cambrian times, and that the rocks themselves are by no means deficient in phosphoric acid. The same number of the *Quarterly Journal* contains a paper by Mr. Davis⁽¹³⁾ on a remarkable bed of phosphatic nodules at the top of the Bala limestone in North Wales, which was then being worked, and to which Dr. Voelcker had directed the attention of the British Association in 1864.

The earliest known phosphatic deposits are those which occur in the Cambrian of Nuneaton (Warwickshire), New Brunswick, and Sweden. The Nuneaton deposit occurs a few feet below the *Hyolithus*-limestone. Pebbles of quartz and slate lie in a matrix containing glauconite, oxides of iron and manganese, and 14 per cent. of phosphate of lime.⁽²⁵⁾ The New Brunswick deposit, described by Mr. Matthews⁽²⁹⁾ consists of small round or oval nodules, about one half inch in diameter, set in a sandy matrix of glauconite and quartz. The nodules have always a trilobite-test or a number of fragments near the centre. Under the microscope they are seen to consist of amorphous phosphate containing fragments of trilobites (*Protolenus*), spicules of sponges, and the tests of protozoa resembling foraminifera. It is extremely interesting to note at this very early period the association of nodular

phosphates and glauconite under conditions that have been reproduced throughout the entire series of geological formations down to the present day.

Phosphatic deposits occur at many horizons in the Cambrian and Ordovician rocks of Sweden. They have been carefully studied and well described by Gunner Andersson.⁽¹⁾ The oldest Lower Cambrian deposit belongs to the zone of *Torrellella laevigata*. It is represented by a boulder of the basal conglomerate found on the island of Gotska Sandon. The matrix is composed of glauconite and quartz cemented by calcite. Numerous small and often fragmentary specimens of the characteristic fossil, filled with compact phosphate, occur in the matrix together with pebbles of granophyre and quartz, and nodules of phosphatic sandstone and compact phosphorite. *The quartz grains in the nodules are smaller than those in the matrix.* Andersson especially calls attention to the last mentioned fact, which appears to be not uncommon in phosphatic deposits of all ages.

The Middle and Upper Cambrian periods are represented in Sweden by the lithologically monotonous black shales, usually known as alum-shales, containing beds and lenticles of bituminous limestones. These alum-shales exhibit a rich series of palæontological zones which have been worked out in great detail by the Swedish geologists. Here and there the regular succession of black shales is broken by the occurrence of conglomeratic deposits—I use Andersson's term, but I am by no means sure that nodular deposits would not, in some cases, be more appropriate—and this phenomenon is always associated with a break in the faunal sequence. Moreover, the matrix of these conglomerates contains a mixture of faunas due, in part at least, to the wearing away of older deposits by submarine erosion.

One of the most interesting of the conglomeratic deposits is termed the *Acrothele granulata*-conglomerate. It occurs between the zones of *Paradoxides ölandicus* and *P. tessini* in the island of Öland. The matrix is composed of grains of quartz and glauconite cemented with calcite. Fragments of trilobites and other fossils occur. *Acrothele granulata* is abundant, and the two valves are generally found together. The conglomerate contains green coated pebbles of limestone apparently due to the destruction of an older deposit, but as *Acrothele granulata* occurs in these pebbles it cannot have been much older. Phosphates are present as nodules or pebbles, and also, to a certain extent, as the infilling material of the fossils in the matrix—a fact which proves that the formation of the phosphate was contemporaneous with the deposit.

Another and different mode of occurrence of phosphate is to be found at the junction of the Cambrian and Lower Silurian (Ordovician) in Nerike and Westergothland. The surface of the Cambrian limestone has been worn into pits and depressions as if

corroded by chemical action. The overlying Lower Silurian deposit is a limestone rich in glauconite containing phosphatic fragments. It descends into the hollows of the underlying floor. Corrosion phenomena are not limited to the surface of the Cambrian limestone. They occur in the phosphatic bed, and in overlying limestone; but at these higher horizons they are more tube-like and may be due to boring organisms. The phosphatic fragments are merely detached portions of the underlying floor in which the original carbonic acid has been replaced by phosphoric acid. Lower Silurian fossils occur in the matrix; Cambrian fossils in the fragments. In one case a thin crust of phosphate was observed on the surface of the underlying limestone. Almost everywhere in the Baltic region the Lower Silurian begins with glauconitic deposits which contain phosphates, especially where there are important breaks in the zonal succession.

Andersson recognises two types of phosphatic deposit in the lower Palæozoic rocks of Sweden. One, the conglomeratic, he regards as a littoral facies; the other, represented by the deposit at the base of the Ordovician in Nerike, as a shallow sea facies. The nodules and pebbles of the conglomeratic deposits consist of phosphatic sandstone or compact phosphorite—sometimes also of foreign rocks, such as quartz and granophyre. The phosphatic nodules have probably been formed by some kind of concretionary action from water charged with phosphatic matter derived from brachiopoda, such as *Acrothele* and *Obolus*, which secrete phosphate of lime in their tests.

The fact that the sand-grains in the nodules are, as a rule, smaller than those of the matrix of the conglomeratic beds suggests that the concretionary action did not take place under the conditions which finally prevailed; but it is not necessary to suppose that the nodules were washed into the littoral zone from an area of deeper water, as our author suggests. This fact might be explained by a shallowing of the sea or by an increase in current action and the consequent winnowing away of the finer matrix in which the nodules were originally formed.

In the case of the deposits at the base of the Lower Silurian in Nerike and Westergothland, little or no concretionary action has taken place. The phosphates are merely portions of the underlying limestones in which a substitution of phosphoric for carbonic acid has taken place.

I have referred to this important work by Andersson at some length because it is based on a careful study of the stratigraphical, palæontological, and petrographical characters of the deposits. It is only by a combination of these various methods of research that we can hope to work out the natural history of our sedimentary rocks; a branch of research which I recommend to any of the younger members of the Association who are looking out for work to do.

Phosphatic deposits of Lower Silurian age have recently (1896) been discovered in Tennessee, and have suddenly become of considerable commercial importance.⁽³⁴⁾ The Capitol limestone, a "granular current-formed and hence laminar limestone, showing cross-stratification" has been locally phosphatised and subsequently enriched by the leaching out of the more soluble carbonate. At what date and under what conditions the phosphatisation took place has not been ascertained.

The Upper Palæozoic rocks of this country are not known to contain any important phosphatic horizons; but this is merely a local character, for in Tennessee deposits of great interest and some commercial importance occur in the Devonian. These deposits have been described by Mr. Hayes.⁽¹⁷⁾ They were worked for a few years, but have now been almost entirely abandoned for the more profitable Silurian phosphates above referred to.

At the western margin of the great Silurian inlier, which forms such a striking feature on the geological map of the State, the Devonian period is represented by only 10 or 12 ft. of strata, intercalated between the Silurian limestone below and the Carboniferous shales and limestones above.

Several feet of black carbonaceous shale, representing the edge of the Chatanooga black shale, a well marked Devonian horizon, traceable over about 40,000 square miles and attaining a thickness of several hundred feet in Virginia, separate two phosphatic horizons. The lower is formed of a bedded phosphate, the upper is a nodular deposit containing glauconite—the faithful companion of phosphate in all geological formations from the Cambrian period to the present day.

The bedded phosphates are the most valuable, the richest portion yielding from 70 to 80 per cent. of tricalcic phosphate. Four varieties are described by Hayes under the terms oolitic, compact, conglomeratic and shaly. Speaking of the oolitic variety he says:

"On close examination of the unweathered rock the constituent grains are seen to be small, round or flattened ovules, giving it an oolitic structure. The ovules are bluish black or grey with a glazed surface. Associated with them are many fragmentary casts of very small coiled shells, generally well rounded and with the same glazed surface as the ovules, so that they add to the appearance of oolitic structure. These ovules and casts are embedded in a fine grained or structureless matrix." Under the microscope the ovules and fossil casts are seen to be composed of a light amber or yellowish brown, amorphous phosphate of lime. In addition to the casts of shells there are numerous fragments of corals, and perhaps other organisms, all well rounded. It is clear from the description given by Mr. Hayes that this deposit has many points of resemblance to the phosphatic chalks and to the Tertiary phosphates of Tunis and Algeria.

The Chatanooga black shale separates the bedded phosphates from the nodular layer at the base of the Carboniferous, which is traceable as a phosphatic and glauconitic horizon over an enormous area, occurring in Eastern Tennessee, Middle Tennessee, and Arkansas. "The nodules vary in size and shape from nearly spherical bodies, $\frac{1}{2}$ to $1\frac{1}{2}$ inches in diameter, to irregular flattened ellipsoids sometimes 2 ft. in length, and a third or a quarter as thick. They have smooth surfaces, separating readily from the enclosing matrix, and show no external evidence of organic origin.

. . . Thin sections of the nodules examined under the microscope show them to be composed chiefly of an amber-coloured amorphous substance with grains of pyrite and carbonaceous matter, and in some cases showing a concretionary structure consisting of very minute, radial, globular, and mammillary forms."

Phosphatic nodules are not limited to the well-marked layer at the top of the black shale, but occur on certain horizons in the shale itself, thus reminding one very forcibly of the relation which the Cambridge Greensand bears to the Gault.

These Devonian rocks of Tennessee furnish a striking case of the association of phosphates with areas of minimum sedimentation, accompanied in all probability, in the case of the nodular band, with a certain amount of submarine erosion. Traced towards the north-east into the folded zone of the Appalachians, the Devonian sediments swell out into an important formation, measuring hundreds and even thousands of feet in thickness.

MESOZOIC PHOSPHATES.

The phosphatic deposits of the Mesozoic period are too numerous to mention in detail. Phosphates are present in the Rhætic bone-bed. Nodules and phosphatised fossils occur in the three important argillaceous deposits belonging to the Jurassic period, the Lias, Oxford and Kimeridge Clays.

The Lower Lias, north of the Mendip Hills, about Radstock, furnishes an interesting case of the occurrence of phosphatic nodules in an area of minimum sedimentation. Mr. Tawney⁽³⁸⁾ proved that several ammonite-zones are here crowded together into a small thickness. The deposition of sediment acts on the zonal succession and on the distribution of phosphatic matter very much as a prism acts on the rays of light. It supplies a kind of dispersive power. When this is slight the zonal forms are crowded together, and the phosphates, which would otherwise be scattered through a considerable thickness of sediment, become locally concentrate^d.

A bed of nodules is recorded by Mr. H. B. Woodward⁽⁴⁰⁾ in the Middle Lias of Lincolnshire, and another occurs near the base of the Inferior Oolite (Dogger) in Yorkshire.

On the Continent phosphatic nodules have been recognised in the Upper, Middle, and Lower Lias of Lorraine. The most important deposits occur approximately on the same horizon as that at which phosphates are found at Radstock. The nodules have been microscopically examined by M. Bleicher,⁽³⁾ who has proved that many, especially those of the Lower Lias, have been formed by the accumulation of phosphatic matter round sponges. They are similar to the phosphatised sponges from the Cambridge Greensand described by Prof. Sollas.

Phosphatic nodules probably occur in the Oxford Clay of this country, but I am not able to give actual instances. Mr. Newton and I have, however, described their occurrence, on this horizon, in Franz Josef Land, from the collections made by Dr. Koettlitz during his stay there as a member of the Jackson-Harmsworth expedition. We have pointed out that some of these nodules are largely composed of minute oval bodies similar in form and size to the coprolites observed by Messrs. Strahan, Renard, and Cornet in the phosphatic chalks of England, France, and Belgium. I have since found similar bodies in a large coprolite ($3\frac{1}{2} \times 1\frac{1}{2}$ inches) with spiral groove, collected by myself many years ago from the nodular bed at the base of the Red Crag in Suffolk. This curious occurrence of coprolites within a coprolite may possibly be explained by supposing a large animal to have eaten smaller ones.*

The Kimeridge Clay also contains phosphatic concretions, and a fairly persistent bed occurs at its base in Lincolnshire and Cambridgeshire, marking the junction with the underlying Amptthill Clay.⁽³²⁾

Next in order come the nodular deposits of the *Belemnites lateralis*-zone of Lincolnshire and Yorkshire, described by Mr. Lamplugh.^(23, 24) These include the bed at the base of the Spilsby Sandstone in Lincolnshire, that at the base of the Speeton Clay in Yorkshire, and the interesting compound nodular band in the middle of the Speeton Clay at the top of the *B. lateralis*-zone, where a remarkable change of fauna takes place, due, in part at least, to the intermingling of northern and southern forms.

The records of the Cretaceous period contain still more important nodular deposits. There are, for example, the deposits of Wicken, Potton, and Brickhill, of Lower Greensand age, described by Brodie, Walker, Seeley, Keeping,⁽²²⁾ myself,⁽²⁹⁾ and others; and the remarkable Cambridge Greensand so well studied by Seeley, Fisher,⁽¹⁵⁾ Sollas,⁽³⁵⁾ and Jukes-Browne.⁽²¹⁾ Nodules also occur in the Gault and in the Chalk. A well-marked bed is

* Since this was written Mr. Allen has directed my attention to a paper by Dr. Rust, in which similar oval bodies are described as occurring in certain coprolites from the Gault (*Paleontographica*, Band xxxiv, 1887-1888, p. 184). Dr. Rust considers that two explanations are possible. The oval bodies may be either the coprolites of small animals which have been eaten by the large animal, or the casts of the follicles of the intestines of the larger animal.

found in the *Ammonites mammillatus*-zone at West Dereham in Norfolk, and Folkestone in Kent. This is one of the most widely-distributed phosphatic horizons in Europe, for it is traceable all round the northern part of the Paris basin, and is found also in the basin of the Rhone.⁽⁵⁾

I will not attempt to give an account of these various deposits, but content myself with some general remarks on the phosphatic nodules and the conditions under which they were probably formed. The "nodules"—I use the term in a broad and general sense—include :

- (1) Casts of fossils, such as cephalopods, lamellibranchs, gasteropods, brachiopods, echinoderms, etc.
- (2) Phosphatised sponges and pieces of wood.
- (3) Concretionary masses.
- (4) Well-rounded or sub-angular pebbles of phosphatic sandstone and compact phosphate.
- (5) Bones, teeth, and occasionally coprolites of fish and saurians.

The nodules are mainly composed of phosphate of lime with only small quantities of phosphate of alumina and iron. They invariably contain more or less of the sediment which was accumulating on the sea-bed at the time of, or shortly before, their formation. This sediment may be a quartzose sand, a glauconitic sand, a loam, clay, marl, or organic ooze. It may or may not agree in composition with the matrix in which the nodules are embedded. Not unfrequently the sand-grains in the nodules are smaller than those in the matrix, and different nodules in the same bed may contain sediment of different types. Thus the nodules of the Potton deposit, so far as I have examined them, contain smaller grains than the matrix ; those of the West Dereham deposit, on the other hand, contain grains of the same size as the matrix, and are, in part at least, merely phosphatic concretions in the sand.⁽³⁹⁾

The shapes of the nodules have been determined by many causes ; by the form of the original concretion, by that of the organism of which the nodule is a cast, or around which the phosphate has accumulated, and lastly by chemical corrosion or mechanical attrition. Boring organisms have also affected the forms of many nodules, a fact which clearly proves that they must have lain exposed on the sea-floor.

Mr. Lamplugh has called attention to the complex character of the nodules from the bed which occurs in the middle of the Speeton Clay. Fragmentary casts of ammonites in black phosphate are often encrusted with a brownish phosphate containing grains of quartz and glauconite. Both types of phosphate are sometimes enclosed in a grey limestone which seems also to have had a concretionary origin. All these facts point to the

conclusion that the nodule-beds represent a considerable period of time.

Much discussion has taken place as to the nature of the fossils occurring in the Cretaceous phosphatic nodules. Are they indigenous or derived? I do not propose to enter into this discussion, but I will point out that most of the so-called derived fossils belong to the age of the missing zones. This has been conclusively established by Mr. Jukes-Browne for the Cambridge Greensand, and by Mr. Lamplugh for the two coprolite beds at Speeton, and for the bed at the base of the Spilsby Sandstone.

A more careful determination of the species of other deposits will, as Mr. Lamplugh maintains, probably strengthen this conclusion. Thus, in my paper on the Potton and Wicken phosphatic deposits, I called attention to the extraordinary abundance of rolled casts of *Ammonites biplex*, which I regarded as having been washed out of the Kimmeridge Clay.

Mr. Lamplugh assures me that, at any rate, the majority of the ammonites in question are not *A. biplex*, Sow., but a form of *Okostephanus*, characteristic of the missing beds, and unknown in the Kimmeridge Clay. This I am quite prepared to accept, and in support of it I may mention that the casts of this ammonite are formed of phosphatic sandstone which would not be the case if they had been derived from the Kimmeridge Clay as I supposed.

Everything points to the conclusion that the nodule beds represent long periods of time, and that they occur in areas of minimum sedimentation, or where sediment once formed has been subsequently removed by submarine erosion, probably not long after its accumulation.

But the Cretaceous phosphates do not always occur in the form of detached nodules or as nodular and more or less conglomeratic deposits. There are the remarkable phosphatic chalks of Taplow⁽³⁶⁾ and Lewes⁽³⁷⁾ described by Mr. Strahan, and the corresponding deposits of France which have engaged the attention of Messrs. Lasne,⁽²⁶⁾ de Mercey,⁽²⁷⁾ Cornet, Renard,⁽⁸⁾ and Cayeux.⁽⁷⁾ They consist of brown phosphatic grains, made up of more or less phosphatised foraminifera and prisms of *Inoceramus*, together with fragments of the bones, teeth, scales, and coprolites of small animals. The matrix is a fine calcareous powder largely composed of coccoliths, discoliths, and rhabdoliths. That the phosphatisation is not later than the deposit is proved by the fact that the matrix is calcareous.

The origin of the phosphatic matter has given rise to some discussion. M. de Mercey regards it as having come up from below, M. Lasne attributes it to the influx of rivers bringing down apatite in solution, Messrs. Renard, Cornet, and Strahan, suppose it to have been derived from the organisms of which such abundant traces occur in the deposit. In England I imagine we

shall all accept the last mentioned view, notwithstanding the fact, pointed out by M. Lasne, that the substance is a fluo-phosphate practically agreeing with apatite in composition.

CAINOZOIC PHOSPHATES.

The phosphatic deposits of Cainozoic age remain to be considered. They are the most important from a commercial point of view, for they include the enormous deposits of South Carolina, Florida, Algeria, and Tunis. In this country they are feebly represented by the interesting conglomeratic bed at the base of the Crag, particulars of which together with full references to the extensive literature will be found in Mr. Reid's *Geological Survey Memoir* on the Pliocene.⁽³¹⁾ The curious box-stones containing a Pliocene fauna somewhat older than the Crag deserve more than a passing notice. They are nodules of brown phosphatic sandstone, which usually contain hollow moulds of *Pectunculus* or other calcareous shells.

The origin of nodules of this kind has been satisfactorily explained by Dr. Herman Credner.⁽⁹⁾ In Suffolk they are evidently *remanié*, but in the Oligocene of Saxony precisely similar nodules occur in place. There the phosphatic matter, mainly phosphate of lime, has been concentrated round calcareous shells and fish remains; but the shells have entirely disappeared as in the box-stones of the Crag, and the fish are represented only by the denser and more insoluble portions of their skeletons and by their teeth and scales. Most of the bones have disappeared. As Dr. Credner points out, carbonic acid and ammonia are formed in connection with the decomposition of animal matter. Phosphate of lime is soluble in water charged with carbonic acid, and still more so in water containing ammonium carbonate. A solution of ammonium phosphate is thus formed at the expense of the fish bones, and one of calcium carbonate at the expense of the shells. The shells and the fish embedded in the porous sand thus become surrounded by water highly charged, in the one case with calcium carbonate, in the other with ammonium phosphate. When these two solutions react there is a precipitation of calcium phosphate together with some carbonate, and in this way the loose sand becomes cemented into a hard nodule enclosing, in the one case, a hollow mould of a shell, and in the other case, the more insoluble portions of the fish. The forms of the nodules, their microscopic structure and chemical composition, are all in accordance with the theory, which has been still further strengthened by experiments proving the solubility of fish-bones in a solution of ammonium-carbonate, and the precipitation of calcium phosphate on the addition of a saturated solution of calcium bicarbonate.

In some such way the box-stones in the Crag must have been

formed in an early Pliocene deposit of which they are now the sole survivors. The chemical reactions to which Dr. Credner has called attention have doubtless played an important part in the formation of many other phosphatic concretions.

Phosphates occur in greater or less abundance in many Tertiary deposits, the most important being those of Algeria, Tunis, South Carolina, and Florida. The richest deposits of North Africa occur near the base of the Tertiary Series, associated with marls and limestones. They contain bones and teeth of fishes and reptiles, often of considerable size and in great abundance.⁽²⁾ Apart from this they have a general resemblance to phosphatic chalks. The matrix in which the larger constituents are embedded is made up of brown phosphatic grains, grains of glauconite, a few of quartz, and a calcareous paste. The phosphate occurs as more or less spherical grains, reminding one, as regards form and size, of oolitic grains. I have not been able to recognise with certainty either foraminiferal casts or small coprolites in the specimens I have examined from Djebel Kouif (Algeria), but they have been described as occurring in the corresponding rocks from Tunis.⁽⁴¹⁾ The calcareous paste is composed of minute idiomorphic rhombs of calcite.

These phosphatic limestones have been traced over wide areas in Tunis and Algeria. The individual beds vary in thickness from a few centimètres to three mètres, and the richest contain over 60 per cent. of tricalcic phosphate.

The Tertiary phosphatic deposits of North America are of Pliocene—possibly in some cases of Pleistocene age. They are found at intervals all along the Atlantic coast from Virginia to the extremity of Florida, and it is interesting to note that phosphatic concretions are now forming in the sea off the same coast. The well-known deposit of South Carolina⁽³⁰⁾ consists of irregularly shaped nodules which are sometimes cemented together so as to form masses weighing a ton or more. Associated with the nodules are “many sharks’ teeth and cetacean bones, as well as the remains of the mastodon, megatherium, elephant, deer, horse, cow, hog, musk-rat, and other land animals.” The matrix may be either sand or clay. The deposit rests on sands or marls, the latter containing from 55 to 95 per cent. of calcium carbonate. It is covered by Quaternary sands, clays, or marls. Many of the nodules are phosphatised portions of the underlying marl containing Miocene fossils.⁽¹⁰⁾ The bones of land animals are never found embedded in the phosphate. The nodules are often more or less rounded, and bored by marine organisms. They contain from 25 to 70 per cent. of calcium phosphate.

Apart from its exceptional richness, the South Carolina deposit reminds one very much of that at the base of our own Crag. The Florida deposits are of a somewhat different character. The “rock phosphates” are phosphatised portions of the underlying Eocene

and Miocene limestones. Sometimes the phosphatisation has taken place without serious disturbance of the beds, but more frequently the component materials lie in the utmost confusion. Irregularly shaped boulders of all sizes up to 10 ft. in diameter lie in a matrix of soft phosphate or of clay and sand. In addition to the "rock-phosphates" there are, according to Dr. Dall, also pebble phosphates of Pliocene age. The latter rest uncomfortably on Eocene and Miocene rocks, and give therefore some clue to the age of the phosphatisation.

What was the nature of the phosphatising agent? The descriptions by Eldridge,⁽¹⁴⁾ Wyatt,⁽⁴⁵⁾ and others do not mention any facts pointing to submarine action. It was in all probability, as Darton⁽¹¹⁾ supposes, due to guano-deposits and therefore a surface phenomenon.

We have now passed in review illustrations of the principal types of deposits. Calcium phosphate may be formed by the accumulation of animal remains, by the replacement of carbonic by phosphoric acid through the action of solutions arising from the leaching of guanos, or the decomposition of animal matter, by direct deposition from solutions of calcium phosphate and by chemical precipitation, due to the interaction of solutions containing ammonium phosphate and calcium bicarbonate.

Deposits containing both calcium phosphate and calcium carbonate, such as the phosphatic chalks, may be enriched by the action of water charged with carbonic acid, owing to the comparative insolubility of the former.

The formation of phosphatic deposits may take place on the surface of the land, or beneath the waters of the ocean. In the latter case they appear to be limited to continental borders where deposition is slight, and where current action is often well marked.

From the earliest time down to the present day the physical and chemical conditions under which phosphatic deposits have been formed have remained essentially the same.

My duties as your President are at an end. I thank you most heartily for the honour you conferred upon me in electing me to the post, and I assure you that I shall carry away the most pleasant recollections of my two years of office. I desire also to thank the Officers with whom it has been a pleasure to serve, and to whose enthusiasm and ability the continued prosperity of the Association is so largely due.

My successor needs no introduction. He is not only a distinguished geologist, but also an old and tried friend of the Association, and we are all delighted that he has consented to act as our President. I have now great pleasure, mingled with regret that my own term of office is over, in asking Mr. Whitaker, President of the Geological Society, to take the Chair.

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ORDINARY MEETING.

FRIDAY, FEBRUARY 2ND, 1900.

W. WHITAKER, B.A., F.R.S., President, in the Chair.

George F. Brown and R. W. Gray were elected Members of the Association.

There being no further business the meeting then terminated.

ORDINARY MEETING.

FRIDAY, MARCH 2ND, 1900.

W. WHITAKER, B.A., F.R.S., President, in the Chair.

George Gibbens was elected a member of the Association.

A paper was read by Mr. F. A. Bather, M.A., F.G.S., on "Wind-worn Pebbles in the British Isles."