On Natural Phosphates.*

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When your President and Treasurer did me the honor to request me to read a paper on "Phosphates" before the Ottawa Field Naturalists' Club I hesitated in complying "Phosphates" in a general way, as we employ the word in this locality, implies the crystallized Mineral Apatite so abundant in certain parts of our Laurentian formation. The good work done by the Geological Survey, has from time to time, through its officers, kept us well informed of the localities and peculiarities of occurence of the Canadian apatite, by valuable contributions from the pens of Sir Wm. Logan, Sterry Hunt, Vennor, Dr. Geo. Dawson, Torrance, Dr. Robt. Bell and others. At the present time, I understand that Mr. Ingalls also, who has been in charge of a special study of our Canadian apatite fields, is about to terminate and publish his preliminary report, so with deference to his opportunities and approaching publication, I could not presume to undertake a paper purely on Canadian phosphates or apatites as was proposed, but thought it might be acceptable to our members here to give their attention to a more extended and general consideration of natural mineral phosphates, and hence the title of my paper this evening, instead of being "Canadian Apatite" is "Natural Phosphates" in a more general way. My present occupations prevent me from giving much time and study to the preparation of this work, but if by some generalizations of facts we can awaken a healthy discussion and exchange of ideas, my humble attempt will not have been useless.

Natural phosphates owe their commercial value to the proportion of phosphoric element contained in them, and are employed as raw material for the manufacture of phosphatic fertilizers, being also sometimes applied in the natural and raw state direct to the soil by the farmer. They are also in demand for the manufacture of phosphorus, baking powders, and some other chemical products. By far the greatest demand for them, however, is made by the manufacturers for agricultural requirements, and this demand is yearly increasing at a very rapid rate. The occurence of natural phosphates presents the most varied and interesting modes of formation, as may be surmised by finding their deposits not only in nearly every geological system but in many different groups of the same system: Now in beds, which may be, have a fresh water or marine origin; now appearing as hardened conglomerate or rocks; and sometimes as sand and loose gravel: then again in vein formation or pockets, sometimes amorphous, at other times crystalised.

In the matter of texture, color and other physical characters, we find the same endless variation.

The origin of the demand for these phosphatized products is comparatively of recent date. It was only in the commencement of the present century that crushed bones were employed as a fertilizer in agriculture, and, strange to say, only then on account of the gelatine or organic matter they might contain.

The following curious statement, which appeared in a scientific journal in the year 1830, apropos of the employment of crushed bones in England, exposed the ignorance on the subject at that day, and read as follows: "As to the earthy matter or phosphate of lime contained in the bones, we may disregard it. It is insoluble and indestructible, and *canno serve as a manure*, even in a damp soil, and in immediate contact with the rootlets of the plant."

The suggestion of Liebig, to treat the bones with sulphuric acid, opened a new era to the utilisation of phosphatic materials in agriculture, and the manufacture of artificial manure was soon established.

The illustrious Eli de Beaumont thus expressed himself with regard to the commencement of the mining of mineral phosphates. "Colbert has said that France would be lost for want of forests, and everyone perceives that without coal, his prediction would soon be accomplished.† In his day, one would have failed to comprehend how a great country might disappear."

Natural Phosphatic Deposits.

These valuable provisions of nature are the result of various causes and agencies familiar to the geological observer, and their contained phosphoric acid is mostly due to animal life; and when we say "due" to animal life we wish to imply that animal life is the assimilating and concentrative medium of *pre-existing* phosphoric acid. Whether as sea and fresh water shells, as fish and animal bones, as excreta of birds and saurians, etc., animal organisms have been from the beginning of life, and still are, the silent but mighty laboratory of nature, never resting to collect and store up the dispersed molecules of phosphoric acid. Among such are the guano beds of recent epochs, coprolitic deposits, bone beds, shell beds, etc.

Nature's operations of bringing these materials or their debris together to form whole geological areas are equally varied, but the esturaries and depressions of the sea bottoms of the different and respective geological periods are recognized to have been the receptacles or store houses of these wonderful supplies. A curious disposition to concretionary action, displayed by nuclei of certain organisms to absorb and accumulate phosphatic matter, with which the ancient seas abounded, is more easily seen in its effects than explain ed.

* Paper read before the Ottawa Field Naturalists' Club.

† Jean Baptiste Colbert, born 1619, Minister of Finance to Louis XIV.

Such is the origin of many odd species of nodules, some varities of which exist in immense quantities.

The abrupt or imperceptible, but never ceasing operations of geological rearrangement, follow the aforementioned accumulations, and we then have new forms of mineralized phosphatic matter, giving rise to conglomerates, breccias, phosphatic limestone, shells and marls, sandy and ablation deposits, etc., and most of the known natural deposits of mineralized phosphate display examples of two or more of these products. For instance, the perplexities experienced just now with some of the exploratory workings of the lately discovered Florida deposits, are chiefly occasioned by the character of these beds containing boulders, and nodules from pea size to masses of several hundred pounds in weight, fish bones, shark teeth and fossil bones, in fact *debris* from several geological epochs, each of these materials naturally varying in their purity, and therefore their commercial value, so that the more successful enterprises may be looked for where regular and homogeneous deposits occur, or some cheap and efficient mechanical means are applied for the separation of the marketable products from the less valuable or worthless intermixtures.

The classification of natural phophates of lime is, as remarked by Dr. Penrose in Bulletin No. 46 of the U.S. Geological Survey, "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 blend into one another, thus often rendering it uncertain to which class a special deposit should be referred;" and he adopts the following classification, based mainly on the chemical composition of the deposits, and grouped under the headings thus:—

MINERAL PHOSPHATES.	*Apatites.*	*Fluor-Apatites.*
	Phosphorites.	*Chlor-Apatites.*
ROCK PHOSPHATES	*Amorphous Nodules.*	*Loose Nodules cemented (conglomerates).*
	Phosphoric Limestone Beds.	
	Guanos.	*Soluble Guanos.*
		Leached Guanos.
	Bone Beds.	

We shall recognize, as we proceed with the study of the various phosphatic deposits formed during the different geologic periods, that by far the greater part owe their origin to animal or organic remains, and we shall see that as soon as the organic compounds of a guano, for example, are dissipated and resolved into their elements, we may consider that the residual products, to all intents and purposes, revert to the mineral state, in accordance with the familiar expression "earth to earth."

We pass over, for the present, the guano of various localities, which however, will be observed to lie mostly within 10 to 20 degrees of the Equator.

We should remember, however, that this product has probably obtained its zenith, both as to quality and quantity, and must cede its commercial importance ultimately to the mineral resources of phosphoric acid, which are before us for our more particular consideration.

We shall find the diagram on the wall, which shows the approximate geological position or age of the different phosphate deposits, very useful to our present purpose, and we will commence with the more recently formed or mineralized products:—

Occurrence of Natural Phosphates in the Geological Epochs.

Post Tertiary or Quarternary System.

- True guanos.
- Crushed or "leached" guanos.
- West Indian and Pacific phosphates.

Tertiary System:

- West Indian Rock Phosphates.
- Nassau or Lahn nodular concretions.
- Suffolk Coprolites in the Red crag and Coralline crag; (reposing on Lower Eocene).
- South Carolina beds, resting upon Eocene.
- Deposition of Florida phosphate, *debris* and organic remains.
- North Carolina, overlying Eocene marl.
- Fundamental rock of Florida phosphate deposits.
- Clays and *debris* of Bordeaux phosphates.

Cretaceous System:

- Belgian (Liege) Hesbaye nodules.
- American Alabama amorphous nodules.
- New Jersey marls.
- Belgian (Mons) Ciply nodules (Mæstricht beds).
- Somme deposits, arenaceous and nodules.
- Russian "Samorod" nodules Desna-Don.
- Cambridgeshire and Bedfordshire Coprolites.
- French nodules of Ardennes, Meuse.
- French nodules of Montpellier and Bellegrade.

Oolitic or Jurassic System.

- Bordeaux Phosphorites and nodules overlain by Tertiary (Eocene) clays and *debris*.
- Algerian Phosphates.

Triassic System.

- Highly phosphatic beds, (between Trias and below Lias), containing exuviæ of huge reptiles as well as remains of fish and crustaceans.

Permian System:

- (Appearance of Reptilia.)

Carboniferous System:

- (Appearance of Amphibia.)

Devonian or Old Red Sandstone:

- Highly phosphatic beds in junction with Lower Carboniferous.
- Highly phosphatized bed in Shropshire, containing oldest known remains of vertebrate life associated with crustaceans.

Silurian System:

- (Appearance of Vertebrata.)
- Welsh Bala beds; Berwyn Phosphate mine.
- Lingula flags (Quebec), 40% Tribasic.
- Angers slates (France).
- Phosphate limestone of Kentucky.
- Logrosan (Spain) Phosphorites. (Apatites?)
- Caceres (Spain) Phosphorites.
- Portugal Phosphorites.

Cambrian System:

- (Appearance of Protozoa, Mollusca, Annuloida and Crustacea.)

Laurentian System:

- Canadian Apatite.
- Norwegian Apatite.

Thus at the present time, we have mineral phosphates of lime in process of formation, and principally known in commerce as "Grust Guano."

Looking at the chemical composition of average bird guano, we find it to be composed of the following constituents:—

Moisture........	15.8
Organic matter and Ammoniacal Salts....	52.5
Phosphates of Lime......................	19.5
Phosphates of Iron and Alumina.........	3.1
Alkaline Salts......	7.6
Silica and Sand..................	1.5
	100.0

This typical analysis is from the average of 15 samples, made by Nesbit on the Chinchas inland guano.

An elementary knowledge of chemistry will assist us to perceive what a large proportion of the above constituents will be leached out by water, or dissipated by prolonged exposure to ordinary atmospheric influences, especially when we remember that the organic matter above mentioned comprises uric, oxalic and phosphoric salts of alkalis and ammonia, and even about one-third of the phosphate of lime is found to be soluble in water. Given a deposit of guano on a limestone soil or rock, and it is readily perceived that every shower will contribute to the steady but continual process of the transmutation of the carbonate of lime into phosphate of lime in consequence of the discharge of the weaker carbonic acid by the stronger phosphoric acid.

The exhausted guano then becomes phosphatic in distinction to being nitrogenous and ammoniacal ("leached"), and the subjacent limestone undergoes a metamorphosis, by a double decomposition, into phosphate of lime. If the absorbing limestone is pure, the phosphate of lime thereby formed will be correspondingly pure; and on the other hand, if the calcareous base is intermixed with clay or sand, or ferruginous material, the newly formed product will contain alumina, silica, oxide of iron, etc., in like proportions.

Such has been the undoubted origin of the deposits of Aruba rock phosphates, samples of which are on the table, and which are typical of this kind of metamorphosis, and will serve to illustrate many similarly formed deposits, notably those of Curacao, Sombrera, Navassa and Redondo, (in which latter case the subsoil must have been aluminous, since the mineral is a phosphate of alumina).

In some cases, the phosphatic principle may have been derived from animal *debris*, such as bones.

The composition of animal bones varies somewhat, according to the animal furnishing them, and even with the particular part of the same animal, but the following analysis, expressed in 100 parts, may be taken as an average:—

	Green Bones.	Bone Ash.
Moisture .... } Organic matter....... }	33 (gelatine)	
Phosphate of Lime.....	56	} 70/75%
Phosphate of Magnesia..	3	
Carbonate of Calcium...	3	
Alkaline Salts.........	4	
Silica..................	—	

The bones of birds are even richer in phosphoric acid than those of mammals, but bones of the *Amphibia* and fish contain less than those of birds and mammals.

Amongst other animal organisms rich in phosphoric acid or phosphate of lime, may be mentioned certain shell fish, or rather their shell remains, notably the shells of *Lingula* and *Orbicula*, which consist for the greater part of phosphate of lime, and are found in accumulated beds in the Lower Silurian rocks, being thus described by Sir Wm. Logan (Geology of Canada, 1863). Those coming from the Chazy formation at Alumette Island left after calcination, 61% of fixed residue, consisting of:—

Phosphate of Lime	85.7
Carbonate of Lime......................	11.7
Magnesia................................	2.6
	100.0