IV. On the Existence of Phosphoric Acid in Rocks of Igneous Origin. By George Fownes, Ph. D., Chemical Lecturer in the Middlesex Hospital Medical School. Communicated by Thomas Graham, Esq., F.R.S., &c. &c.

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THE important although obscure functions attributed to the elementary body phosphorus, both in the vegetable and in the animal kingdoms, and the well-known fact that rocks of nearly every description afford on disintegration soils more or less capable of supporting the life of plants, and from which consequently phosphoric acid cannot possibly be absent, seemed to render a search for that substance in rocks of igneous origin generally very desirable, because if there found, an easy and satisfactory explanation of the origin and first source of the element in question would be given. As I am not aware that any direct researches on this subject have yet been made, or at least placed on record, I venture to submit to the notice of the Royal Society the results of a few experiments made by myself, which, so far as they go, resolve the question in the affirmative.

The first substance tried was the fine white porcelain-clay of Dartmoor, Devon, the result of the disintegration of the felspar of the granite of that district. This is one of the chief components of porcelain and of the finer kinds of English earthenware, and was found on analysis to correspond very closely in composition with that of the material employed in the manufacture of the Sèvres porcelain. It was thought that phosphoric acid, if present, would be in combination with a portion of the alumina; and as the phosphate of that earth is readily soluble in dilute mineral acids, while the silicate offers great resistance to these agents, mere digestion with acid would suffice to extract the whole, or the greater part of the phosphate, which could be afterwards precipitated by an alkali, and examined.

With this view, 1000 grains of the clay were boiled during several hours in a flask with a quantity of pure dilute hydrochloric acid; a large bulk of distilled water was then added, and the whole allowed to rest until perfectly clear. The acid liquid was then carefully decanted from the undissolved clay, evaporated in a porcelain basin to a small bulk, and precipitated by a slight excess of pure ammonia. The scanty, reddish precipitate obtained, which consisted chiefly of alumina and oxide of iron, was collected upon a little filter, thoroughly washed with distilled water, dried, and ignited. It was next reduced to fine powder, and mixed with an equal weight of pure silica in a finely-divided state, and six times as much anhydrous carbonate of soda. This mixture was heated to fusion in a platinum crucible. When cold, the melted

mass was acted upon by boiling water, and the soluble and highly alkaline portion separated by a filter from the insoluble silicate of alumina. The solution was mixed with excess of nitric acid, evaporated to dryness, water added, and the product filtered. The liquid thus obtained was divided into two portions; one of these was carefully neutralized by a little ammonia, and mixed with a few drops of solution of nitrate of silver; a distinct yellow precipitate appeared, which was freely soluble in dilute nitric and in acetic acids. The second portion was mixed with excess of ammonia and some hydrochlorate of ammonia, and a few drops of solution of sulphate of magnesia added. After a short interval, a crystalline, granular, white precipitate, the ammonio-magnesian phosphate, made its appearance, which increased in quantity by agitation.

This experiment, which demonstrates the presence of a small quantity of phosphoric acid in the clay, in a most unequivocal manner, was several times repeated with a like result. The purity of the acids, carbonate of soda, and other materials employed, were rigorously tested, and filtration through paper of the original acid liquid purposely avoided, lest a trace of earthy phosphate should have been dissolved from the paper.

The porcelain-clay is extracted from the disintegrated granite by mere washing with water, and subsidence, and the water of the district in which it is found is, in all probability, exceedingly pure. It was thought worth while, however, to examine in the same manner the decomposed rock which had not been subjected to any artificial treatment, and a specimen taken by myself from the quarry was chosen for the purpose. The result showed the presence of phosphoric acid as in the clay, and apparently to about the same extent, allowance being made for the quartz-grains, mica, &c.

In the examination of unaltered felspar, I failed, unfortunately, in getting a conclusive result. The mineral, although reduced to very fine powder by trituration in a mortar of Swedish porphyry, was found to be so hard and dense as to resist completely the action of the acid at a boiling temperature. An insignificant quantity of oxide of iron was dissolved out, in which no phosphoric acid could be detected. 200 grains of the powdered felspar were then fused with a large excess of carbonate of soda; the mass was treated with water, filtered, the solution supersaturated with nitric acid, and evaporated to dryness; water was poured upon the residue, and the whole placed upon a filter. The solution was then examined, as before, for phosphoric acid, but with an indistinct and doubtful result. Too small a quantity of the felspar had been used, and the mass of nitrate of soda present interfered too seriously with the action of the tests to render their evidence of any value. A far better mode of investigation would be, to act upon the powdered mineral with hydrofluoric acid, in the manner recommended by some analysts in the examination of natural silicates containing an alkali; not being, however, in possession of the necessary platinum vessels, I was obliged to abandon the attempt.

Other substances were then tried with very decisive results. The method of proceeding adopted was very much the same as that already described. The minerals were very finely powdered in the porphyry mortar and boiled, as before, with dilute hydrochloric acid. All were much more readily attacked than the porcelain-clay, and yielded solutions containing a large quantity of alumina and oxide of iron. The liquid was separated from the insoluble part by decantation, evaporated nearly to dryness, water added, and then an excess of ammonia. The copious, bulky precipitates obtained were washed and digested in dilute acetic acid, which has the property of dissolving with great facility both oxide of iron and alumina, while it leaves untouched the phosphates of those bases. The undissolved residue was dried, ignited, fused with silica and carbonate of soda, and the product examined in the manner already described. The addition of silica is indispensable to the retention of the whole of the alumina in an insoluble condition. Phosphate of alumina is not decomposed by carbonate of soda by fusion, or only partially, and is besides soluble in an aqueous solution of that salt.

The results of the examination may be thus briefly stated:—

Dark grey vesicular lava from the Rhine, used at Cologne as a building-stone, being exceedingly strong and durable.—Enough phosphate of soda was extracted from 1000 grains of this substance to exhibit the yellow phosphate of silver, and the phosphate of magnesia and ammonia upon a large scale. The phosphoric acid might be said to be here very abundant, that is, comparatively speaking. No attempt was, however, made to estimate it quantitatively, as the operation is attended with great difficulty, and the result of doubtful value from the unavoidable errors of experiment bearing too large a proportion to the quantity of the substance.

White trachyte of the Drachenfels, near Bonn, on the Rhine.—This rock is apparently as rich in phosphoric acid as the preceding; nothing could be more distinct and satisfactory than the indications of the reagents.

Dark red, spongy, scoriaceous lava from Vesuvius.—This was tried in the same manner, and yielded abundance of phosphoric acid.

Compact, dark green basalt, or toadstone, from Cavedale, Derbyshire.—This substance was very tough, and difficult to powder. Enough phosphate of soda was, however, extracted from 750 grains of the rock to exhibit very unequivocally the characteristic tests described.

Dark blackish-green, extremely strong basalt from the neighbourhood of Dudley, termed *Rowley-ragg*, gave a very similar result. Phosphoric acid is not so plentiful in these substances as in the lava, although its presence is easily rendered evident.

An ancient porphyritic lava containing numerous crystals of hornblende, from Vesuvius.—The phosphoric acid was here very distinct, but not so abundant as in the more recent lava.

A specimen of tufa, or *volcanic mud*, also from Vesuvius, was found to contain phosphoric acid in notable quantity.

These were all the substances tried; they were taken, as is at once seen, indiscriminately from igneous formations of many localities and many ages, and they all, with one doubtful exception, in which practical difficulties interfered with the inquiry, yielded phosphoric acid. It is highly probable, therefore, that this substance is a very usual, although small, component of volcanic rocks.

It is not unlikely that the remarkable fertility possessed by soils derived from the decomposition of some varieties of lava may be, in part at least, due to the presence of this phosphate in the original rock, although much must of course be ascribed to the alkali, especially potash, which these substances contain, and which is gradually brought by the continued process of disintegration into a soluble state. be little doubt that the matter erupted from time to time from the interior of the earth, in a state of fusion, is thus destined to renew the surface from which the more valuable and more soluble components have gradually been removed by the action of water and other causes constantly in operation. If it should hereafter be found on a more extended investigation that phosphoric acid, although present in all igneous rocks, is most abundant in those of modern date, the fact will thus receive an explanation, the more ancient lavas having been most changed by the slowly-acting and almost imperceptible causes in question. One might be tempted to consider lava as a kind of fundamental material, from the subsequent alteration of which all others are derived, and expect it to contain, here and there at least, traces of all the elementary bodies known, even those most rare. In the present case, it cannot be altogether devoid of interest to trace to its first source the enormous quantities of phosphoric acid, for the most part locked up in a temporarily insoluble condition in the vegetable and animal kingdoms, and in the various strata of calcareous and sedimentary deposits, in the formation of which organized beings have played so prominent and so important a part.

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