XLI.—*Chemical Researches on some new and rare Cornish Minerals.*

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I. *Hydrated Cerous Phosphate.*

The hydrous phosphate which forms the subject of the present communication, occurs as a thin crust closely investing a quartzose matrix. This crust is made up of very minute crystals, generally occurring in fan-like aggregations of single rows of prisms. The faces of union of these groups are parallel to the larger lateral prismatic planes. Occasionally the structure is almost columnar, or in radiating groups, presenting a drusy surface and a general appearance somewhat resembling that of wavellite. The mode of attachment of the crystals is such that only one of the end-faces of the prisms can be studied fully. It would appear that the crystals belong to the oblique system, and are prismatically developed forms. The end-face, 001, presents the aspect of an unmodified rhomboid; occasionally, however, its diagonally opposite acute angles are replaced. Whether the appearances then presented by the crystal are due to a truncation of the solid acute angle, or to a bevelling of the acute prismatic edge, it is difficult to say, owing to the microscopic size of the crystals, and their parallel mode of aggregation.

The plane of cleavage most easily obtained is parallel to the end-face 001; this cleavage is very perfect. Other cleavages are obtainable; one parallel to the plane previously referred to as replacing the acute solid angles or acute prismatic edges of the crystal, the other parallel to the larger lateral prismatic planes. The crystals are fragile.

Other surfaces besides the faces of union and the flat cleavage planes are occasionally shown in breaking a crystal; these surfaces indicate a distinctly conchoidal fracture.

As seen under the microscope, the crystals are transparent to translucent.

The general lustre of the mineral is vitreous. But the conspicuousness of the end-faces with a brilliant pearly lustre, causes the general aspect of the grouped crystals to be splendent. The crystals are doubly refractive, but owing to their minute size, I have not yet obtained a specimen capable of affording indications as to the number and direction of the optic axes. For the same reason they have not been examined as to the presence or absence of pleochroism.

The colour of the mineral is a pale smoke-grey, with a faint tinge of flesh-red. The streak and powder are white.

The hardness of the mineral slightly exceeds 3. It distinctly abrades a cleavage-surface of calcite. The density of the mineral has not been determined with exactness. In an experiment with a small fragment, the density was found to be 3·14, but the quantity of the material was quite insufficient for anything more than an approximative result.

The following are the blowpipe reactions of the new species. Heated alone in a tube, the mineral becomes opaque, and gives off water, having a very faint acid reaction. Exposed to the oxidising flame, the mineral becomes reddish in colour, and then presents the difficult solubility of cryptolite. It melts and dissolves completely in borax; in the oxidising flame the colour of the bead is opaline and orange-yellow when hot, and colourless or slightly amethystine when cold.

Half of my specimen of the mineral was carefully removed from the gangue, and then picked over with the aid of the microscope. Portions submitted to qualitative analysis shewed the presence of phosphoric acid, lime and water, also of an earth resembling alumina. But it was soon found that this earth, as precipitated by ammonia, became orange-brown on ignition, and dissolved in hydrochloric acid with evolution of chlorine. The chloride thus formed when heated with oil of vitriol, gave a soluble sulphate, which was at once precipitated by potassic sulphate as an insoluble double salt. In the solution of the chloride, oxalate of ammonia produced a copious pale pink precipitate, curdy at first, but rapidly becoming crystalline. From these indications and the blowpipe reactions, it was evident that the earth resembling alumina was in reality the mixed hydrates of the metals of the cerium group.

The results of the quantitative analyses were perfectly accordant and satisfactory.

A few words as to the processes of separation adopted may not be out of place here.

The mineral was finely pulverised, and the water determined by the loss on ignition. The residue was gently warmed with a few drops of oil of vitriol. When complete decomposition had been thus effected, the mass was extracted with boiling water; the insoluble residue was insignificant, but was collected and weighed. To the clear, warm solution, containing phosphoric acid, the sulphates of cerium and calcium, and some excess of the sulphuric acid employed, ammonia was added, till a barely perceptible cloudiness was produced, then a few drops of oxalic acid were introduced, and, lastly, excess of oxalate of ammonium. After standing 12 hours, the precipitated oxalates of cerium and calcium were collected on a weighed filter, washed, dried, weighed, ignited, and then weighed again. The ignited mass, which was of a lemon-yellow* tint, was then dissolved in hydrochloric acid, the hydrates of the cerium metals precipitated by ammonia, and then ignited and weighed. The lime was precipitated as oxalate from the filtrate. The phosphoric acid was finally removed as the ammonio-magnesium salt, from the liquid filtered from the original oxalates. In a second analysis the phosphoric acid was first of all separated by the molydic acid method.

The following are the details of the analytical results :—

I.	·534	gramme	gave	·241	gramme	$Mg''_2P_2O_7$.
I.	·534	„	„	·051	„	$Ca''CO_3$.
II.	·33	„	„	·05	„	H_2O.
II.	·33	„	„	·178	„	Ce''_3O_4.
III.	·246	„	„	·024	„	$Ca''CO_3$.
III.	·246	„	„	·036	„	H_2O.
III.	·246	„	„	·136	„	Ce''_3O_4.
III.	·246	„	„	·108	„	$Mg''_2P_2O_7$.

The following percentages are deduced from the above numbers :—

	I.	II.	III.
$Ce''O$	—	51·21	52·52
$Ca''O$	5·34	—	5·49
P_2O_5	28·88	—	28·08
H_2O	—	15·15	14·71

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* The oxalates of the cerium metals, if a little oxalate of calcium be present, exhibit this lemon-yellow colour on ignition.

† The small quantity of insoluble gangue, mainly silica, left on dissolving the mineral for analysis has been deducted in all cases.

The following are the mean percentages:—

$Ce''O$	51·87
$Ca''O$	5·42
P_2O_5	28·48
H_2O	14·93
	100·70

Assuming the calcium to be an essential and not intruding element in the mineral (and the strict accordance of the two determinations of calcium made in different parts of the specimen confirms the assumption), we may deduce from the analytical results the formula

$$5Ce''O.Ca''O.2P_2O_5+8H_2O.$$

This formula demands the following percentages:—

	Theory.		Mean of Experiments.
$5Ce''O$	540	52·73	51·87
$Ca''O$	56	5·47	5·42
$2P_2O_5$	284	27·73	28·48
$8H_2O$	144	14·07	14·93*
	1024	100·00	100·70

Adopting the older atomic weights, the mineralogical formula may be given thus:—

$$(\dot{\mathrm{Ce}}_{\frac{5}{6}}\dot{\mathrm{Ca}}_{\frac{1}{6}})_3\overset{\cdot\,\cdot}{\overset{\cdot\,\cdot\,\cdot}{\mathrm{P}}}+4\dot{\mathrm{H}}.$$

The oxygen of the base, acid, and water shows the ratio

$$3 \quad : \quad 5 \quad : \quad 4$$

resembling in this respect scorodite and possibly hureaulite also, if part of the water in the latter mineral may be regarded as basic.

The present species may be easily distinguished from all the allied minerals by several of the characters already given. The occurrence of a British mineral rich in cerium is, of course, of considerable interest, but the complete novelty of the species as a *hydrated* phosphate of the metal attracts particular attention, the

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* The excess of water is perhaps due to hydrofluoric acid, but the proportion of fluorine present is very small, and the formula which its occurrence suggests is not confirmed by the determinations of P_2O_5 or CeO. By analogy the formula which might be proposed is—$3CeO,P_2O_5 + 4aq. + \frac{1}{3}CaF_2$.

known phosphates, cryptolite, monazite, &c., being, when quite unaltered and pure, completely anhydrous. Calcium also does not occur in cryptolite, and in monazite never exceeds 1·5 per cent.

The mineral is a Cornish species. It was found by Mr. Talling, of Lostwithiel, some time ago.

It may be as well to add that the mineral under review exhibits no signs whatever of being an altered substance. It occurs in a copper lode on quartz and killas.

II. *Hydrated Calcium-aluminic Phosphate* (?).

I lately obtained from Mr. Talling a mass of quartz crystals mixed with iron- and copper-pyrites, partly coated with childrenite, and containing, moreover, in numerous cavities and fissures a light and soft white powder. This powder was found to contain lime, alumina, phosphoric acid, and water, together with a trace of iron. When free from impurities it presents the appearance of a pearly powder of perfect whiteness, rather difficultly soluble in acids. Under the microscope it is seen to consist of minute acicular crystals, transparent to translucent, and fragile. Sometimes these crystals are sparsely scattered in irregular stellate groups upon the quartzose matrix. By very careful selection under the microscope, a sufficient amount of the pure white crystals was obtained for analysis, but the quantity at my disposal was quite inadequate for a determination of density, while the physical condition of the substance precluded me from ascertaining its exact hardness.

The mineral gives no colour (unless childrenite be present) to the borax bead. Heated alone it incandesces and becomes opaque. After ignition it gives a distinct blue colour with nitrate of cobalt.

The following are the results (after deduction of insoluble gangue,* &c.) of the quantitative analysis. The phosphoric acid was determined by the molybdic acid method:—

·1875 gramme gave
·0225 gramme H_2O
·068 „ $Ca''O$ (weighed caustic)
·042 „ $Al_2'''O_3$
·089 „ $Mg''_2P_2O_7$

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* Chiefly silica, which I have assumed to be an intruding material, perhaps without sufficient reasons Yet, while the lime, alumina, and phosphoric anhydride exhibit a definite and constant ratio, the silica does not.

These results lead to the following oxygen ratio of base, acid, and water—

$$6 : 5 : 3$$

This is the ratio of dufrenite, and of several other native phosphates.

The experimental percentages are as follow :—

$Ca''O$	36·27
Al'''_2O_3	22·40
P_2O_5	30·36
H_2O	12·00
	101·03

These numbers lead to the formula

$$3Ca''O.P_2O_5.Al'''_2O_3 + 3H_2O,$$

which may be thus abbreviated by the adoption of the lower atomic weights and the mineralogical notation—

$$\overset{\cdot}{\mathrm{Ca}}_3\overset{\cdot\,\cdot}{\overset{\cdot\cdot\cdot}{\mathrm{P}}} + \overset{\cdots}{\cancel{\mathrm{Al}}}_2 3\overset{\cdot}{\mathrm{H}}.$$

The theoretical percentages demanded by this formula are

$Ca''O$	35·97
Al'''_2O_3	22·06
P_2O_5	30·41
H_2O	11·56
	100·00

The only known mineral phosphate resembling the present species is one examined by Damour in 1853, and believed by him to be a hydrous phosphate of alumina and lime. I am not aware that any quantitative analytical result was obtained by Damour, save a determination of water in the mineral. This amounted to 12·7 per cent. Damour's phosphate was found in the diamond sands of Bahia. It occurred in rounded pebbles. Its hardness exceeded that of glass, and in other physical characters it differed widely from the species now described. Our present mineral is from Tavistock, Devonshire: the specimen in the British Museum is placed with wavellite.

III. *Hydrated Plumbo-cupric Arsenate.*

A Cornish specimen, supposed to be arsenate of copper, was submitted to special examination on account of its high density and strong resinous lustre. Qualitative analysis at once revealed the presence of lead. Although many mineral species are double compounds of copper and lead (caledonite, chileite, linarite, vauquelinite, &c.), yet I am not aware of any double arsenate of lead and copper, definite and constant in composition, having been yet discovered and described. The following details concerning such a compound may therefore not be without interest. I may state at the outset that I propose the name "Bayldonite" for this species, in honour of my friend and former colleague, Dr. John Bayldon.

Bayldonite occurs in minute mammillary concretions, having a drusy surface: the structure of the masses is often somewhat reticulated after the manner occasionally observed in certain travertines.

The fracture is slightly conchoidal, uneven. Translucent on the edges. The lustre is more or less distinctly resinous. Colour grass-green to blackish-green. Colour of the powder siskin-green to apple-green.

The hardness of Bayldonite is about 4·5.

Its specific gravity is 5·35.

It gives in the oxidising flame a blue borax bead. On ignition it gives off water only, and becomes black. On charcoal it readily fuses to a black bead, and then suddenly gives off fumes of arsenic with deflagration: a metallic bead (a hard white alloy of lead and copper) remains on the charcoal. Nitric acid is the best solvent for Bayldonite: by the aid of heat and subsequent addition of hot water, the finely powdered mineral dissolves, though with some difficulty; a residue, chiefly consisting of quartz and amounting to from 1 to 3 per cent., remaining unacted on.

The analyses were made as follows:—The excess of acid in the nitric acid solution of the mineral having been removed, the lead was precipitated by means of sulphuric acid and the subsequent addition of a little alcohol. From the filtrate from the sulphate of lead the alcohol was removed by evaporation to dryness. To the nitric acid solution of this residue ammonia was added in excess, and then magnesia-mixture: the precipitate was collected on a weighed filter. In the filtrate, after suitable treatment, the copper was determined. In one case the arsenic acid was precipitated by molybdate of ammonia. The following are the analytical results :—

I. ·617 gramme gave ·249 $Pb''SO_4$.
I. ·617 „ „ ·193 $Cu''O$.
I. ·617 „ „ ·026 H_2O.
II. ·62 „ „ ·2565 $Pb''SO_4$.
II. ·62 „ „ ·189 $Cu''O$.
II. ·62 „ „ ·3225 $Mg''_2(NH_4)_2 2AsO_4 + H_2O$.
II. ·62 „ „ ·031 H_2O.
III. ·773 „ „ ·32 $Pb''SO_4$.
III. ·773 „ „ ·409 $Mg_2(NH_4)_2 2AsO_4 + H_2O$.
III. ·773 „ „ ·038 H_2O.
IV. 1·05 „ „ ·044 H_2O.

The above numbers correspond to the following percentages :—

	I.	II.	III.	IV.
$Pb''O$	29·64	30·45	30·31	—
$Cu''O$	31·28	30·48	—	—
*As_2O_5	—	31·49	32·02	—
H_2O	4·21	5·00	4·92	4·19
		97·42		

The mean experimental percentages are therefore as follow :—

$Pb''O$	30·13
$Cu''O$	30·88
As_2O_5	31·76
H_2O....................	4·58
Ferric oxide, lime and loss..	2·65
	100·00

These numbers lead to the oxygen ratio, between base, acid, and water, of

4 : 5 : 2 nearly,

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* In Analysis II. the ammonio-magnesian arsenate was specially examined for phosphoric acid. It was dissolved in HCl, the arsenic removed by hyposulphite of sodium, and the phosphoric acid precipitated as ammonio-magnesian phosphate ; ·013 grm. of the pyrophosphate was thus obtained, corresponding to ·76 p. c. P^2O^5.

very similar to that of konichalcite and of pseudolibethenite,—perhaps identical with it. The formula deduced from the analysis is—

$$Pb''O.3Cu''O.As_2O_5 + 2H_2O,$$

which may be arranged thus:—

$$Pb''O,2Cu''O,As_2O_5 + Cu''H_2O_2 + aq.$$

or tricupric arsenate in which $\frac{1}{3}$ of the copper is replaced by lead; together with 1 atom of cupric hydrate and 1 atom of water. One reason for disallowing the expression

$$3Cu''O.As_2O_5 + Pb''O + 2aq.$$

is the evident decomposition of the substance on heating, with change of colour: the cupric hydrate, outside the arsenate itself, becoming anhydrous and black. Olivenite, however, in which it is believed there likewise exists 1 atom of hydrate of copper, becomes olive-green only on gentle ignition, and at a bright red heat assumes an emerald tint, no separation of cupric oxide being apparent. The present species differs in amount of water from olivenite, or I should have thought it to be that species in which 1 atom of copper had been replaced by lead. All the so-called varieties of olivenite, even the light "wood" arsenate, contain no more than 3·38 per cent. of water, corresponding exactly to the formula—

$$3Cu''O.As_2O_5 + Cu''H_2O_2.$$

The theoretical values demanded by the formula $Pb''O,2Cu''O,As_2O_5 + Cu''H_2O_2$ + aq. are as follow:—

$Pb''O$	223·0	30·65
$3Cu''O$	238·6	32·79
As_2O_5	230·0	31·61
$2H_2O$	36·0	4·94
	727·6	100·00

It should be stated that in some analyses not here recorded the percentage of $Pb''O$ in the mineral was as high as 33·1. It is also worthy of note that almost all the determinations of water are below the percentage demanded by the accepted formula, though they agree much more nearly with it than with any other simple expression.

Minute traces of chlorine and sulphuric acid have been found in some specimens of Bayldonite, in addition to the ferric oxide and lime, to which allusion has been already made.

I am indebted to Mr. Talling for this mineral species also.