On Dufrenite from Cornwall.

By Prof. EDWARD KINCH, F.C.S., F.I.C., &c., Royal Agricultural College, Cirencester.

[Read May 8th, 1888.]

SOME of the published analyses of specimens of Dufrenite have afforded results not in good accord with the chemical formula $2Fe_2O_3$, P_2O_5, $3H_2O$, usually ascribed to that species.

Moreover, since analyses of a crystallised Dufrenite from Cornwall[1] gave results showing a higher ratio of acid to base than demanded by the above formula, a re-examination of the ordinary botryoidal variety of the mineral seemed desirable.

The samples selected for analysis were from Wheal Phœnix, Cornwall, and occurred as more or less isolated, dark olive-green, internally radiated globules, seated on the surface of a highly quartziferous, bluish to brown ferruginous veinstone.

Some ten or a dozen good specimens were most kindly placed at my disposal by my friend Mr. F. H. Butler, M.A., A.R.S.M.

The globules, after removal from the gangue, were broken up, and any portions showing change of colour,—due to a tendency to become converted into limonite, to which Dufrenite is often altered in bands throughout its structure,—were carefully eliminated, together with any particles of enclosed quartz or other derivatives from the matrix which were visible under a lens.

These specimens were originally much freer from limonite than the older specimens of the mineral to be seen in most collections. Their specific gravity was found to be 3·08 and the hardness about 4. They contained no arsenic nor manganese, and very little alumina.

In the first samples examined there were always traces, but traces only, of copper ; in the latest and purest of the specimens copper was entirely absent.

On ignition the mineral becomes of a bright red colour.

The analytical results were as follows :—

Loss at 100° C.—Very slight ; for example : 2·6804 grams lost ·0044 = ·16 per cent. All the following numbers were obtained on samples dried at 100° C.

---

[1] *Mineralogical Magazine*, Vol. 1886, VII. p. 65.

Loss on ignition.

·730	gram lost	·0778 = 10·65 per cent.	Mean
·3163	,,	·0340 = 10·75 ,,	*Loss on*
·3376	,,	·0364 = 10·78 ,,	*ignition*
·5605	,,	·0608 = 10·84 ,,	10·72
·6654	,,	·0704 = 10·58 ,,	per cent.

Water.—Loss on ignition 10·72 per cent. + gain in weight of oxygen by FeO on ignition ·75 per cent. = 11·47 per cent.

Silica, consisting mainly of quartz, with a few minute flakes of gelatinous silica.

·730	gram gave	·0037 = ·50 per cent.	Mean
·3163	,,	·0014 = ·44 ,,	*Silica*
·5605	,,	·0025 = ·44 ,,	·43
1·1132	,,	·0038 = ·34 ,,	per cent.

Phosphorus pentoxide.

$\cdot$2433 gram gave ·1171 $Mg_2P_2O_7$ = 31·19 per cent. of P_2O_5.

·3163	,,	·1534 ,,	= 31·02	,, ,,
·3648	,,	·1758 ,.	= 30·82	,, ,,
·5605	,,	·2752 ,,	= 31·40	,, ,,
·4959	,,	·2411 ,,	= 31·09	,, ,,

Mean *Phosphorus pentoxide* 31·10 per cent.

Ferrous oxide, volumetrically after dissolution of the mineral under an atmosphere of carbon dioxide.

·6118 gram gave ·043318 FeO = 7·08 per cent.   Mean FeO
·6934   ,,   ·045224 FeO = 6·52   ,,   6·80 per cent.

Equivalent to 7·55 per cent. ferric oxide.

Total *oxides of iron,* as ferric oxide, volumetrically.

·305 gram gave ·16666 Fe_2O_3 Mean Fe_2O_3
·1217   ,,   ·066332 Fe_2O_3 54·58.

Ferric oxide.—54·58 — 7·55 = 47·03 per cent. Fe_2O_3.

Ferric oxide and *Alumina.*—·5605 gram gave ·3108 = 55·45 per cent. $Fe_2O_3 + Al_2O_3 = Alumina$ ·87 per cent.

Lime.—1·1132 gram gave ·0187 = 1·68 per cent. CaO.

Magnesia.—1·1132 gram gave ·0054 $Mg_2P_2O_7$ = ·17 per cent. MgO.

The results collected give :—

H_2O	... ...	11·47 per cent.
SiO_2	... ...	·43 ,,
P_2O_5	... ...	31·10 ,,
FeO	... ...	6·80 ,,
Fe_2O_3	... ...	47·03 ,,
Al_2O_3	... ...	·87 ,,
CaO	... ...	1·68 ,,
MgO	... ...	·17 ,,

99·55

Eliminating the silica we obtain the following numbers :—

		Per cent.		Oxygen.
H_2O	...	11·52	...	10·24
P_2O_5	...	81·23	...	17·59
FeO	...	6·83	...	1·52
Fe_2O_3	...	47·23	...	15·74
Al_2O_3	...	·87	...	·40
CaO	...	1·69	...	·48
MgO	...	·17	...	·07
		99·54		

These figures point to the oxygen ratio between bases, acid, and water, 5 : 5 : 3, or the formula $5Fe_2O_3$, $3P_2O_5$, $9H_2O$: allowing one-seventh of the iron to be as ferrous oxide, it may be written $3Fe_2O_3$, FeO, $2P_2O_5$, $6H_2O$.

The formula usually given to Dufrenite and the above two require the following percentages:—

Per cent.	Per cent.	Per cent.
$2Fe_2O_3$ = 62·0	$5Fe_2O_3$ = 57·64	$3Fe_2O_3$ = 50·85
P_2O_5 = 27·5	$3P_2O_5$ = 30·69	FeO = 7·62
$3H_2O$ = 10·5	$9H_2O$ = 11·67	$2P_2O_5$ = 30·09
		$6H_2O$ = 11·44
Oxygen ratio 6 : 5 : 3	5 : 5 : 3	5 : 5 : 3

The last differs from Maskelyne's formula for Chalkosiderite,[1] $3Fe_2O_3$, CuO, $2P_2O_5$, $8H_2O$, only in containing less water by two molecules, and FeO in the place of CuO.

The Dufrenite from Rockbridge County, Virginia, analysed by F. A. Massie[2] and by T. L. Campbell,[3] resembles this closely in composition, excepting that it contains about 8 per cent. less water and 8 per cent. more ferric oxide. The Cornish botryoidal mineral is much purer than any Rockbridge specimens I have seen.

There seems no reason for doubt that pure specimens of the species Dufrenite contain a higher ratio of acid to base than in the formula usually ascribed to the species, and the oxygen ratio of base to acid appears to be 1 : 1, as in the Cornish mineral described by myself and Butler (Vol. VII. p. 65). Indeed, in some specimens ascribed to this species, as Kurlbaums, from Allentown, New Jersey, the ratio of $3Fe_2O_3$: $2P_2O_5$, the same which is given to Beraunite and Cacoxenite, and with alumina replacing ferric

[1] *Chem. Soc. Jour.* 1875 [2], XIII. 586.

[2] *Chem. News.* 1880, p. 181.

[3] *Amer. Journal of Science*, 1881 [3], XXII. 65.

oxide to Wavellite, seems possible. It is not unlikely that the first two minerals and Dufrenite differ from each other only in containing more or less water and in ferrous oxide sometimes replacing ferric oxide.

$3Fe_2O_3$, $2P_2O_5$, $6H_2O$, requires Fe_2O_3 55·05, P_2O_5 32·57, H_2O 12·38.

In any future analyses of Dufrenite or allied species it would be very desirable to ascertain the temperatures at which different molecules of water are given off.

Church[1] has observed that Dufrenite is usually so mixed with hæmatite that it is difficult to separate it for analysis; this, I think, may account for the higher proportion of ferric oxide found in most of the older analyses.

The formula I would suggest, after full consideration, for the pure Cornish botryoidal Dufrenite, is $3Fe_2O_3$, FeO, $2P_2O_5$, $6H_2O$.

A point which may be sometimes overlooked or undervalued in the analysis of phosphates, and especially of iron phosphates, is their decomposibility by water, and especially if this contains salts or alkalies in solution. In an investigation arising from the above analyses it was found that ferric phosphate was decomposed by washing with a dilute solution of ammonia (·75 per cent.), and phosphoric acid removed continuously until the ratio of base to acid was $16Fe_2O_3 : 1P_2O_5$; this is practically the same ratio as found by Rammelsberg,[2] after digesting precipitated ferric phosphate with dilute caustic potash solution.

---

[1] *Chem. News*, X. 157.

[2] *Pogg. Ann.* LXIV. 418.