

*On a New Variety of Mineral from Cornwall.*

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*With a Note on the Crystallographical Characters.*

By H. A. MIERS, M.A., &amp;c.

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SOME two years since the authors received from East Cornwall examples of a crystallised mineral presenting features dissimilar to those of any species previously known to them, but presumably referable to Dufrenite. The specimens obtained were from the central part of a narrow neck of "dead ground" (compact ferruginous quartz rock) connecting the much broader E. and W. continuations of a lode, yielding respectively copper and tin ores.

The freshest crystals have a vitreous lustre, and vary in colour from almost black to a light apple-green, their sections, however, being of a yellow brown to yellow. Where, as commonly, some superficial chemical change has taken place—seemingly into limonite—the colour is from red to brown or yellowish brown. The crystals are aggregated for the most part to form squarish fasciculi, somewhat like files of bills, which are confusedly grouped together or incipiently stalactitic. From the definitely crystallised groups one may observe a passage into merely scabrous nodules and botryoidal masses on the smooth spherules of apparently ordinary Dufrenite. Where compact the mineral shows in section, not infrequently, a sequence of curved strongly contrasted red and green bands, doubtless the result of interstitial change along lines of accretion.

The unaltered (green) crystals have a hardness of about 4·5, and a specific gravity, in the powdered condition, of 3·233. Their qualitative analysis revealed the presence of ferric oxide, phosphoric anhydride, water, minute siliceous granules (gangue), a little CuO and CaO, and a slight trace of MgO, but no FeO or MnO. Neither uranium nor vanadium was detectable, and Al<sub>2</sub>O<sub>3</sub> was absent except in the matrix. On ignition the crystals become red, and before the blowpipe they melt without much difficulty.

Quantitative analysis yields the following results:—

*Water.* No loss *in vacuo* over sulphuric acid. Loss at 100° C. traces only, 1·1502 grs. yielding ·0012 after some hours. By ignition

1·1485	lost	·1228	=	10·69	per cent.	}	Mean	H <sub>2</sub> O	
1·0073	"	·107	=	10·62	"				
·9016	"	·095	=	10·54	"				
							10·62	per cent.	

*Silica* (Quartz sand, none combined) :—

1·1485 gave	·0056 =	·48 per cent.	} Mean	SiO <sub>2</sub>
1·0078 "	·0058 =	·57 "		
·9016 "	·005 =	·55 "		
			·53 per cent.	

*CuO* :—

1·1485 gave	·0102 =	·89 per cent.	} Mean	CuO
1·0078 "	·0112 =	1·11 "		
·9016 "	·0078 =	·86 "		
			·95 per cent.	

*P<sub>2</sub>O<sub>5</sub>* :—

·4594 gave	·217 Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> =	30·21 per cent.	} Mean	P <sub>2</sub> O <sub>5</sub>
·4029 "	·1922 "	= 30·51 "		
·9016 "	·424 "	= 30·08 "		
			30·26 p. cent.	

*Fe<sub>2</sub>O<sub>3</sub>* (Dry method) :—

1·1485 gave phosphate pp.	·9794 =	85·28 per cent.	} Mean	Fe <sub>2</sub> O <sub>3</sub>
1·0078 "	" "	·866 = 85·97 "		
·9016 "	" "	·779 = 84·96 "		
			85·40 per cent.	

whence by difference 55·14 per cent. Fe<sub>2</sub>O<sub>3</sub>.

Volumetrically (1 cc. K<sub>2</sub>Mn<sub>2</sub>O<sub>8</sub> solution = ·00785 Fe<sub>2</sub>O<sub>3</sub>) :—

·2297 =	16·5 cc. =	56·88 per cent.	} Mean	Fe <sub>2</sub> O <sub>3</sub>
·2014 =	14·2 cc. =	55·85 "		
·839 =	59·1 cc. =	55·28 "		
·5944 =	42·4 cc. =	56·16 "		
			55·63 per cent.	

*CaO* :—

1·0078 gave	·016 CaO =	1·59 per cent.	} Mean	CaO
·9016 "	·0227 CaCO <sub>3</sub> =	1·41 "		
			1·50 per cent.	

Collecting the above results we have :—

H <sub>2</sub> O =	10·62
SiO <sub>2</sub> =	·53
CuO =	·95
P <sub>2</sub> O <sub>5</sub> =	30·26
Fe <sub>2</sub> O <sub>3</sub> =	55·63
CaO =	1·50
MgO =	traces

99·49

Eliminating the ·53 per cent. of SiO<sub>2</sub> we obtain the following proportions :—

		Oxygen.
H <sub>2</sub> O =	10·68	9·49
CuO =	·96	·19
P <sub>2</sub> O <sub>5</sub> =	30·42	17·14
Fe <sub>2</sub> O <sub>3</sub> =	55·93	16·78
CaO =	1·51	·43

99·50

Calculated as  $\text{Fe}_2\text{O}_3$  the CaO and CuO give respectively the numbers 1.44 and .65 = 2.09. Correcting for the amount .38 lost by conversion of CaO and CuO, we get finally the percentages:—

$$\begin{array}{r} \text{H}_2\text{O} = 10.72 \\ \text{P}_2\text{O}_5 = 30.54 \\ \text{Fe}_2\text{O}_3 = 58.24 \\ \hline 99.50 \end{array}$$

These numbers lead to the formula

$$\begin{array}{r} 8 \text{H}_2\text{O} = 10.51 \\ 3 \text{P}_2\text{O}_5 = 31.09 \\ 5 \text{Fe}_2\text{O}_3 = 58.40 \\ \hline 100.00 \end{array}$$

Three principal formulæ have been applied or are applicable to minerals under the name of Dufrenite, viz.:—

(1)	(2)	(3)
per cent.	per cent.	per cent.
$2 \text{Fe}_2\text{O}_3 = 62.0$	$3 \text{Fe}_2\text{O}_3 = 56.21$	$5 \text{Fe}_2\text{O}_3 = 58.40$
$\text{P}_2\text{O}_5 = 27.5$	$2 \text{P}_2\text{O}_5 = 33.25$	$3 \text{P}_2\text{O}_5 = 31.09$
$3 \text{H}_2\text{O} = 10.5$	$5 \text{H}_2\text{O} = 10.54$	$8 \text{H}_2\text{O} = 10.51$
Oxygen ratio 6 : 5 : 3	9 : 10 : 5	15 : 15 : 8

[Or the last with  $7\frac{1}{2}$  molecules of water =  $\text{Fe}_2\text{O}_3$  58.78,  $\text{P}_2\text{O}_5$  31.3,  $\text{H}_2\text{O}$  9.92 = 2 : 2 : 1.]

The first of these is adopted by Maskelyne<sup>1</sup>, Church<sup>2</sup> and others, and agrees with the analyses of Karsten<sup>3</sup> and Diesterweg<sup>4</sup> of the dark green mineral from near Siegen, and those of some others.

Our results point, undoubtedly, to the third formula, and this is supported, at all events so far as the ratio of base to acid is concerned, by analyses of Streng, Boricky, and others, though most of these show rather less water than in our Cornish specimens, and always included ferrous oxide.

Apart from chemical considerations, from the description given by Streng<sup>5</sup> of the physical characters of crystallised Kraurite (Dufrenite), from Waldgirmes, near Giessen, there can be little hesitation in concluding

<sup>1</sup> *Journ. Chem. Soc.* 1875 [2]. XIII. 586.

<sup>2</sup> *Chem. News*, 1864, X. 157.

<sup>3</sup> *Arch. f. Bergb. u. Hütt.* XV. 243.

<sup>4</sup> *Berg. u. Hütt. Zeitung*, XXII. 257.

<sup>5</sup> *Neues Jahrb. f. Min.* 1881 (1), p. 101.

that it is identical with the mineral now under consideration. Streng's analytical results, however,—

$$\begin{aligned} \text{Fe}_2\text{O}_3 &= 60.20 = .376 = 3.35 \text{ or } 5.0 \text{ or } 3.00. \\ \text{FeO} &= 1.53 = .021 = 0.02 \\ \text{P}_2\text{O}_5 &= 31.82 = .224 = 2.00 \text{ or } 3.0 \text{ or } 1.78. \\ \text{H}_2\text{O} &= 8.03 = .446 = 4.00 \text{ or } 6.0 \text{ or } 3.50. \end{aligned}$$

101.58

answering to the formula  $5 \text{ Fe}_2\text{O}_3, 3 \text{ P}_2\text{O}_5, 6 \text{ H}_2\text{O}$ , differ from the authors' in the presence of FeO and the absence of CaO and CuO, in containing less water by  $2\frac{1}{2}$  per cent., and in being, moreover, too high by over  $1\frac{1}{2}$  per cent. ; Boricky's<sup>1</sup> analyses of Dufrenite (Kraurite) from St. Benigna, Bohemia, giving—

Dark-green variety.	Light-green variety.
Per cent.	Per cent.
$\text{P}_2\text{O}_5 = 30.05 = 1.7 \text{ or } 2.0$	$\text{P}_2\text{O}_5 = 32.09 = 1.87 \text{ or } 2.0$
$\text{Fe}_2\text{O}_3 = 59.82 = 3.0 \text{ or } 3.6$	$\text{Fe}_2\text{O}_3 = 57.93 = 3.0 \text{ or } 3.2$
$\text{H}_2\text{O} = 9.33 = 4.1 \text{ or } 5.0$	$\text{H}_2\text{O} = 9.04 = 4.1 \text{ or } 4.8$
$\text{FeO \& Mn}_2\text{O}_3 = \text{traces.}$	$\text{FeO \& Mn}_2\text{O}_3 = \text{traces.}$
<hr style="width: 50%; margin: 0 auto;"/> 99.2	<hr style="width: 50%; margin: 0 auto;"/> 99.06

and C. A. Kurlbaum's<sup>2</sup> of radiated Dufrenite from Allentown, New Jersey,

Per cent.
$\text{SiO}_2 = 0.72$
$\text{Fe}_2\text{O}_3 = 53.74$
$\text{FeO} = 3.77$
$\text{P}_2\text{O}_5 = 32.61$
$\text{H}_2\text{O} = 10.49$

100.95 (*sic*, but = 101.33)

more closely resemble those obtained for the Cornish crystallised mineral in question. It would appear, in fact, that Kurlbaum's specimens contained some Vivianite, probably as a result of commencing chemical change. Calculating all the iron oxide as  $\text{Fe}_2\text{O}_3 = 57.51$  per cent. he deduces the formula :

$3 \text{ Fe}_2\text{O}_3$	$2 \text{ P}_2\text{O}_5$	$4 \text{ H}_2\text{O}$
$57.31 \text{ per cent.}$	$31.10 \text{ per cent.}$	$8.59 \text{ per cent.}$
$\text{but } 3 \text{ Fe}_2\text{O}_3$	$2 \text{ P}_2\text{O}_5$	$5 \text{ H}_2\text{O}$
$56.21$	$33.25$	$10.54$
,,	,,	{ per cent. seems more probable.

<sup>1</sup> *Bericht. Ak. Wien.*, 1867, LVI. 6.

<sup>2</sup> *Silliman's Am. J. of Science*, 1857 [2], XXIII. 423.

Another American specimen from Rockbridge County, Virginia, occurring in nodular masses with a radiated structure, being made up of slender prisms closely compacted, of a very dark blackish green colour and greyish green streak, has been analysed by F. A. Massie<sup>1</sup> and by L. Campbell<sup>2</sup> with almost identical results. The former found  $H_2O$  8.85,  $SiO_2$  .20,  $P_2O_5$  31.66,  $Fe_2O_3$  50.89,  $FeO$  6.06,  $Al_2O_3$  .29,  $MnO$  .24,  $MgO$  2.16.

It may be noted here that the percentage of water given for Dufrenite by Church, 10.5 per cent. is almost exactly the same as that found by the authors of the present paper. Maskelyne's formula requires this percentage of water, but a lower proportion of  $P_2O_5$  and a higher proportion of  $Fe_2O_3$  than in the mineral now in question. The identity of the two seems therefore far from clear.

Further chemical examination of pure examples of the ordinary Cornish Dufrenite is perhaps desirable, and one of us is now at work on this.

The crystallised phosphate just described is the only Dufrenite (?) in which copper has been noted, though the occurrence of Dufrenite with Chalcosiderite and its resemblance to that mineral have been noticed. The latter mineral contains over 8 per cent. of copper, and a higher percentage, 15, of water, and also about  $4\frac{1}{2}$  per cent. of alumina, but there is a similarity between our formula for the mineral forming the subject of this paper and Maskelyne's (*loc. cit.*) for Chalcosiderite, 3  $Fe_2O_3$ ,  $CuO$ , 2  $P_2O_5$ , 8  $H_2O$ , the oxygen ratio of base to acid being the same in each case, 1 : 1.

Also the evidence of certain specimens in the possession of the authors points pretty conclusively to the occasional origin of brilliantly crystallised Chalcosiderite in the decomposition of this phosphate—presumably by the infiltration of a solution of some copper salt, and replacement thereby of an equivalent amount of ferric oxide by copper oxide, with simultaneous addition of water.

From Maskelyne's Andrews site the crystals under consideration differ in composition chiefly in the absence of ferrous oxide, and in containing less than a tenth as much cupric oxide.

We submit that there is evidence that this mineral (as well as others described under the head Dufrenite) contains a larger proportion of phosphoric acid to base than is compatible with the usual formula given for Dufrenite, 2  $Fe_2O_3$ ,  $P_2O_5$ , 3  $H_2O$ ; and that (unless it should be afterwards shown that some of the earlier analysed specimens contained iron oxides

<sup>1</sup> *Chemical News*, 1880, XLII. 181.

<sup>2</sup> *Amer. J. Science*, 1881 [3], XXII. 65.

as impurities) the species must be divided into two, one having the formula  $5 \text{Fe}_2\text{O}_3, 3 \text{P}_2\text{O}_5, 8 \text{H}_2\text{O}$  (or possibly in some cases less water).

Having regard to the conclusions we have so far arrived at, it is not our intention to propose a new name for this mineral.'

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*Note by H. A. MIERS.*

THE crystals occur in the form of rectangular tables about 1 to 2 mm. in length and breadth, and  $\frac{1}{4}$  to  $\frac{3}{4}$  mm. in thickness; they may be regarded in all probability as orthorhombic plates formed by the macropinakoid faces  $\{010\}$ , bevelled at the sides by small faces of the prism  $\{110\}$ , and bounded at top and bottom by the basal planes  $\{001\}$ , the latter, however, sometimes rounded into a low brachydome. The best measurements gave an angle of  $86^\circ 26'$  for the prism, and  $12^\circ 45'$  for the inclination of the flat dome to the basal plane; but the crystals are so invariably grouped into penetrating bundles that it is almost impossible to find one which can be regarded as strictly a single individual, consequently neither the system nor the dimensions could be determined with certainty. The groups are generally sheaf-like aggregates, in which the plates radiate from a central axis and have their basal planes nearly parallel; the crystals are also frequently heaped together into confused rounded masses, in which the basal planes all lie outwards, and these again pass into smooth spherical and botryoidal concretions of radial structure. Sections parallel to the macropinakoid show marked dichroism, and between crossed nicols extinguish parallel and perpendicular to the prism edges. The crystallographic characters agree closely with those of Dufrenite from Waldgirmes, near Giessen, described by A. Streng (*Op. cit.* p. 110), and the habit is nearly that of fig. 7 in the plate accompanying his description.