

The composition of francolite.

By E. B. SANDELL, Ph.D.

Department of Analytical Chemistry, University of Minnesota,
Minneapolis, Minnesota,

M. H. HEY, M.A., D.Sc.

Assistant-Keeper, Department of Mineralogy, British Museum, London,
and DUNCAN McCONNELL, Ph.D.

Department of Geology, University of Texas, Austin, Texas.

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Introduction.

IN 1850, T. H. Henry¹ published an imperfect analysis of francolite, a supposed new mineral, previously named by H. J. Brooke. Henry stated that his material was similar to the material from Wheal Franco, Tavistock, Devon, but he does not show how he was in a position to know the composition of the material from this mine, because there is no record to indicate that the mineral from Wheal Franco had been analysed. Henry did not report CO₂ for the material he analysed, but M. H. N. Story-Maskelyne and W. Flight² analysed material, supposedly similar, and obtained a significant amount of CO₂. Their determinations are as follows:

CaO.	P ₂ O ₅ .	CO ₂ .	F.	H ₂ O.	Na ₂ O.	FeO+MnO+Fe ₂ O ₃ .
54.09	38.14	2.25	3.34	1.59	0.69	0.91

These authors state that the mineral from Wheal Franco contains CO₂ also, but they do not give any determinations for material from this mine. Their material is now known to have come from the Fowey Consols mine, St. Blazey, Cornwall.³ H. Robinson⁴ analysed, under the name francolite, material from the Levant mine, St. Just, Cornwall.

Although Brooke apparently proposed the name francolite and although he seemingly did not publish any description of the mineral,

¹ T. H. Henry, *Phil. Mag.*, 1850, ser. 3, vol. 36, p. 134.

² M. H. N. Story-Maskelyne and W. Flight, *Journ. Chem. Soc. London*, 1871, vol. 24, p. 3.

³ R. H. Solly, *Min. Mag.*, 1886, vol. 7, p. 57.

⁴ H. Robinson, *Min. Mag.*, 1886, vol. 7, p. 59.

Henry's description is not the earliest appearance of the name. A printed sale catalogue, issued by the mineral dealer H. Heuland, lists francolite among the minerals offered for sale on May 15, 1843.

Thus it seems that, although three analyses have been recorded for francolite, none of the specimens came from Wheal Franco, and there remained some doubt as to the composition of the mineral named by Brooke.

In 1866, C. A. Stein¹ described the phosphorite from Staffel, Nassau, introducing the name staffelite for a calcium phosphate containing carbon dioxide, and this was done prior to the appearance of a reliable analysis of francolite. From the data for francolite given by Story-Maskelyne and Flight and for staffelite given by Stein, A. Lacroix² has supposed francolite and staffelite to be identical. This view is confirmed by a new analysis of staffelite recently given by J. W. Gruner and D. McConnell³ and by the new analysis of francolite to be presented below.

The specimen now investigated is B.M.61342 of the British Museum collection, which was found unlabelled and was registered in 1883, but which is almost certainly identical with B.M.15628, a specimen obtained at Heuland's sale in 1843 and the specimen referred to in his sale catalogue (lot 154). It is therefore almost certainly from Wheal Franco, and the actual specimen to which the earliest public ascription of the name francolite was made.

Physical and Optical Properties.

The specimen consists of clear, colourless francolite, forming a thin, confusedly crystalline crust on a fibrous quartz mass which is heavily impregnated with haematite.

The density was determined by flotation in Clerici solution as $D_4^{21} = 3.178 \pm 0.006$, and by the micro-pyknometer⁴ as 3.173 ± 0.020 (calculated probable error for a single determination). The material was separated from haematite and quartz through the use of bromoform and Clerici solution and with an electromagnet. A microscopic examination showed the material to be free from impurities except for small amounts of haematite and quartz, which could not readily be removed without considerably reducing the small samples available. Failure to remove

¹ C. A. Stein, *Jahrb. Ver. Naturk. Nassau*, 1866, vol. 19-20, p. 41; *Neues Jahrb. Min.*, 1866, p. 716.

² A. Lacroix, *Compt. Rend. Acad. Sci. Paris*, 1910, vol. 150, p. 1213.

³ J. W. Gruner and D. McConnell, *Zeits. Krist.*, 1937, vol. 97, p. 208. [M.A. 7-88.]

⁴ F. A. Bannister and M. H. Hey, *Min. Mag.*, 1938, vol. 25, p. 30.

quartz completely is of little significance. The failure to remove haematite completely probably accounts for most, if not all, of the soluble iron obtained on analysis. These impurities together represent the insoluble matter shown in the analysis. No trace of calcite or other carbonate could be seen, and all grains alike can be seen to give off bubbles of carbon dioxide during solution in acid. There is certainly no admixture of free calcite or other carbonate, as suggested by J. Thewlis, G. E. Glock, and M. M. Murray,¹ in this material.

The material is not well suited to optical examination as individual crystals cannot be isolated. Most of the grains show sharp extinction and no appreciable departure from uniaxiality. A few show division into sectors extinguishing at about 60° to one another with very weak birefringence and a small optic axial angle; none of these grains showed crystal faces, and the boundary between adjacent sectors is mostly irregular and useless for a reference line, hence no measurements on the optic orientation could be made. A few basal grains showed division into sectors, each sector being subdivided into fine lamellae of irregular width, arranged parallel to the edges of the basal plane, the lamellae having alternately weak and very weak birefringence, straight extinction, and positive elongation. The refractive indices were determined by the immersion method, which gave ω 1.629, ϵ 1.624, both ± 0.002 .

Chemical Data.

The specimen available was sufficient only for semi-micro methods of analysis. The most abundant constituents were determined by the semi-micro methods on an analysed specimen of staffelite before attempting them on the small sample of francolite from Devon. The staffelite had been analysed by Dr. R. B. Ellestad (in Gruner and McConnell, 1937, loc. cit.), and the results obtained by the semi-micro methods compare with his results as follows:

	CaO.	P ₂ O ₅ .	CO ₂ .	H ₂ O+.	H ₂ O-.
Macro (Ellestad)	54.88	37.71	3.36	1.14	0.04
Micro (E. B. S.)	54.78	38.05	3.24	1.25	0.03

These determinations are sufficiently similar to indicate that the semi-micro methods used for this work are quite comparable to the methods which required larger samples. The results agree within 0.1%, except for P₂O₅, where the semi-micro method yielded a result about 0.3% higher than the macro method.

¹ J. Thewlis, G. E. Glock, and M. M. Murray, *Trans. Faraday Soc.*, 1939, vol. 35, p. 358. [M.A. 7-352.]

Calcium, magnesium, and phosphorus were determined essentially by the method given by Hoffman and Lundell¹ for the analysis of phosphate-rock. Calcium was separated by double precipitation as the oxalate at a *pH* of 3 to 4 and weighed as the carbonate by igniting the precipitate at 475–525° C. In the determination of magnesium, calcium was first separated as sulphate in alcoholic solution, and magnesium was then precipitated in the filtrate as magnesium ammonium phosphate in the presence of citrate after removal of the alcohol; the magnesium ammonium phosphate was weighed as the hexahydrate after washing with acetone and air-drying. Phosphorus was separated from the other constituents of the sample by two precipitations with magnesia mixture in the presence of ammonium citrate, without preliminary precipitation with molybdate, and weighed as magnesium pyrophosphate.

Carbon dioxide was determined gravimetrically by absorption in 'ascarite' (soda-asbestos) after liberation with dilute hydrochloric acid. Total water was determined by the Penfield method, lead oxide being used as a retainer for fluorine. Insoluble material was determined by treating the sample with dilute hydrochloric acid and drying the residue at 105° C. Iron in the hydrochloric acid solution of the sample was obtained by precipitating as sulphide in ammoniacal solution containing tartrate, dissolving the precipitate in hydrochloric acid, oxidizing with bromine water, and finally applying the colorimetric thiocyanate method.

Twenty milligram samples were used in the determination of calcium, phosphorus, and total water, and a 40 mg. sample for carbon dioxide. The filter-stick technique was applied in the determinations involving precipitation, and when the precipitate was to be ignited at a high temperature a porcelain filter-stick was employed in conjunction with a 10 ml. platinum crucible as the precipitation vessel.

Dr. W. D. Armstrong kindly determined the fluorine on several samples weighing between 5 and 10 mg. through the use of his modification² of the method of H. H. Willard and O. B. Winter.³ The end-points were quite distinct because interfering substances were apparently absent. The value reported is an average of three determinations: 3.69, 3.68, and 3.77.

The results of the analysis are given in table I, and are discussed below. A spectroscopic analysis of the specimen was obtained and it indicated the presence of Mg, Cu, Be, Fe, Mn, Sr, Pb, Si, Bi, and Zn, but none of these were determined chemically except Mg and Fe, and there is no reason to believe from the intensities of the lines on the spectrogram that any of these elements are present in greater abundance than 0.1% (except Fe) and most of them are probably less abundant than 0.01%.

X-Ray Data and Interpretation.

The specimen was examined by the powder diffraction method⁴ and the lattice constants were obtained as a 9.34, c 6.89 Å. (both \pm 0.01),

¹ J. I. Hoffman and G. E. F. Lundell, Journ. Res. Nat. Bur. Standards, U.S.A., 1938, vol. 20, p. 607.

² W. D. Armstrong, Journ. Amer. Chem. Soc., 1933, vol. 55, p. 1741.

³ H. H. Willard and O. B. Winter, Ind. Eng. Chem. (Anal.) 1933, vol. 5, p. 7.

⁴ We are indebted to Mr. Lynn Gardiner, of the University of Minnesota, for the preparation of the powder diffraction photograph.

$c/a = 0.738$. The interplanar distances obtained with Fe- K_{α} radiation in a camera of 57.3 mm. radius are given in table II, where they are compared with an analysed sample of fluor-apatite from Hastings Co., Ontario.¹

TABLE I. Chemical analysis (by E. B. Sandell) of francolite (B.M.61342) from Wheal Franco, Buckland Monachorum, Tavistock, Devon.

		Weight per cent.	Unit-cell contents*			
			i.	ii.		
CaO	...	53.94	Ca	...	9.83	9.73
MgO	...	0.10	Mg	...	0.02	0.02
P ₂ O ₅	...	38.13	P	...	5.49	5.43
CO ₂	...	3.40	C	...	0.79	0.78
F	...	3.71	F	...	1.99	1.97
H ₂ O+	...	0.46	OH	...	0.52	0.52
H ₂ O-	...	0.01	O	...	23.90	23.70
Fe ₂ O ₃	...	0.34	Total	...	42.54†	42.16†
Insol.	...	1.83	O+OH+F	...	26.41	26.19
		101.92	C in Ca positions	...	0.28	0.21
Less O	...	1.56				
Total	...	100.36‡				

* Calculated from the cell sides, density, and analysis; (i) assuming a density of 3.178, (ii) a density of 3.145.

† ± 0.30 .

‡ SO₃, Cl, absent.

From these cell sides, the density, and the chemical analysis, the number of atoms of each kind in the unit cell may be computed, and the results of these calculations are included in table I. Unfortunately, the presence of haematite films on the crystal fragments makes it almost certain that the observed density of 3.178 is distinctly too high. If the whole of the 1.83% insolubles found could be taken as haematite, the corrected density would be 3.145 ± 0.006 , and calculations were therefore made based on both these densities; the true figures must be somewhere between these extremes.

If, instead of calculating the cell contents from the density and other experimental data, the density is calculated from the cell sides and chemical analysis on the assumption that the unit cell contains 42 atoms altogether, a value of 3.139 ± 0.015 is obtained; calculating on a basis of $26(O+OH+F)$ in the unit cell, the density should be 3.129 ± 0.015 .

From these calculations, which show reasonably good agreement, two

¹ A. S. Dadson, Univ. Toronto Studies, Geol. Ser., 1933, no. 35, p. 51. [M.A. 5-480.]

conclusions may be drawn. First, it is probable that the 0.46% of H_2O+ shown in the analysis is not wholly water of constitution; if it is assumed that the unit cell contains 42 atoms altogether and 26

TABLE II. Powder diffraction diagram of francolite.

Unfiltered Fe radiation; $R = 57.3$ mm.

No.	Indices.	Fluor-apatite.		Francolite.	
		d .	I .	d .	I .
1.	(002)	3.432	2	3.428	3
2.	(102)	—	—	3.157	$\frac{1}{2}$
3.	(120)	3.060	3	3.058	3
4.	(300) β	2.975	$\frac{1}{2}$	2.965	$\frac{1}{2}$
5.	(202) β	2.884	$\frac{1}{2}$	—	—
6.	(121)	2.798	10	2.795	10
7.	(112)	2.769	4	2.765	3
8.	(300)	2.702	6	2.694	6
9.	(202)	2.616	3	2.618	3
10.	(301)	2.517	$\frac{1}{2}$	—	—
11.	(130) β	2.477	$\frac{1}{2}$	—	—
12.	(122)	2.289	$\frac{1}{2}$	2.286	$\frac{1}{2}$
13.	(130)	2.248	2	2.244	2
14.	(131)	2.135	1	2.130	1
15.	(113)	2.057	1	*	—
16.	(123) β	2.026	$\frac{1}{2}$	2.024	1
17.	(203)	2.001	$\frac{1}{2}$	*	—
18.	(222)	1.937	3	1.934	4
19.	(132)	1.883	1	1.883	1
20.	(123)	1.838	6	1.837	6
21.	(231)	1.795	3	1.795	2
22.	(140)	1.769	3	1.768	2
23.	(402)	1.745	3	1.746	2
24.	(004)	1.720	3	1.722	3
25.	(232)	1.637	1	1.635	1
26.	(133)	1.605	$\frac{1}{2}$	—	—
27.	(240)	1.533	$\frac{1}{2}$	—	—
28.	(331)	1.521	$\frac{1}{2}$	—	—
29.	(124)	1.498	1	1.502	$\frac{1}{2}$
30.	(502)	1.468	2	1.470	1
31.	(304)	1.452	1	1.456	1

* Indistinct lines occurred in these positions.

(O+OH+F), and that the remainder of the analysis is accurate, the essential water should be only 0.11%, and the calculated density 3.141 ± 0.015 . Secondly, it is clear that there is a definite substitution of calcium by carbon, to the extent of approximately 0.2 atoms per unit cell,¹ the remainder of the calcium (about 0.6 atom per unit cell) replac-

¹ Calculations of atomic ratios have also been made to bases of (O+OH+F) = 26, of (Ca+Mg+P+C) = 16, and of total atoms = 42; all agree in showing approximately 0.2 atom carbon replacing calcium.

ing phosphorus. This type of substitution has been demonstrated also for francolite (staffelite),¹ ellestadite,² and dahlite,³ while a recent analysis by H. C. G. Vincent⁴ (T. Deans, 1938) of francolite from Robin Hood quarry, Thorpe-on-the-Hill, Leeds, indicates carbon replacing phosphorus, but not calcium. In the present case, definite evidence was obtained that the material was quite free from calcite or other carbonates.

N. V. Belov⁵ suggests that it is structurally improbable that carbon should replace calcium atom for atom, but quite possible that one carbon may replace two of those calcium atoms which lie on the three-fold axes, and such an interpretation is quite consistent with the present analysis. But while the data clearly demonstrate that carbon does replace calcium, they are not sufficient to decide whether the replacement is $C \rightleftharpoons Ca$ or $C \rightleftharpoons 2Ca$.

Conclusions.

Francolite and staffelite are identical, and the name francolite has priority. A specimen obtained from the British Museum has been analysed by semi-micro methods and a general description of the method is given. The lattice constants and physical and optical properties have been measured and found to be mutually consistent within the limitations of the methods. Carbon was found to enter the apatite lattice in the calcium and phosphorus positions (as previously postulated for several other carbonate-apatites) on the basis of the analysis, to form CO_3 -groups similar to those found in calcite and aragonite in the first instance, and CO_4 -groups with a tetrahedral configuration in the second instance. This is the fourth analysis of a carbonate-apatite to confirm these conclusions.

¹ J. W. Gruner and D. McConnell, 1937, loc. cit.

² D. McConnell, Amer. Min., 1937, vol. 22, p. 977. [M.A. 7-14.]

³ D. McConnell, Amer. Journ. Sci., 1938, ser. 5, vol. 36, p. 298. [M.A. 7-351.]

⁴ T. Deans, Min. Mag., 1938, vol. 25, p. 135.

⁵ N. V. Belov, Compt. Rend. (Doklady) Acad. Sci. URSS, 1939, vol. 22, p. 89. [M.A. 7-351.]