Francolite from sedimentary ironstones of the Coal Measures.

By T. Deans, B.A.

With a chemical analysis by H. C. G. Vincent, M.A.
Department of Mineralogy and Petrology, University of Cambridge.

[Read June 9, 1938; communicated by Prof. C. E. Tilley, F.R.S.]

THE sedimentary iron ores of Britain all contain small amounts of phosphorus which is generally present in the colloform mineral collophane. In a rather uncommon class of oolitic ironstones recently described from the Yorkshire coalfield (1), a crystalline phosphate was found which has now been identified as francolite and forms the subject of this paper. These oolitic ironstones occur in the immediate roofs of coal seams, are of freshwater origin, and consist of ooliths of kaolinite and isotropic clay in a groundmass of chalybite. During the later stages of their diagenesis, francolite, associated with quartz, calcite, pyrite and blende, and much kaolinite, crystallized within the ooliths (fig. 1) and in the shrinkage cracks (fig. 2) of the ironstone, and sometimes replaced the ooliths and groundmass. The francolite is present in all of the three oolitic ironstone occurrences described from Yorkshire, and also in the similar rock from Derbyshire in the Geological Survey's collection of iron ores. Details of these localities are given in the ironstones paper (1). The writer has also found similar francolite in an ironstone nodule from a parting in the Mühlenbach coal seam of south Limburg, Netherlands. Although not recorded, it may be expected to occur in some of the blackband ironstones and other rocks closely associated with coal seams. The following account is based entirely on material from Robin Hood quarry, Thorpe-on-the-Hill, 4 miles south of Leeds.

Physical characters.—Pseudo-hexagonal by twinning. The crystals are hexagonal plates, consisting of the basal plane and a low pyramid, twinned in six triangular sectors. Minute re-entrant angles are frequent at the corners of the plates; they are too small to measure accurately, but are close to 120°. The crystals range up to half a millimetre across, and sometimes up to one millimetre, but the latter are usually rounded and covered with smaller crystals. Cleavage indistinct. Fracture conchoidal. Brittle. Specific gravity 3·21. Lustre vitreous. Colourless to pale yellow-brown. Soluble in cold dilute acid.

Optical properties.—Biaxial negative, with $\alpha = c$, and the extinction-angle, γ to the hexagonal edge, showing two different values, one about 40° (fig. 3), the other about 50°. The two values frequently occur in different sectors of the same crystal. 2V, determined with the universal stage, varies from 25° at the centre of the crystal to 40° at the hexagonal edge, but the general value around the centre of the triangular sectors is about 37°. α 1·620, β 1·627, γ 1·628, $\gamma - \alpha = 0{\cdot}008$. Cross-sections of the plates indicate further twinning about a composition-plane parallel to the basal plane, but the differences in optical orientation about this plane are very slight. Many crystals show anomalous wavy extinction.

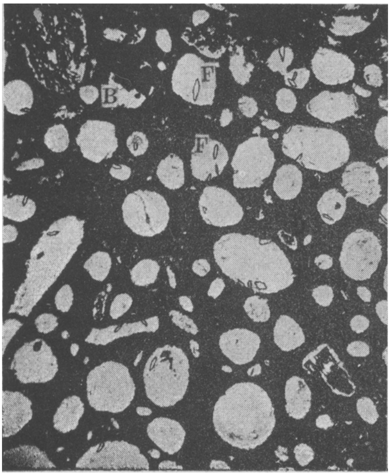

FIG. 1.

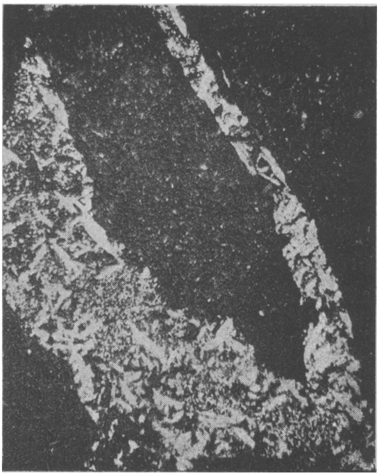

FIG. 2.

FIG. 1. Oolitic ironstone, Robin Hood quarry, near Leeds, Yorkshire. Crystals of francolite (F) and one of dark blende (B) in kaolinite ooliths. The groundmass is chalybite. Ordinary light, × 16.

FIG. 2. Shrinkage cracks in the ironstone infilled with francolite and kaolinite (fine-grained). Crossed nicols, × 16.

The refractive indices agree closely with previous data. In francolite from the Vosges, however, Lacroix records the optic axial plane as parallel to the hexagonal edge (2). Oblique extinctions on the hexagonal edge occur in carbapatites and alkali-apatites. The anomalous orientation of the optic axial plane producing two extinction positions appears to be analogous to the variable orientations within the same crystal recorded in pyromorphite and endlichite by Bowman (3) and Lietz (4). The variation in the optic axial angle from the centre to the margin of the crystals is paralleled in carbapatites (5) and alkali-apatites (6) described with uniaxial cores and biaxial margins.

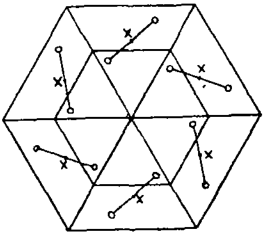

FIG. 3. Optical orientation of francolite on the basal plane.

Chemical composition.—A mixture, almost pure, of kaolinite and francolite was scraped from septarian cracks in the ironstone. After washing to remove the finer kaolinite and crushing to pass a 400-mesh sieve, the material was centrifuged in mixtures of methylene iodide and bromoform, and the fraction with density between 3·15 and 3·21 taken for analysis. The francolite thus obtained contained inclusions of kaolinite but little other impurity. The analysis is shown in table I.

TABLE I. Francolite from oolitic ironstone, Robin Hood quarry, near Leeds.

CaO	54·64	SiO_2	nil
SrO	0·13	TiO_2	nil
MgO	trace	Al_2O_3, Fe_2O_3	trace
P_2O_5	38·25	FeO	nil
CO_2	1·98	Cr_2O_3	nil
H_2O+ ...	0·66	V_2O_3, As_2O_3	nil
H_2O- ...	0·06	MnO	nil
F	2·80	BaO	nil
Insol.	2·19	Na_2O	nil
	100·71	K_2O	nil
Less O = F ...	1·18	Cl, SO_3	nil
	99·53		

In calculating the composition of the francolite the moisture and insoluble residue are ignored, and since the latter is mainly kaolinite an approximate content of 10 % H_2O+ (i.e. 0·22 %) is assumed and deducted from the combined water of the analysis, leaving 0·44 % H_2O+ for the francolite. The distribution of atoms within the molecule is calculated on the assumption that the structure is analogous to that of fluorapatite, $Ca_{10}P_6F_2O_{24}$, with 42 atoms in the molecule, and

(O,OH,F) 26. Ca, Sr, P, and C are therefore brought to a total of 16 atoms, the OH and F adjusted in the same ratio, and O obtained by difference. The composition, thus calculated, is shown in table II.

TABLE II. Atomic ratios in francolite.

	Weight %	Mol. ratios.	Atomic ratios.		Atoms to 26(O,OH,F).		Positive charges.	Negative charges.
CaO ...	54·64	9·743	Ca	9·743	9·999	10·012	19·998	
SrO ...	0·13	0·013	Sr	0·013	0·013		0·026	
P_2O_5 ...	38·25	2·695	P	5·390	5·531	5·993	27·655	
CO_2 ...	1·98	0·450	C	0·450	0·462		1·848	
H_2O+	0·44	0·244	OH	0·489	0·502	2·013		0·502
F ...	2·80	1·473	F	1·473	1·511			1·511
			O	—	23·982			47·964
					42·000		49·527	49·977

The francolite may therefore be given the formula:

$$(Ca,Sr)_{10}(P,C)_6(F,OH)_2O_{24}, \text{ with the ratio } F:OH = 3:1.$$

Gruner and McConnell recently investigated a francolite (staffelite) from Staffel (7), and deduced the formula $(Ca,Mg,C)_{10}(P,V,C)_6F_2(O,OH,F)_{24}$. There is a mathematical error in their calculation, however,[1] and, corrected, the distribution of ions in the Staffel mineral is: $10Ca = 9{\cdot}810Ca + 0{\cdot}077Mg + 0{\cdot}113C$; $6P = 5{\cdot}322P + 0{\cdot}026V + 0{\cdot}625C$; $2F = 2{\cdot}000F$; $24O = 22{\cdot}832O + 1{\cdot}000OH + 0{\cdot}168F$. The formula for this distribution is therefore better expressed as

$$(Ca,Mg,C)_{10}(P,V,C)_6F_2OH(O,F)_{23}.$$

McConnell proposed that francolite is 'a suitable name for an apatite which contains an appreciable amount of CO_2 but which also contains more than one per cent of fluorine. It may or may not contain OH-ions' (8, p. 9). The Yorkshire material conforms to this definition of francolite, but differs distinctly from previously analysed specimens in its particularly low content of OH-ion, and relatively low C and F values. These differences probably account for the high density of this francolite as compared with previous data. The differences are to be expected, not only on account of the varied substitutions possible within the apatite group, but also on account of the different modes of origin of the francolites investigated. Some are from hydrothermal ore-deposits, others (including the Staffel material) from marine phosphorites, while the present occurrence is the first record from freshwater sediments.

---

[1] In table I, p. 210, of their paper, HO is 0·90 per cent., so the ionic ratio for OH should be 1·000, not 0·100 as given.

Hey has pointed out ((8), footnote p. 9) that the original francolite from the Wheal Franco mine has never been analysed, so that the validity of the name as applied to materials from other localities is always doubtful. The name francolite is still used here, however, as it would be premature to propose a new name which might have to be withdrawn should the Wheal Franco mineral be analysed.

The author is indebted to Professor C. E. Tilley for laboratory facilities in the Department of Mineralogy and Petrology, Cambridge, and for advice and criticism.

References.

1. T. Deans, Trans. Leeds Geol. Assoc., 1936, vol. 5, pp. 161–187.
2. A. Lacroix, Minéralogie de la France, 1910, vol. 4, p. 558.
3. H. L. Bowman, Min. Mag., 1903, vol. 13, pp. 324–329.
4. J. Lietz, Zeits. Krist., 1931, vol. 77, pp. 437–498. [M.A. 5–38.]
5. A. F. Rogers, Amer. Journ. Sci., 1912, ser. 4, vol. 33, pp. 475–482.
6. E. S. Larsen and E. V. Shannon, Amer. Min., 1930, vol. 15, pp. 307–337. [M.A. 4–343.]
7. J W. Gruner and D. McConnell, Zeits. Krist., 1937, vol. 97, pp. 208–215. [M.A. 7–88.]
8. D. McConnell, Amer. Min., 1938, vol. 23, pp. 1–19. [M.A. 7–88.]