

Francolite, a Carbonate-Apatite from Milburn, Otago.

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INTRODUCTION.

FRANCOLITE, a carbonate-apatite, with the formula $(\text{Ca,C,Na,K})_{10}(\text{P,Si,C,Al})_6(\text{OH,F})_3\text{O}_{22.7}$ has been recognized in a quartz-sandy type of phosphorite from near Milburn, Table Hill Survey District, Otago Land District. The phosphorite has been described by Ongley (1939, p. 83) as sandstone, but its true nature has more recently been pointed out by Macpherson (MS.).

The mineral has been separated from the phosphorite in the pure state, analysed and optical and chemical properties determined. These facts are compared with similar data obtained from literature available to the writers. Finally, the petrography of the francolite-bearing rock is given and attention is drawn to its similarity with the Russian phosphorites of the Briansko-Kurski area.

PHYSICAL PROPERTIES.

The phosphate mineral occurs in stumpy hexagonal, or pseudo-hexagonal prisms, usually terminated at one extremity only by basal plane and low pyramids. The crystals rarely exceed 0.6 mm. in length. They are colourless, but show clouds of minute 'dust-like' inclusions of haematite or limonite. The inclusions are commonly regularly arranged so that a central hexagonal zone is heavily charged, leaving the periphery quite clear. The refractive index of the central portion appears to be very slightly less than that of the peripheral zone, although no other differences in optical properties were noticeable.

In a hexagonal section, γ of the refractive index ellipsoid is observed to be parallel with the hexagonal edge in each triangular sector of the twinned crystal, and not at an angle to it as found by Deans (1938, p. 136). Thus the Milburn francolite appears to be similar to that described by Lacroix (1910, p. 558) from the Vosges, and by Sandell, Hey and McConnell (1939, p. 397) from the mine Wheal Franco, Tavistock, Devon. In other cases basal sections do not show any evidence of repeated twinning and, therefore, are isotropic or extinguish uniformly. The refractive indices are closely comparable with previous data, some of which are given in Table I.

TABLE I.
Optical Properties of Francolite.

	α	β	γ	$\gamma-\alpha$	Reference.
1.	1.620	1.627	1.628	0.008	Deans, 1938.
2.	1.624	—	1.629	0.005	Sandell, Hey and McConnell, 1939
3.	1.619	—	1.628	0.009	McConnell, 1938B.
4.	{1.614— 1.617	1.627	{1.627— 1.630	0.013	de Villiers, 1942.
5.	{1.620— 1.622	{1.624— 1.627	{1.625— 1.627	0.005	This work.

The mineral is negative with an optic axial angle ranging from $0^\circ-25^\circ$ ($\pm 2^\circ$). Measurement of the angle on the universal stage

was a matter of some difficulty because of the fine grain-size and low birefringence. However, it was clearly seen that the optic axial angle varied from grain to grain, and sometimes within individual grains. The acute bisectrix is normal to the basal plane, hence prismatic crystals have negative elongation.

CHEMICAL PROPERTIES.

The characteristic feature of francolite or the carbonate-apatites in general as compared with normal apatites, is that the carbonate-apatites are soluble in warm dilute hydrochloric acid with liberation of bubbles of CO_2 .

In order to prepare a pure sample of francolite for analysis, the phosphorite was first crushed carefully and the larger quartz grains were screened out. The concentrated material was then ground to pass through a 200-mesh screen and the product elutriated carefully to rid the product of some of the clay fraction. Finally, the concentrate was centrifuged in bromoform-methylene iodide mixtures. The authors consider that a pure product was obtained, except that it was not possible to free the fine francolite particles entirely from minute inclusions of iron-ore. Close inspection of the purified product did not reveal any grains of quartz. In Table 2, the analysis of the Milburn francolite is compared with other data obtained from the literature, and it will be noted that a very close correspondence exists between these analyses and that of the Milburn mineral. The classification of the mineral as francolite rather than dahllite is based on McConnell's (1938A, p. 9) suggestion that dahllite should be limited to those types containing less than one per cent. of fluorine while francolite has more than this amount. The specific gravity, as determined with centrifuged material is 3.15-3.18. These figures may be a trifle high on account of the presence of tiny inclusions of iron-ore in the francolite.

Gruner and McConnell (1937) have shown that the structure of francolite is essentially similar to that determined by Náray-Szabó (1930) and Mehmel (1930, 1931) for fluor-apatite; and, further, Gruner and McConnell (1937) have demonstrated that the CO_2 present could be accounted for in terms of the structure of apatite. Therefore, the analysis of francolite from Milburn has been recalculated (Table 3) on this basis, after excluding Fe_2O_3 and FeO ; that is, assuming 42 atoms to the molecule, and with (O,OH,F) equal to 26. The main group, Ca, P and C, has been calculated to a total of 16 atoms to the unit cell, with F and OH calculated in the same ratio.

In this analysis (Table 3) we find additional evidence of the types of substitution shown to occur in ellestadite (McConnell 1937, p. 977), francolite (Gruner and McConnell 1937) and dahllite (McConnell 1938B). Silicon and aluminium, together with 0.353 atoms of carbon, the latter forming CO_4 -groups with a tetrahedral configuration, are assigned to phosphorus positions in order to make up the group to the theoretical figure of six. Sodium and potassium, together with the remainder of the carbon ions enter the lattice in the calcium positions. Although Si-ions enter the lattice in the phosphorus positions, S-ions, which might be expected, are not present. The amount of substitution by carbon in the calcium and

phosphorus positions, viz. 0.395 and 0.353 atoms per unit cell, appears to bear out the fact that as carbon goes into the calcium positions the birefringence of the mineral becomes lower. The scanty data available suggest that in a francolite in which calcium only is replaced by carbon, the birefringence may be reduced to a negligible figure. However, as de Villiers (1942, p. 446) points out, information on this is not yet available.

TABLE 2.
Analyses of Francolite.

	A.	B.	C.	D.	E.	F.
CaO	51.30	51.02	54.88	54.64	53.94	54.84
SrO	—	—	—	0.13	—	—
MnO	tr.	—	—	nil	—	—
MgO	0.41	0.47	0.31	tr.	0.10	0.53
Na ₂ O	0.46	0.71	—	nil	—	0.20
K ₂ O	0.17	0.57	—	nil	—	—
CO ₂	3.20	5.79	3.36	1.98	3.40	4.43
P ₂ O ₅	34.63	33.01	37.71	38.25	38.13	35.01
SiO ₂	2.27	tr.	—	nil	—	—
SO ₂	nil	1.77	nil	nil	nil	—
Al ₂ O ₃	1.18	0.20	—	—	—	—
Fe ₂ O ₃	2.11	0.66	—	tr.	0.34	0.25
FeO	0.27	—	—	nil	—	nil
TiO ₂	0.06	—	—	nil	—	—
F	3.66	3.55	4.11	2.80	3.71	5.60
Cl	nil	tr.	nil	nil	nil	0.03
H ₂ O+	1.18	3.16	1.14	0.66	0.46	1.51
H ₂ O—	1.02	0.54	0.04	0.06	0.01	0.16
Others	—	0.77	0.24	2.19	1.83	0.10
	101.92	102.22	101.79	100.71	101.92	102.66
O for F.	1.54	1.49	1.73	1.18	1.56	2.36
	100.38	100.73	100.06	99.53	100.36	100.30

- A. Francolite, Milburn, Otago; F. T. Seelye, Analyst.
- B. Francolite = grodnolite, near Grodno, Poland; W. Wawryk, Analyst (McConnell, 1938A, p. 6, Table 2, analysis 2).
- C. Francolite = staffelite, Staffel on Lahn, Nassau, Germany; R. B. Ellestad, Analyst (McConnell, 1938A, p. 6, Table 2, analysis 8).
- D. Francolite, Robin Hood Quarry, near Leeds; H. C. G. Vincent, Analyst (Deans, 1938, p. 137).
- E. Francolite, Wheal Franco Mine, Buckland Monachorum, Tavistock, Devon; E. B. Sandell, Analyst (Sandell, Hey and McConnell, 1939, p. 399).
- F. Francolite, Farm Annisfontein, Richtersveld, Namaqualand, Cape Province; C. J. Liebenberg, Analyst (de Villiers, 1942, p. 445).

TABLE 3.
Atomic Ratios in Francolite.

	Wt. %.	Mol. ratios.		Atomic ratios.	Atoms to 26 (O.O.H.F.).	
CaO	51.30	9.148	Ca	9.148	9.419	} 10.003
Na ₂ O	0.46	0.074	Na	0.148	0.152	
K ₂ O	0.17	0.018	K	0.036	0.037	
CO ₂	3.20	0.727	C	0.727	0.748	} 0.395
P ₂ O ₅	34.63	2.438	P	4.876	5.020	
SiO ₂	2.27	0.378	Si	0.378	0.389	} 6.000
Al ₂ O ₃	1.18	0.116	Al	0.232	0.238	
F	3.66	1.926	F	1.926	1.983	} 3.332
H ₂ O	1.18	0.655	OH	1.310	1.349	
			O	—	22.665	
					42.000	

The formula for francolite would approximately be:—
(Ca,C,Na,K)₁₀ (P,C,Si,Al)₆ (OH,F)_{2.3} O_{22.7}

Considering the amount of fluorine present, the figure for H_2O given off above $105^\circ C.$ appears to be very much too high and is certainly not wholly water of constitution. In the case of dahllite, McConnell (1938B, p. 301) suggests that water obtained above $300^\circ C.$ is present as OH-groups, but that the amount of water obtained between $110^\circ-300^\circ C.$ is, to some extent, dependent on the texture of the mineral and is greatly affected by the way in which the sample has been prepared. This water, McConnell believes, is not present as OH-groups in the lattice. From the calculations shown in Table 3, it seems likely that constitutional water would not exceed about one-eighth of the water given off above $105^\circ C.$, if the number of (OH,F) atoms is to be 2.

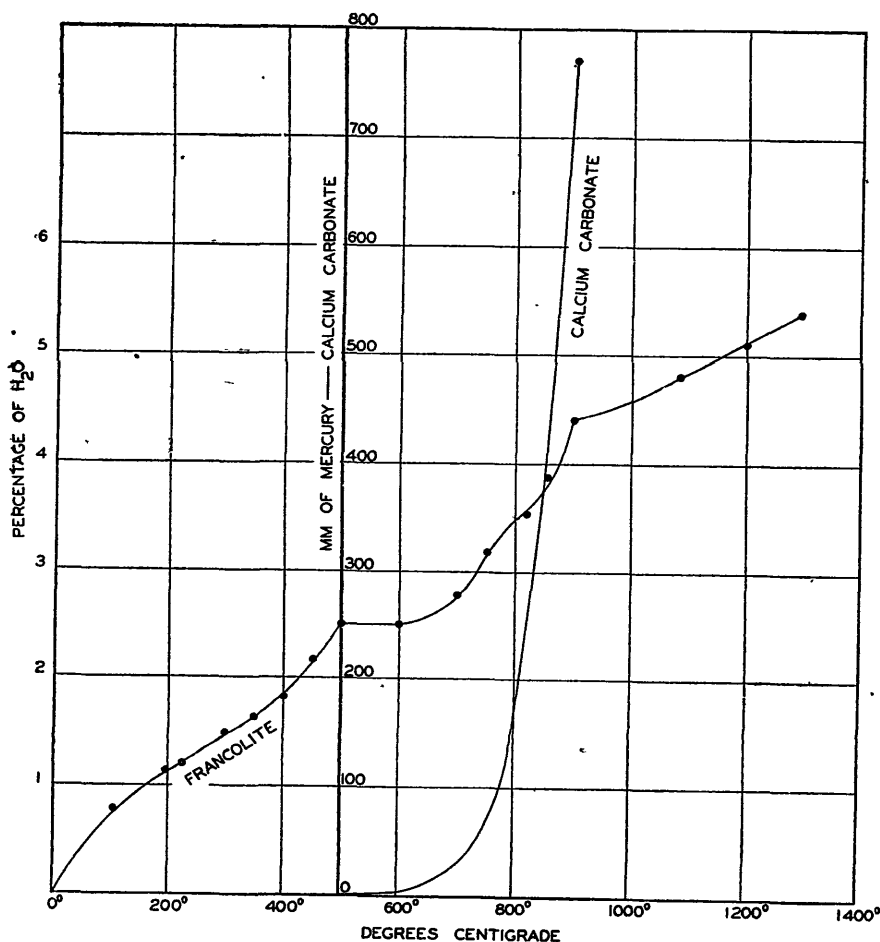


FIG. 1.

Curves showing loss on ignition of francolite (H_2O and CO_2), and dissociation pressures of $CaCO_3$ at given temperatures. The points at 1200° and 1300° on the francolite curve are approximately $\pm 100^\circ C.$

With a view to obtaining some information as to the condition of the water in francolite at various temperatures, a dehydration experiment was carried out and the results are represented in text-figure 1. In the experiment only 0.3 gms. of pure francolite was available after the main analysis had been completed; hence, because of this small quantity, it was only possible to find the loss of weight of francolite on heating and not the weight of water evolved at the various stages. Therefore, while fully aware of the complication introduced because of loss of CO_2 in addition to water, the writers record this data, because, as future workers obtain more information on the carbonate-apatites, some more exact interpretation of the curve may be possible. However, it may be pointed out that at a temperature of 500°C ., the loss of weight is 2.5%, that is 0.3% in excess of the weight of total water in the mineral. Therefore, it would seem that even at 500°C . some CO_2 must have been released from the francolite.* This point is of interest because a study of the dissociation pressures of CaCO_3 at given temperatures indicates the very small amount of CO_2 evolved at low temperatures such as 500° – 600°C ., when the carbonate is heated for brief periods. Not until a temperature of 800° – 900°C . is reached is CO_2 given off in large amount. This seems to be evidence against the possibility that the carbonate-apatites in general, and francolite in particular, are a mixture of $\text{Ca}_{10}\text{P}_6\text{F}_2\text{O}_{24}$ and CaCO_3 , as the theories of Machatschki (1939) and Thewlis, Glock and Murray (1939) demand.

The platform between 500° – 600°C . may be significant, but unfortunately the writers do not know what percentage of CO_2 has been driven off from the francolite. Nevertheless, a study of the CO_2 curve (text-fig. 1) and the curve obtained by heating francolite suggests that the amount of OH present in the lattice of the Milburn francolite is very small.

PETROGRAPHY.

The phosphorite is a pale yellow or buff-coloured rock, composed chiefly of well-rounded and strikingly polished grains of quartz, albite and minor glauconite set in a cement of crystalline francolite. Microscopically, however, it is seen that these minerals are associated with stained prochlorite, green hornblende, sphene, ferruginous epidote, clay, fragments of quartz-albite-epidote-muscovite-schist and some fossil material. The rounded grains of quartz and albite are associated with smaller, but less well rounded grains of the same minerals (text-fig. 2A); the average grain-size is 0.5–0.7 mm. Practically every granule of quartz shows very marked undulatory extinction and, in some cases, even incipient fracture.

The crystallography of the francolite has been described earlier, and it is only sufficient now to describe the microstructure. At least three modes of occurrence, each with transitional stages, are to be seen.

(1) As narrow crusts of prismatic crystals of francolite, up to 0.1 mm. in width, radially directed towards the plane of accumulation and surrounding minerals.

* It is possible that some of the loss of weight may be the result of expulsion of SiF_4 .

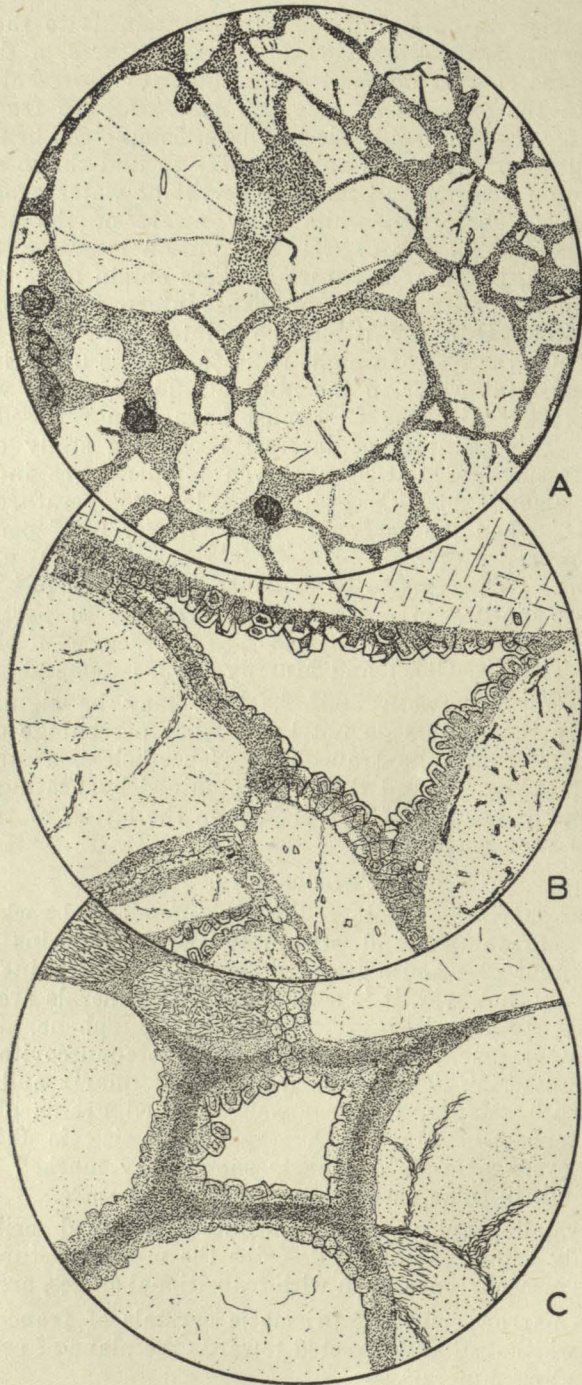


FIG. 2.

- A. Grains of quartz, with some albite and glauconite set in a finely crystalline base of francolite. X 24.
- B. A geode-like form of crystals of francolite radiating outward from quartz and albite. X 105.
- C. A geode of francolite between quartz grains; also some areas completely filled by francolite adjacent to grains of glauconite. X 105.

(2) As geode-like structures due to radial growth of francolite crystals inwardly towards cavities between adjacent groups of quartz and feldspar grains (text-fig. 2B and C).

(3) As areas of dense aggregates of crystalline francolite formed by the complete filling up by phosphate of the geode-like structures mentioned above (text-fig. 2C).

This mode of occurrence of the phosphate mineral is closely similar to that described by Bushinsky (1935, p. 86) in the Cenomanian Phosphorites of the Briansko-Kurski district of Russia.

The heavy mineral residues with a specific gravity > 3 were separated from the phosphorite and the grain-count was found to be as follows: garnet (mostly pink) 12, epidote 34, clinozoisite 3, sphene 38, tourmaline 1, zircon 12. Microchemical tests made on three garnets gave positive reactions for manganese. A study of the main and accessory constituents of the Milburn phosphorite makes it clear that the Otago Central schists have supplied practically all the detritus for these sediments. Strained and fractured quartz, a sodic feldspar, in this case nearly pure albite, fragments of quartz-albite-epidote-muscovite-schists, and all of the heavy residue minerals are essentially common to the Otago schist area. The question of the origin of the phosphatic material has been dealt with by other workers.

CONCENTRATION OF PHOSPHATE.

A number of experiments have been carried out in order to determine to what extent francolite may be concentrated by light crushing and screening. The clue to the problem is to be found in a comparison of the grain-sizes of the chief components of the phosphorite, viz. of quartz and albite, and of francolite. The average diameter of the quartz and albite is 0.5–0.7 mm., while the francolite crystals do not exceed 0.06 mm. in length. With gentle crushing or rubbing by such means as passing between rollers and subsequent screening through 90-mesh and 200-mesh sieves, a notable concentration of francolite results. Thus, when the original phosphorite containing 12.5% P_2O_5 was crushed and screened through 200-mesh, 23% of the crushed material was passed. A quantitative analysis of this product indicated 24% P_2O_5 . Investigation of the material remaining on the 200-mesh screen proved that further careful crushing yielded more concentrate with approximately the same P_2O_5 content. Similar operations were carried out using a 90-mesh sieve, and in this case 31% of the material passed through, and this was found to have a P_2O_5 content of 21%. Crushing tests on a specimen that had been naturally baked (P.4187) by overlying igneous rocks appeared to indicate greater friability than in the case of the unbaked material. Therefore it is suggested that initial roasting of the phosphorite might facilitate a more complete separation of the mineral particles on crushing, resulting in better concentration of francolite.

Thus it is evident that the arenaceous phosphorite of the Milburn-Clarendon areas might, by careful crushing and screening, supply a product with at least a content of 80% of francolite (28% P_2O_5). However, it is of economic importance to remember that the phosphate mineral is francolite with a maximum P_2O_5 content of 35%, whereas in the case of Nauru Island or Ocean

Island phosphatic material, the maximum P_2O_5 value obtainable would be about 39–40%, while an analysis of a typical guano from Christmas Island shows 39–44% P_2O_5 . On the other hand, when apatite is the raw material used, such as that from the Kukisvumchorr or Yukspor mines of Northern Russia, the P_2O_5 percentage reaches 41–42%.

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