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MINERALOGY OF THE FRENCH PHOSPHORITES.

INTRODUCTION.

In two recent publications,[1] Lacroix has described the mineralogy of the phosphorites of France and its colonies. These descriptions present so clearly the mineralogical composition of the phosphorites that I thought it would be of interest to students of the American phosphate deposits to present briefly the results reached by Lacroix. The data here given are, therefore, a free translation and compilation of his papers.

TYPES OF PHOSPHORITES.

The French phosphorites are of three types—

(1) Holocrystalline, fibrous; (2) amorphous (isotropic), homogeneous; (3) mixture of the amorphous and holocrystalline.

(1) The holocrystalline, fibrous type is composed of either dahllite or francolite. Dahllite is a hydrous carbonate and phosphate of lime, free from fluorine, and was first found in Norway, its occurrence there being described by Brögger and Bäckstrom[2] in 1888. Tschirwinsky's podolite, described[3] as a new mineral in 1907, is probably identical with dahllite.[4] Francolite was described in 1850 from Tavistock, Devonshire, England,[5] but has hitherto been considered a variety of apatite. Staffelite[6] is considered by Lacroix as identical with francolite, but the name is kept for the fibrous variety of francolite. Damour's hydroapatite[7] also is francoline. Francolite is similar to dahllite in composition, but contains a notable amount of fluorine.

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[1] Lacroix, A., Sur la constitution minéralogique des phosphorites françaises: Compt. Rend., vol. 150, 1910, p. 1213; Minéralogie de la France, vol. 4, second part, 1910, p. 555.

[2] Brögger, W. C., and Bäckstrom, H., Dahllite, a new mineral from Odegarden, Bamle, Norway: Abstracted in Zeitschr. Kryst. Min., vol. 17, 1890, p. 426; also in Dana's system of mineralogy, 6th ed., 1892, p. 866.

[3] Tschirwinsky, W., Podolite, a new mineral: Centralbl. Min. Geol. Pal., 1907, p. 279. For some earlier but incomplete descriptions in Russian publication, see abstract thereof in Zeitschr. Kryst. Min., vol. 46, 1909, p. 296.

[4] Lacroix, op. cit. See also the following paper in this volume.

[5] Henry, T. H., On francolite, a supposed new mineral: Philos. Mag., vol. 36, 1850, p. 134. The CO_2 present in the mineral was not detected by Henry. A better analysis of francolite from Cornwall was later given by Story-Maskelyne, N., and Flight, W., Mineralogical notes—3, Francolite, Cornwall: Jour. Chem. Soc. (London), vol. 24, 1871, p. 3.

[6] Stein, C. A., Ueber das Vorkommen von phosphorsauren Kalk in der Lahn- und Dill-gegend mit besonderer Berücksichtigung des Vorkommens bei Staffel, Amts Limburg: Jahrb. Ver. Naturk. Herzogthum Nassau, vols. 19-20, 1864-1866, p. 41. Abstracted in Jahrb. Min., 1866, p. 716.

[7] Sur l'hydro-apatite, espèce minérale: Annales des mines, vol. 10, 1856, p. 65.

(2) The amorphous, perfectly isotropic type is composed of the mineral collophanite, which is a hydrous carbonate and phosphate of lime, generally free from any appreciable amount of fluorine, but rarely containing a small amount (fluocollophanite).

(3) The third type is composed of the following minerals, in variable amounts:

(*a*) Dahllite; (*b*) francolite (var. staffelite); (*c*) an unknown mineral, similar to dahllite and francolite in chemical composition but differing optically from them; (*d*) collophanite.

This type of phosphorite, composed of an amorphous mineral and one or more crystalline minerals, is called quercyite. If the unknown mineral ((*c*) above) is absent, the subtype is called α–quercyite; if the unknown mineral is present, the subtype is called β–quercyite. Quercyite is often formed of alternating layers of α–quercyite and of β–quercyite.

DESCRIPTION OF MINERALS.

DAHLLITE.

Dahllite occurs as fibrous crusts, stalactites, or concretions with a radiating or confused fibrous structure, and also in a pure state as nodular masses and concretions, some resembling the fungus polypore having formed against the sides of pockets in the phosphorite. It is colorless, white, yellow, or greenish, and is transparent in thin pieces. The streak is white, and the luster vitreous, dull, silky, or slightly greasy in the very pure specimens. The fibrous concretions are very tenacious. The fracture yields a dull white surface, sometimes showing a regular fibrous structure, but more often the fibers are radiating or intermingled. From the similarity of the shape of the nodular masses of dahllite, quercyite, and collophanite, the dahllite may have formed by the dehydration of the quercyite or the collophanite.

Optically the mineral is hexagonal, uniaxial, and negative, the fibers being elongated parallel to the least index of refraction. It shows the helicoidal optical grouping. The birefringence is slightly greater than that of apatite. The mean refractive index $(n) = 1.625$ approximately; the hardness is 5, and the density ranges from 2.97 (on confused fibrous masses more or less porous) to 3.053. When heated in a closed tube, it decrepitates without fusion, giving off water. It is readily soluble in cold dilute acids, with evolution of CO_2. The formula is given as $2Ca_3(PO_4)_2.CaCO_3.\frac{1}{2}H_2O$, but is more probably $3Ca_3(PO_4)_2.CaCO_3.H_2O$. See discussion in the following papers in this volume. For analyses see the table at the end of this paper.

FRANCOLITE.

Francolite is found as minute hexagonal crystals showing the forms *c* {0001} and *m* $\{10\bar{1}0\}$. These are tabular, flattened parallel to *c* {0001}, and are generally grouped in rosettes or confused masses. More frequently it forms the fibrous variety staffelite, as mammillated fibrous crusts or as very pure spherolites which were formerly considered to be apatite. These spherolites occasionally show minute crystals, about 1 millimeter in length, with free ends. They are colorless, white, yellow, or greenish, with a vitreous luster which tarnishes or becomes dull on exposure to air, the specimens changing from translucent to opaque. The streak is white.

The hexagonal crystals show a division of the basal section into six sectors, each normal to an acute negative bisectrix, the trace of the large axial angle being, in each sector, parallel with the prism edge. By superposition of biaxial plates the crystals often appear uniaxial. The birefringence is, like that of dahllite, 0.004 to 0.005, and the mean refractive index $(n) = 1.625$ approximately. The hardness is 4 to 5, and the density 3.09 to 3.128. In its pyrognostic and chemical properties, it is similar to dahllite, except that it shows the presence of fluorine. The formula given for it is $(CaF)_2Ca_8(PO_4)_6.CaCO_3 + H_2O$. Analyses are given at the end of this paper.

UNKNOWN MINERAL.

The unknown mineral, mentioned as forming the characteristic component of β-quercyite, has not been found in a pure state, so that its chemical composition is not accurately known, but from analyses of specimens of β-quercyite rich in this unknown mineral (analyses Nos. 11 and 12 of this paper), its composition is doubtless near that of dahllite and francolite. The distinguishing test, however, is its optical character, for it is positive while both dahllite and francolite are optically negative. The birefringence of this positive mineral is about double that of the negative ones.

COLLOPHANITE.

The amorphous mineral collophanite forms concretionary masses, resembling opal or gum, and has a conchoidal fracture. An earthy variety is called monite. Some of the nodules or masses are nearly transparent, and others are only translucent, but most of them are opaque. The nearly transparent kind looks like carnelian stone, the others more like enamel. It is colorless, white, yellow, brown, or reddish. It has a vitreous luster, a little resinous or earthy in the variety monite. It is isotropic. The index of refraction is not constant for different specimens. Two different samples gave for sodium light the values 1.569, 1.612. The hardness is 4.5, and the density of the common variety 2.69–2.82, though that of monite is as low as 2.1. One variety is very poor in or entirely free from fluorine; a second variety (fluocollophanite) contains fluorine ranging up to an amount, in proportion to the P_2O_5 content, equal to that present in apatite. Its pyrognostic and chemical properties are like those of the crystallized compounds. Collophanite is often impure from admixed substances. It may be distinguished from similar minerals, such as opal, by its ready solubility in acids with evolution of CO_2, and by its P_2O_5 reaction. The formula given for it is $x[Ca_3(PO_4)_2]$ or $x[(CaF)_2Ca_8(PO_4)_6]+yCaCO_3+zH_2O$. See following papers. Analyses are given at the end of this paper.

QUERCYITE.

The name quercyite is applied to mixtures of the amorphous collophanite and the crystalline dahllite, francolite, and the unknown mineral. The most common type of the French phosphorites is this variable mixture called quercyite. Only a small portion of the phosphorites are composed of either collophanite or one of the crystallized phosphates. The mixture in quercyite is so intimate that it is impossible to separate the constituents mechanically. If the crystalline mineral present is optically negative the mixture is called α-quercyite; if the unknown mineral (optically positive) is present, the mixture is called β-quercyite. Quercyite is often composed of alternating layers of α- and β-quercyite. Some of the layers may be nearly free of any crystalline material when they are composed of only collophanite. The density of α-quercyite is 2.83 to 2.87, and the mean refractive index about 1.608.

SUMMARY OF PROPERTIES.

This completes the list of minerals forming the French phosphorites. For convenience their chief diagnostic properties, including those of α-quercyite and of fluorapatite, are here tabulated:

Properties of phosphorite minerals.

	Dahllite.	Francolite.	Unknown mineral.	Collophanite.	α-Quercyite.	Fluorapatite.
Density	2.97–3.05	3.09–3.13	(?)	2.69–2.82	2.83–2.87	3.2
Mean refractive index	1.625	1.625	(?)	1.569–1.612	1.608	1.63
Birefringence	0.005 (approx.).	0.005 (approx.).	0.009 (approx.).	0.000	0.005	0.004
Optical character	Negative.	Negative.	Positive.	Isotropic.		Negative.
Distinguishing chemical component	CO_2,H_2O	F,CO_2,H_2O	(?)	CO_2,H_2O	F,CO_2,H_2O	F.

CHEMICAL COMPOSITION.

The chemical composition of the minerals and of their mixture—quercyite—can be seen by the analyses given below. They have been grouped together in this way in order to render the comparison more easy.

Dahllite analyses	1.	Original analysis, Bamle, Norway.
	2.	Mouillac, Quercy, France.
	3.	Podolite, crystals, Podolie, Russia.
	4.	Podolite, crystalline aggregate, Podolie, Russia.
Francolite analyses	5.	Cornwall, England.
	6.	d'Encourtiech, Ariège, France.
	7.	Staffelite, Staffel, Limburg.
Collophanite analyses	8.	Original analysis, Sombrero, Antilles.
	9.	Pouzillac, Gard, Cévennes, France.
Quercyite analyses	10.	α-quercyite, Mouillac, Quercy, France.
	11.	β-quercyite, Mouillac, Quercy, France.
	12.	β-quercyite, Castillo de Belmez, Cordone, Spain.

Analyses of phosphorite minerals.

	Dahllite.				Francolite.			Collophanite.		Quercyite.		
	1	2	3	4	5	6	7	8	9	10	11	12
CaO	53.00	53.65	51.15	51.31	54.09	52.32	54.67	50.70	49.73	51.85	50.45	52.50
P_2O_5	38.44	38.40	39.04	36.44	38.14	40.00	39.05	39.10	37.40	37.60	36.60	37.75
F	....	Trace.	.00	.26	3.34	3.36	3.05	....	.88	1.50	.83	Trace.
CO_2	6.29	5.30	3.90	4.18	2.25	5.30	3.19	3.96	3.75	4.00	4.62	5.70
H_2O	1.37	2.10	(?)	(?)	1.59	....	1.40	5.02	7.05	4.80	6.00	3.20
$(Al,Fe)_2O_3$	....	.57	3.04	2.19	.91	.43	.06	....	.50	....	1.30	.85
MgO	[a].79	....	....	....	....	....	.69	.80	....	....	....	....
$(K,Na)_2O$	1.00	....	....	1.11	....	....	....	....	.30	....	....	....
Organic	....	....	....	.56	....	....	....	....	....	....	....	....
SiO_2 (insoluble)	....	....	....	4.87	....	....	....	....	....	....	....	....
	100.89	100.02	97.13	100.92	101.01	101.41	101.42	99.58	99.61	99.75	99.80	100.00
Less O for F	....	....	....	.11	1.41	1.41	1.28	....	.37	.63	.35	....
	....	....	....	100.81	99.60	100.00	100.14	....	99.24	99.12	99.45	....

[a] FeO.

THE PROBABLE IDENTITY OF PODOLITE WITH DAHLLITE.

A comparison of the properties and chemical composition of podolite and dahllite shows them to be essentially identical. Dahllite was described in 1888 by Brögger and Bäckström,[1] and podolite by Tschirwinsky [2] in 1907, and the summary of the properties of the two minerals given below has been prepared from the printed descriptions.

Properties of dahllite and podolite.

Dahllite.	**Podolite.**
Occurs in crusts with fibrous structure, on apatite.	Occurs in crystalline masses or in prismatic crystals on phosphorite, also in spherulites of prismatic crystals.
Density is 3.053.	Density is 3.077.
Color is pale yellowish white.	Color is yellowish.
Uniaxial, negative.	Apparently hexagonal, crystals show optical anomalies, negative.
Double refraction and index of refraction slightly greater than that of apatite.	Double refraction somewhat greater than that of apatite.
Soluble in cold dilute acid with evolution of CO_2.	Mean index of refraction 1.635.
	Soluble in HCl with evolution of CO_2.
Composition..... $\begin{cases} H_2Ca_{14}P_8C_2O_{39} \text{ or} \\ 2Ca_3P_2O_8.CaCO_3.\frac{1}{2}H_2O \end{cases}$	Composition..... $\begin{cases} Ca_{10}P_6CO_{27} \text{ or} \\ 3Ca_3P_2O_8.CaCO_3 \end{cases}$

To better compare the two formulas, they are given below with Ca given in constant amount.

Dahllite..	$H_{10}Ca_{70}P_{40}C_{10}O_{195}$
Podolite..	$Ca_{70}P_{42}C_7O_{189}$

The analyses of the two minerals are shown in the following table for comparison:

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[1] Brögger, W. C., and Bäckström, H., Dahllite, a new mineral from Odegarden, Bamle, Norway. Abstracted in Zeitschr. Kryst. Min., vol. 17, 1890, p. 426; also in Dana's System of mineralogy, 6th ed: 1892, p. 866.

[2] Tschirwinsky, W., Podolite, a new mineral: Centralbl. Min., Geol. u. Pal., 1907, p. 279; abstracted in Zeitschr. Kryst. Min., vol. 46, 1909, p. 296.

Analyses of dahllite and podolite.

	Dahllite.	Podolite.	
		Crystals.	Crystalline aggregate.
CaO	53.00	51.15	51.31
P_2O_5	38.44	39.04	36.44
CO_2	6.29	3.90	4.18
H_2O	1.37	Not det.	Not det.
Fe_2O_3	[a].79	3.04	1.73
Al_2O_3			.46
K_2O	.11		.45
Na_2O	.89		.66
F		.00	.26
Organic			.56
SiO_2			4.87
Total	100.89	97.13	100.92

[a] FeO.

The above figures show the undoubted identity of the three substances analyzed. The CO_2 values for podolite are slightly lower than that given for dahllite, but the differences are slight. Water was not determined, but it must unquestionably have been present, for such a secondary mineral as podolite would be very likely to contain some, and a small amount, at least, must have been absorbed by the ground sample. The poor summations and the varying values in general lead one to suspect that further analyses of purer material, carefully made, would lead to slightly different results.

THE COMPOSITION OF THE PHOSPHORITE MINERALS.

INTRODUCTION.

The previous paper on the mineralogy of the French phosphorite deposits contains several analyses of these minerals, which, with those already published, furnish sufficient criteria for a determination of their formulas. I have therefore calculated the ratios from the different analyses and by averaging them up, have deduced formulas for the minerals in question. Below the actual ratios obtained, I have given them with CaO taken as 100.

DAHLLITE.

From analyses 1 to 4, given on page 95, the following ratios are obtained:

Ratios from dahllite analyses.

	1	2	3	4
CaO	0.945	0.956	0.912	0.915
P_2O_5	.271	.270	.275	.256
CO_2	.143	.120	.090	.095
H_2O	.076	.117	(?)	(?)
CaO	100	100	100	100
P_2O_5	29	28	30	28
CO_2	15	13	10	10
H_2O	8	12	(?)	(?)

The average values of these yield the formula

$$100(CaO).\ 29(P_2O_5).\ 12(CO_2).\ (10H_2O),$$

which is sufficiently close to the simple one

$$10CaO.\ 3P_2O_5.\ CO_2.\ H_2O.$$

to suggest strongly that this is the correct formula for dahllite.

FRANCOLITE.

From analyses 5 to 7, given on page 95, the ratios shown below are deduced:

Ratios from francolite analyses.

	5	6	7
CaO	0.964	0.933	0.974
P_2O_5	.269	.282	.275
F	.176	.177	.161
CO_2	.051	.084	.072
H_2O	.088	.088	.078
CaO	100	100	100
P_2O_5	28	30	28
F	18	19	17
CO_2	5	9	8
H_2O	9	9	8

The average of these values gives—

$$100(CaO).\ 29(P_2O_5).\ 18(F).\ 7(CO_2).\ 9(H_2O)[\text{minus } 9O],$$

which reduces to the simpler formula

$$10(CaO).\ 3(P_2O_5)\ 2(F).\ (CO_2).\ (H_2O)\ [\text{minus } 1O],$$

which may be written

$$9CaO.\ 3P_2O_5.\ CO_2.\ H_2O.\ CaF_2.$$

The average ratio of P_2O_5 to CaO is 3 to 10.44, being for analysis No. 5, 3 to 10.75; for analysis No. 6, 3 to 9.93; and for analysis No. 7, 3 to 10.63. This value lies almost exactly halfway between the 3:10 ratio required by my formula above and the 3:11 required by Lacroix's formula for francolite.

COLLOPHANITE.

From the values given in analyses 8 and 9, on page 95, the following ratios are deduced:

Ratios from collophanite analyses.

	8	9
CaO	0.904	0.886
P_2O_5	.275	.263
F	....	.046
CO_2	.090	.085
H_2O	.279	.392
CaO	100	100
P_2O_5	30	30
F	....	5
CO_2	10	10
H_2O	31	44

The average formula developed is

$$10CaO.\ 3P_2O_5.CO_2.\ 3+\ H_2O(+F?).$$

SUMMARY.

The three formulas developed are repeated here in order to show their relation to one another. To the list are added those of apatite, both the fluoapatite and the hypothetical hydroxyapatite.

Dahllite..........	$9CaO.3P_2O_5.CaO.\ CO_2.H_2O.$
Francolite.........	$9CaO.3P_2O_5.CaF_2.CO_2.H_2O.$
Collophanite......	$9CaO.3P_2O_5.CaO.\ CO_2.H_2O+nH_2O.$
Fluoapatite	$9CaO.3P_2O_5.CaF_2.$
Hydroxyapatite...	$9CaO.3P_2O_5.CaO.\ H_2O.$

The derivation of dahllite from the dehydration of collophanite becomes very simple, proceeding according to the reaction,

$$\underset{\text{(Collophanite)}}{9CaO.3P_2O_5.CaO.CO_2.H_2O.nH_2O} = \underset{\text{(Dahllite)}}{9CaO.3P_2O_5.CaO.CO_2.H_2O} + nH_2O.$$

By the introduction of fluorine, the reaction would yield francolite instead of dahllite:

$$\underset{\text{(Collophanite)}}{9CaO.3P_2O_5.CaO.CO_2.H_2O.nH_2O} + 2HF = \underset{\text{(Francolite)}}{9CaO.3P_2O_5.CaF_2.CO_2.H_2O} + nH_2O.$$