

*Florencite, a new hydrated Phosphate of Aluminium and the Cerium Earths, from Brazil.*

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*Occurrence.*

FLORENCITE was first discovered as a rare constituent of the cinnabar-bearing sands of Tripuhy, near Ouro Preto, Minas Geraes, Brazil. Here it occurred in well-developed crystals (up to  $\frac{1}{2}$  cm. in length), in association with monazite, xenotime and the titano-antimonates (lewisite and derbylite) previously described.<sup>1</sup> Blowpipe experiments made by Dr. W. Florence showed that the mineral was a phosphate of the cerium earths, while angular measurements of the crystals and observations of the optical characters suggested its close relationship with hamlinite, the new hydrated phosphate of aluminium, barium and strontium, recently described by Hidden and Penfield.<sup>2</sup> From this locality it was not possible to pick out sufficient material for quantitative analysis. In much larger amount, however, and in larger crystals and rounded grains, the same mineral was found later in a sample of diamond-bearing sand from "Matta dos Creoulos" on the Rio Teque-tinhonha, near Diamantina, Minas Geraes, which was collected by Prof. O. A. Derby. The material used in the quantitative chemical analysis was from this source. It consisted of acute rhombohedral crystals, the angular measurements and optical properties of which were in perfect agreement with those of the mineral from Tripuhy.

A third source of the new mineral is the Morro do Caixambú, the well-known locality of the yellow topaz near Ouro Preto and Tripuhy. Here it was found in relatively large amount as a microscopic accessory constituent of the reddish micaceous schists, in the quartz lenticles of which

<sup>1</sup> *Min. Mag.* XI, 80, 176 (1896-7).

<sup>2</sup> *Am. J. Sci.* 1890, XXXIX, 511, and 1897, IV, 313.

occurs the topaz in association with kaolin and hæmatite. Examination of the microscopic crystals, which had been obtained by Prof. O. A. Derby in the heavy residue of the schists, showed that they were rhombohedral and optically uniaxial, and that they contained phosphoric acid and cerium earths. There is therefore little doubt of their specific identity with the mineral from Tripuby and "Matta dos Creoulos."

*Crystallographic and other physical characters* (E. H.).

The crystal system of florencite is rhombohedral (trigonal, ditrigonal-scalenohedral class of Groth).

Axial ratios (calculated from  $r'r'''$ ):— $a : c = 1 : 1.1901$ .

Observed forms and combinations:—

$r = R, (10\bar{1}1)$ , rare.

$f = -2R, (02\bar{2}1)$ , the predominant form with

$c = OR, (0001)$ .

$m = \infty R, (10\bar{1}0)$ , very rare,

and an obtuse positive rhombohedron, probably  $+\frac{1}{2}R(0112)$ .

Measured angles:—

$f'r' = 54^\circ 13'$ , very good reflections.

$r'f'' = 54^\circ 11'$ .

$f''r'' = 54^\circ 13'$ , very good reflections.

$r''f''' = 54^\circ 18'$ .

$f'''r''' = 54^\circ 14'$ .

$r'''f' = 54^\circ 20'$ .

$f'f'' = 108^\circ 26'$ .

$\ast r'r''' = 88^\circ 56'$ .

These angles correspond very closely with those given by Penfield for hamlinite, as seen in the following table:—

Florencite (Husak).			Hamlinite (Penfield).
$r'r''' = 88^\circ 56'$	...	...	$87^\circ 2'$
$f'f'' = 108^\circ 26'$	...	...	$108^\circ 2'$
$r'f' = 54^\circ 13'$	...	...	$54^\circ 1'$
$a : c = 1 : 1.1901$	...	...	$1 : 1.1853$

The rhombohedral faces are generally bright, and give good reflections. The basal plane, on the other hand, is rough and much curved.

Cleavage: basal, fairly perfect. The fracture is splintery to sub-conchoidal. The hardness is about 5. The specific gravity (weight of one cc.)

of the material used for analysis was 3.586 at 17°, as determined on 0.5601 gram. The lustre is greasy to resinous. The colour of the pure mineral is clear pale yellow, but the crystals are often spotted black by included microscopic needles of tourmaline, or are coloured red by oxide of iron. The mineral is transparent, and is optically uniaxial and positive. The double refraction is not very strong.

*Chemical Composition* (G. T. P.).

The mineral is infusible. Heated in the closed tube it gives off acid water, and leaves signs of etching on the tube. As in the case of hamlinite, very strong ignition is necessary before all the water is expelled: 1 0.2043 gram gave off no water at 180°, and only lost  $\frac{1}{2}$  m.gr. after heating for an hour and a half up to 240°.

The mineral appeared to be only partially soluble in hydrochloric acid, a residue being always left even after prolonged digestion. Qualitative analysis showed the presence of phosphoric acid, cerium earths, alumina, water, and somewhat doubtfully of fluorine: no beryllia, yttria earths, thorium or zirconia could be detected.

The results of the quantitative analyses are as follows:—

	I.	II.	III.	Mean.	Mol. Ratios.	Hamlinite (Penfield)
Al <sub>2</sub> O <sub>3</sub> ...	= 32.05	—	32.52	32.28	.316	32.80
Ce earths = 28.20	—	—	27.80	28.00	.080	—
(Molecular weight = 352 <sup>2</sup> )						
Fe <sub>2</sub> O <sub>3</sub> ...	= 0.76	—	—	0.76	—	.90
CaO ...	= 1.31	—	—	1.31	—	—
SiO <sub>2</sub> ...	= 0.48	—	—	0.48	—	.96
P <sub>2</sub> O <sub>5</sub> ...	= 25.08	—	26.04	25.61	.181	28.92
H <sub>2</sub> O ...	= —	10.87	—	10.87	.604	12.00
(Loss on ignition)						
F ...	= undet.	—	—	99.31	—	1.93
					SrO	18.48
					BaO	4.00
					Alkalies	.74
						100.18

<sup>1</sup> An attempt to determine the water directly by igniting the mineral in a porcelain boat in a combustion tube failed owing to the fact that in this way it could not be heated to a sufficiently high temperature.

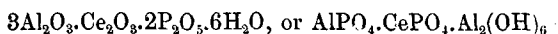
<sup>2</sup> Two determinations of the molecular weight were made, one on 0.0743 gr. and the other on 0.1113 gr. of the ignited oxide, by converting into sulphate and precipitating the sulphuric acid with barium chloride. The two results were in close agreement (352.2 and 352.7), but give a number which is considerably higher than those usually accepted for any of the cerium earths. Examination of the absorption spectrum of a solution of the sulphate suggested that didymium was only present in very small amount, as the characteristic bands in the green and yellow were only faintly visible.

Weight of material used in I, 0.3289 gram; in II, 0.1545 gram; in III, 0.2043 gram.

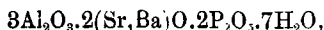
*Method of Analysis.*—The portion soluble in hydrochloric acid and the insoluble residue were treated separately, but the composition of the two appeared to be practically the same. In the soluble portion the cerium earths were precipitated by oxalic acid, the alumina and part of the phosphoric acid in the filtrate by ammonia, and the rest of the phosphoric acid by magnesia mixture. In this way, however, by no means perfect separations were effected, so each precipitate was separately treated, and the phosphoric acid in it determined by the molybdate method. The insoluble portion was fused with sodium carbonate, and the portion soluble in water and the residue were separately treated in the same way as the original solution, in the case of all the precipitates the phosphoric acid being finally determined by the molybdate method. The loss on ignition was determined in a separate portion by igniting with lime according to Penfield's method.<sup>1</sup> A determination of the loss on ignition without the use of lime gave 11.50 per cent.

The cerium earths, which on ignition were of a deep brownish red colour, were tested for yttria earths by converting into sulphates and precipitating with potassium sulphate: in the filtrate only a slight precipitate was obtained with oxalic acid. No precipitate was obtained with sodium thiosulphate in the solution of the sulphate.

The numbers obtained, considering the probability that by the method of analysis on so small an amount of material the alumina may be somewhat over and the phosphoric acid under estimated, suggest the formula—



analogous to that given to hamlinite by Penfield—



in which part of the HO is replaced by F.

The chemical composition of florencite is thus very similar to that of hamlinite, the strontia and baria of the latter being in florencite replaced by cerium earths.

The result of the analysis is, therefore, to support the idea suggested by the similarity in crystallographic and optical properties, cleavage, &c., that the two minerals are really isomorphous.

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<sup>1</sup> *Am. J. Sci.* 1897, IV. 314.

This result is of interest in view of the researches of Wyruboff and others,<sup>1</sup> who have shown the isomorphism of many cerium salts with corresponding salts of calcium and strontium, and have based on these facts arguments for the diad character of the cerium earths.

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<sup>1</sup> Wyruboff, *Bull. Soc. Min.* 1896, XIX, '282; Cossa, *Compt. Rend.* XCVIII, 1884, 990; *Accad. d. Lincei*, 1878 and 1879 [3] and 1886 [4].

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