FLORENCITE, AN OCCURRENCE IN THE ZAIRIAN COPPERBELT*

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ABSTRACT

Florencite has been identified in a sample from the Shituru deposit of Shaba in the Zairian extension of the Central African copperbelt. Its composition is very close to that of the type material $CeAl_3(PO_4)_2(OH)_6$ except for the La content, which is the highest on record. The fact that La is in excess of Ce is unusual, though in the literature, florencite occurrences have been reported where La and Nd predominate. The Shituru florencite occurs as pseudocubic crystals 20 to 30 micrometres in average diameter, in what was originally a chloritic red siltstone, rich in hematite, underlying lagoonal dolomites mineralized in copper and cobalt. The florencite originated during the hydrothermal events that altered the siltstone, transforming the chlorite into a regularly interstratified clay.

Keywords: florencite, rare earths, Shituru deposit, Shaba, Zaïre, Central African copperbelt.

SOMMAIRE

La florencite a été reconnue dans un échantillon provenant du gisement de Shituru (Shaba), qui est localisé dans l'extension zaïroise de la ceinture cuprifère centrafricaine. En composition, elle est très semblable à son type $CeAl_3(PO_4)_2(OH)_6$ sauf en ce qui concerne les proportions relatives des terres rares: la teneur en La est la plus forte connue. Le fait que La soit plus abondant que Ce est rare, quoique la littérature rapporte l'existence de florencite où La et Nd prédominent. A Shituru, la florencite se présente en cristaux pseudocubiques, de 20 à 30 micromètres de diamètre, dans ce qui était originellement un silt chloritique rouge, riche en hématite. Ce silt est recouvert de dolomies lagunaires, minéralisées en cuivre et en cobalt. L'origine de la florencite doit être cherchée dans les phénomènes hydrothermaux qui ont altéré le silt, y transformant la chlorite en une argile régulièrement interstratifiée.

INTRODUCTION

Florencite is a member of a group of isostructural hydrous Al phosphate minerals identified by the ideal chemical formula $XAl_3(PO_4)_2(OH)_6$. In this formula, X is predominantly Ce in florencite, Ca in crandallite, Pb in plumbogummite, Ba in gorceixite and Sr in goyazite. The analyses of florencite reported in the literature show that Ce, La and Nd are the most abundant rare-earth elements in the mineral. Of these Ce is normally predominant; La (this study) and Nd (Milton & Bastron 1971) are, occasionally, the most abundant rare-earths.

Reported occurrences of florencite are numerous; the reports describe the mineral as associated with a wide variety of parageneses. Florencite was first described as a rare constituent associated with monazite and xenotime in placer samples from Ouro Preto in Minas Gerais, Brazil, and as an accessory mineral in mica schists of the same area. Florencite was also observed associated with goyazite and gorceixite in diamond-bearing sands of the Jequitinhonha River near Diamantina, Brazil [all these occurrences were reported by Hussak & Prior (1900)].

Other reported occurrences of florencite in alluvial placers are in Gabon and France (Devismes *et al.* 1968), in the diamond placers of Ubangi, Central African Republic (Trueb & de Wys 1971) and in the Ural Mountains, U.S.S.R. (Semenov & Barinskii 1958). Florencite is abundant in the gold–sulfide deposits and associated placers of the gold-ore fields in the Donets Basin, U.S.S.R. (Kuznetsov *et al.* 1974) and in the North Baikal Mountains, U.S.S.R. (Aleksandrov *et al.* 1975). In these gold deposits, florencite is considered a hydrothermal

mineral probably precipitated from rare-earth carbonate complexes. This origin is possibly similar to the gold–cinnabar–florencite mineralization of the Bondoukou region, Ivory Coast (Casanova *et al.* 1970).

It is generally accepted that rare-earth mineral deposits have a genetic relation to alkalic igneous rocks. In this particular environment florencite, commonly associated with monazite, was recognized in potassic pegmatites (Ramdohr & Thilo 1940, King 1952, Whittle 1954, Rao & da Cunha e Silva 1968, Mitchell & Geitgey 1968), in late hydrothermal alteration (Trace 1960, Mel'nikova *et al.* 1975, Fazekas *et al.* 1975) in tin veins (van Wambeke 1971), and especially in the late ankeritic stage of carbonatite differentiation sequences (Smith 1953, Garson 1958, James 1958, McKie 1962, Somina & Bulakh 1966).

Other occurrences of florencite are in weathered zones (Bain 1970, Milton & Bastron 1971) and, like monazite, in metamorphic rocks in which the mineral is recrystallized (Gapon 1965, Theunissen & Martin 1969, Nikolaeva *et al.* 1971).

Even though occurrences of florencite are relatively widely reported, information on its optical properties, chemistry and structure is limited and often sketchy: sometimes the chemistry is reported, but not the optical properties or structure and *vice versa*. For that reason, the mineral and particularly its chemistry are poorly defined; even though the theoretical formula shows Ce as the major rare-earth element, the reported analyses show that La and Nd may be abundant and sometimes even predominant without apparently changing the crystal structure. As well as describing the new occurrence from Zaïre, the present paper attempts to summarize the available data on florencite and to clarify, on the basis of such data, the identity and characteristics of the mineral.

MODE OF OCCURRENCE OF THE ZAIRIAN FLORENCITE

The florencite discovered in Zaïre occurs in one of the copper deposits of Shaba province. These deposits are located in the Late Precambrian Katangan sequence (Cahen 1974), which is divided into the upper Kundelungu Supergroup and the lower Roan Supergroup. The Roan consists of cyclic successions of continental redbeds and lagoonal dolomites with
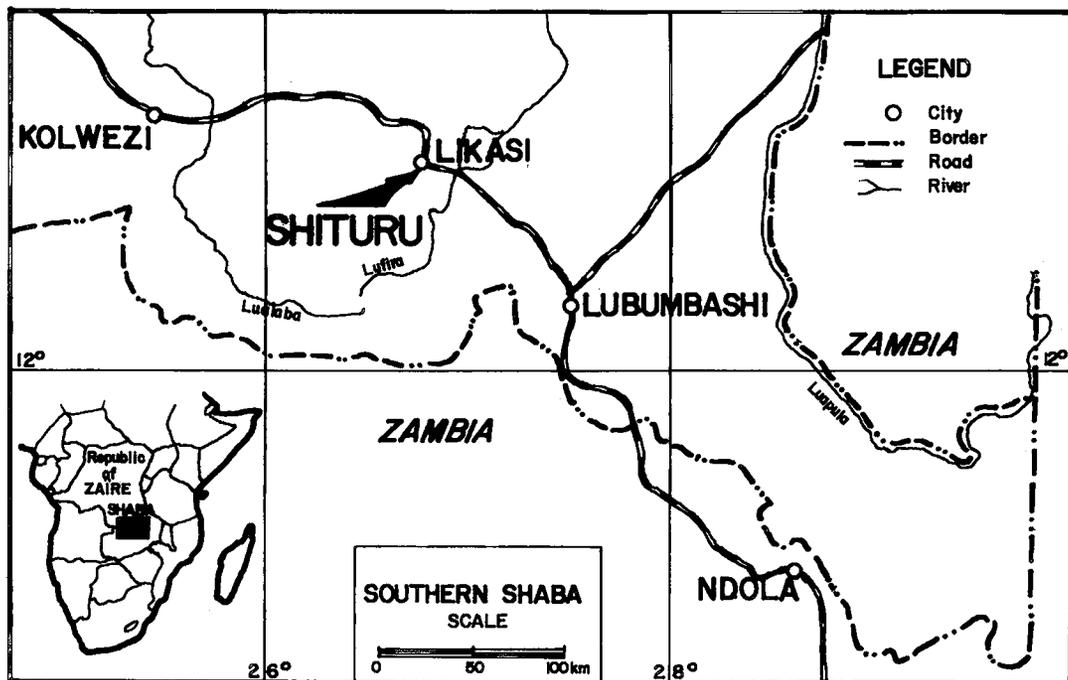
FIG. 1. Location of the Shituru deposit.

some indication of evaporitic material in between. The resulting lithostratigraphy consists of an alternation of sandstones and siltstones, rich in hematite, and dolomite and dolomitic siltstones derived from a reducing environment and containing abundant stromatolites. Interbedded felsic and basic pyroclastic rocks are locally abundant. The copper deposits as well as the uranium deposits and occurrences are located in lagoonal facies at the bottom of the cycles (Lefebvre 1978).

The florencite was found in a piece of drill-core from the Shituru deposit near Likasi (Fig. 1). The rock consists of finely laminated grey to reddish siltstones belonging to an intertidal facies and overlain by lagoonal dolomites of the youngest cycle at the top of the Roan Supergroup (Mwashya Group). Drillhole examination shows that the siltstones are brecciated at the contact with the lagoonal dolomites, and more intensely in a zone that corresponds to the axial plane of the Shituru anticline.

In the siltstone the florencite is relatively abundant: it accounts for approximately 3% by volume of the total sample. Other mineral components of the siltstone are quartz, dolomite, hematite, apatite, rutile, zircon and a regularly interstratified clay mineral of the chlorite–montmorillonite type. As in most of the copper or uranium deposits of Shaba, intense recrystallization in the Shituru deposit appears to be associated with copper mineralization, resulting in the substitution of quartz and a magnesium chlorite (leuchtenbergite) for detrital micas and feldspars. The alteration that accompanies florencite transforms the leuchtenbergite into an interstratified clay mineral without changing the original chemical composition. In the tectonic breccia, the fragments are composed of recrystallized dolomite and quartz associated with traces of talc, whereas the matrix is made of a very fine aggregate of Mg–chlorite, white mica, apatite, quartz, brown tourmaline and rutile together with abundant disseminations of euhedral Ce-rich monazite and hematite. No florencite was found in close association with monazite. The monazite accounts for 8% by volume of the total sample, with a size in the range of 70 to 120 μm.

Monazite is not uncommon in Shaba, as it occurs in the two main occurrences of uranium mineralization of the province. The hydrothermal uranium deposits of Shinkolobwe and Swambo are located 40 and 80 km, respectively, to the southwest of Shituru. In contrast to the majority of the Cu deposits of Shaba, these occurrences of uranium mineralization are post-tectonic. In Swambo as well as in Shinkolobwe, a monazite–chlorite episode follows the crystallization of uraninite (Derriks & Oosterbosch 1958). This monazite forms veins and masses of small yellow crystals and is reported to contain only 0.2% of ThO_2 (Thoreau et al. 1936). In the Swambo deposit, traces of bastnaesite are possibly associated with the monazite (Derriks & Oosterbosch 1958).

CHEMISTRY

The mineral from Zaïre was identified as florencite on the basis of its optical properties (see below) and chemistry (Gasparrini 1980). Qualitative chemical compositions were obtained with the microprobe (1) by collecting X-ray spectra of several micro-areas in six different grains of the florencite under study and (2) by comparing these spectra with those emitted by several micro-areas of a grain of identified florencite from Diamantina, Brazil (ROM M11571). Such spectra, obtained by energy-dispersive spectrometry, show that, except for the proportions of the individual rare-earths, the chemical compositions of the minerals from Zaïre and Brazil are identical (Fig. 2). The spectra also show that the mineral from Zaïre is unzoned and contains La as the most abundant rare-earth element, whereas the mineral from Diamantina is zoned in the rare-earth elements, with the extremes being high Ce – low La and equal amounts of Ce and La (spectrum shown in Fig. 2).

Quantitative chemical analyses of the mineral were difficult to obtain owing to the very small size of the grains, which allowed their study only by electron-microprobe techniques. Some standards, including the one for La, oxidize easily or do not contain the rare-earth elements in amounts comparable to those in the grains under study. A way around such problems was found by using the following techniques: P and Al were analyzed by wavelength–dispersive spectrometry (a more accurate and recommendable method for the production of reliable analyses of new or rare minerals). The counts emitted by the two elements at the P and Al $K\alpha$ wavelengths in several micro-areas of the grains under study were compared with the counts emitted at the same wavelengths by the same elements in standards of analyzed anorthite and apatite. The counts were con-
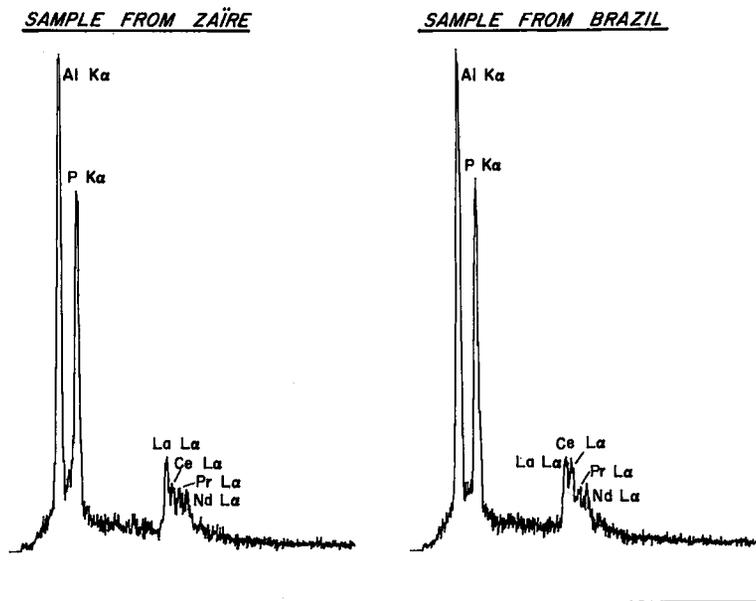
FIG. 2. Electron-microprobe X-ray spectra of florencite from Zaïre and Brazil.

verted into oxide weight percentages by the computer program EMPADR VII (Rucklidge & Gasparrini 1969). The rare earths and other minor elements were obtained by energy-dispersive analysis by using the computer program PESTRIPS (Statham 1975) modified at the

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF FLORENCITE (THIS STUDY) COMPARED WITH THE THEORETICAL COMPOSITION

	1	2	3	4
MgO	0.9	--	2.3	--
Al_2O_3	32.0	31.3	32.0	29.8
SiO_2	1.4	-	0.5	-
P_2O_5	29.1	27.2	28.6	27.7
CaO	0.2	0.5	0.4	-
La_2O_3	19.0	14.3	9.0	-
Ce_2O_3	10.5	14.2	13.4	32.0
Nd_2O_3	0.8	0.7	3.7	-
Sm_2O_3	0.0	0.8	1.3	-
Gd_2O_3	0.9	-	1.0	-
H_2O	nd	nd	nd	10.5
Total RE	31.2	30.0	28.4	32.0

1. Specimen from Zaïre. 2, 3. Specimen from Diamantina (ROM M11571). 4. Theoretical composition. nd: not determined. H_2O is not determined by the microprobe. The grains were too fine for determination of H_2O by other methods. Pr, detected in the qualitative analysis (Fig. 2), was not determined.

Department of Geology, University of Toronto, by M.P. Gorton. With this program, one calculates the oxide weight percentages of the rare-earth elements for which standards were not available by an interpolation of the peak heights in relation to elemental standards other than the ones under study.

The quantitative chemical analyses of the grains of florencite from Zaïre and Diamantina (Table 1) confirm the data found by the qualitative analysis. In addition, La is found to be the major rare-earth element in the sample from Zaïre; the sample from Diamantina is zoned between extremes of composition in which Ce and La are concentrated in similar amounts ($\sim$ 14%) and in which Ce predominates over La (Ce 13.4%, La 9.0%).

Table 2 lists rare-earth elements recalculated to atomic % in the specimen from Zaïre, that from Diamantina and several other florencites obtained from the literature. As mentioned above, Ce is predominant in a large number of occurrences (analyses 4–11). La and Nd can be abundant (more than 20%) and are predominant in the sample from Zaïre (analysis no. 1) and in a sample from Sausalito, California (analysis no. 12). Such a predominance of the two elements is contrary to the normal rare-earth abundances in the earth's crust, where Ce

TABLE 2.   RARE-EARTH ELEMENTS IN FLORENCITE FROM ZAIRE AND OTHER REPORTED LOCALITIES

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
La	61.1	47.7	31.8	37.3	31.1	30.2	30.7	23.4	22.2	30.7	10.1	20.3
Ce	33.6	47.4	47.2	49.6	49.1	47.6	44.2	45.7	44.1	36.6	36.3	5.0
Pr	-	-	-	3.3	4.0	5.4	8.3	6.3	7.9	6.5	3.6	7.0
Nd	2.4	2.4	13.0	9.6	15.1	16.8	12.8	19.7	23.0	21.3	29.5	29.3
Sm	-	2.6	4.4	0.2	0.7	-	1.2	2.6	2.8	2.9	5.6	9.4
Eu	-	-	-	-	-	-	-	-	-	(a)	0.1	6.5
Gd	2.9	-	3.6	-	-	-	2.8	1.9	-	2.0(a)	8.1	13.4
Tb	-	-	-	-	-	-	-	0.4	-	(b)	-	-
Dy	-	-	-	-	-	-	-	-	-	(b)	6.3	6.1
Ho	-	-	-	-	-	-	-	-	-	-	-	0.8
Er	-	-	-	-	-	-	-	-	-	-	0.3	1.7
Tm	-	-	-	-	-	-	-	-	-	-	-	0.1
Yb	-	-	-	-	-	-	-	-	-	-	0.1	0.4
Lu	-	-	-	-	-	-	-	-	-	-	-	-
Y/(Y+Ln).100	-	-	-	-	-	-	-	-	-	1.2(b)	2.8	19.2
Method of Analysis	E.M.	E.M.	E.M.	CH.	O.S.	X.F.	X.F.	-	-	CH.	O.S.	O.S.
Σ=La+Ce+Pr	94.7	95.1	79.0	90.2	84.2	83.2	83.2	75.4	73.6	73.8	50.0	32.3
La-Nd	97.1	97.5	92.0	99.8	99.3	100.0	96.0	96.1	97.0	95.1	79.5	61.6
Sm-Ho	2.9	2.6	8.0	0.2	0.7	-	4.0	4.9	3.0	4.9	20.1	36.2
Er-Lu	-	-	-	-	-	-	-	-	-	-	0.4	2.2
Re_2O_3	31.1	30.0	28.3	19.2	17.6	-	22.8	11.1	-	21,4	8.69*	-
La/Nd	25.46	19.88	2.45	3.88	2.06	1.80	2.40	1.19	0.94	1.44	0.34	0.69

Rare-earth elements have been recalculated in terms of atomic %. * as % RE. (a) Eu+Gd calculated as Gd; (b) Y+Tb+Dy calculated as Y. Methods: O.S. optical spectrography, CH. chromatography, X.F. X-ray fluorescence, E.M. electron microprobe. Specimens: 1. Zaïre (this study). 2, 3. Diamantina (this study). 4. Eastern Sayan, Siberia (Somina & Bulakh 1966). 5. Kangankunde Hill, Nyasaland (McKie 1962). 6. Ural diamond placers, U.S.S.R. (Semenov & Barinskii 1958). 7. Patomsk Highland, Lena area, U.S.S.R. (Gapon 1965). 8. Polar Urals, U.S.S.R. (Mel'nikova et al. 1975). 9. Turkestan Ridge, U.S.S.R. (Nikolaeva et al. 1971). 10. Donets basin, U.S.S.R. (Kuznetsova et al. 1972). 11. North Garden, Virginia (Dagenhart & Maddox 1977). 12. Sausalito, California (Milton & Bastron 1971).

TABLE 3.   REPORTED CHEMICAL ANALYSES OF FLORENCITE

	1.	2.	3.	4.	5.	6.	7.	8.
SiO_2	1.95	7.35	4.54	-	3.48	1.15	0.29	0.48
CaO	-	4.10	1.60	1.60	0.85	1.50	0.50	1.31
MgO	0.81	-	-	-	0.20	0.38	-	-
SrO	7.87	-	2.40	9.00	-	-	-	-
BaO	-	-	-	0.10	-	-	-	-
Fe_2O_3	1.41	6.62	1.40	-	5.64	1.46	-	0.76
Al_2O_3	34.49	26.00	29.78	29.80	24.10	24.39	30.83	32.28
P_2O_5	23.28	33.00	25.52	26.00	23.37	27.27	26.94	25.61
SO_3	-	-	-	1.70	-	-	-	-
F	-	-	-	1.60	-	-	-	-
H_2O+	11.11	-	12.30	12.90		11.46	11.07	10.87
ThO_2	-	-	1.10	-	24.66	-	-	-
RE_2O_3	19.19	22.77	21.40	17.60		31.69	29.25	28.00
	100.11	99.84	100.04	100.30	82.30	99.30	98.88	99.31

1. Eastern Sayan, Siberia (Somina & Bulakh 1966). 2. Patomsk Highlands, Siberia (Gapon 1965). 3. Donets basin, U.S.S.R. (Kuznetsov et al. 1974). 4. Kangankunde Hill, Nyasaland (McKie 1962). 5. Bodaybo, Siberia (Aleksandrov et al. 1975). 6. Koivinite from Urals, U.S.S.R. (Kukharenko 1951). 7. Stiepelmannite from Klein Spitzkopje, S.W. Africa (Ramdohr & Thilo 1940). 8. Minas Gerais, Brazil (Hussak & Prior 1900).

is higher than La and both elements are higher than Nd (Taylor 1964). The amounts recorded probably indicate unusual conditions of crystallization for the mineral (see discussion on the origin of the florencite from Zaïre).

Table 3 shows reported complete analyses of florencite. These show that Mg, Si, Ca, Ba, Sr, Fe, S and Th can be concentrated in the mineral as minor constituents.

OPTICAL AND PHYSICAL PROPERTIES

The florencite discovered in Zaïre occurs in the form of euhedral, colorless to pale yellow crystals normally not exceeding 30 μm in diameter. The crystals always show a darker, commonly isotropic core, the composition of which appears to be identical to that of the transparent edges. This could be due to the fact that the crystals or parts of them have become metamict. The crystals (Fig. 3) have a pseudocubic appearance probably due to the predominance of the $\{02\bar{2}1\}$ rhombohedral habit (Labuntsov 1950). The mineral is uniaxial positive. Indices of refraction for white transmitted light are ω 1.694(2) and ϵ 1.701(2). The hardness is approximately 5 and the fracture is splintery. The density, measured by suspension in a mixture of Clerici solution and distilled water, is 3.52(2) g/cm^3. The mineral is partly soluble in hydrochloric acid. All the above-described data are compatible with those of florencite reported in the literature (Table 4).

X-RAY-DIFFRACTION DATA

The identification of the mineral, as obtained on the basis of its chemistry and optical properties, was confirmed by the X-ray diffraction pattern. For the determination of the chemistry, it was difficult to obtain a good pattern of the florencite under study because of the fine habit of the grains and possibly because of their metamict state. A Debye-Scherrer diffraction pattern (Co $K\alpha$ radiation, Fe filter, camera diameter 114.6 mm) of a concentrate consisting mostly of hematite and florencite gave only one reflection attributable to the mineral (d = 2.93 Å). The small size of the sample in which the florencite was found made it impossible to obtain a richer concentrate capable of yielding a better pattern. However, a crystal measuring 60 μm in diameter extracted from the polished section of the sample and mounted in a Gandolfi camera (Cu $K\alpha$ radiation, Ni filter, camera diameter 57.3 mm) gave a pattern that compared well with that of the florencite from Diamantina and with those reported in the literature (Table 5).

The cell parameters and the indexation of the
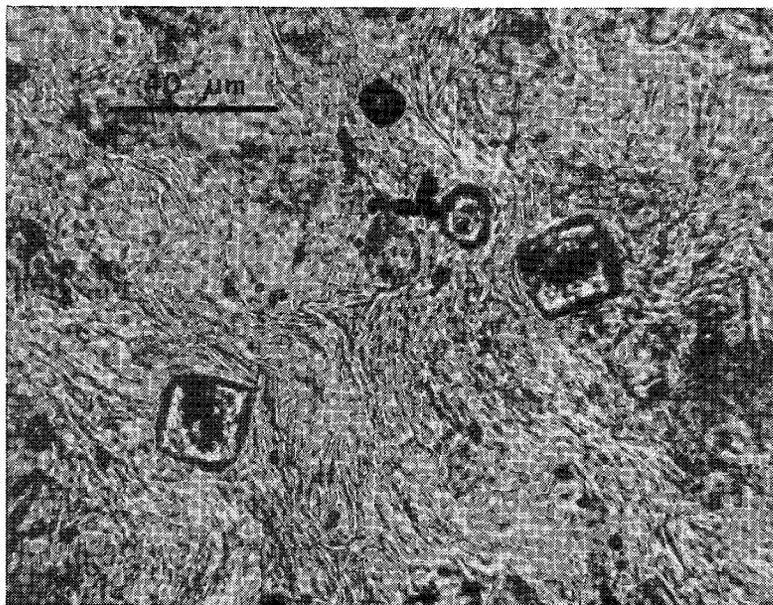
FIG. 3. Pseudocubic crystals of florencite embedded in clay material.

TABLE 4. PHYSICAL AND OPTICAL PROPERTIES OF FLORENCITE FROM ZAIRE AND OTHER REPORTED LOCALITIES

	COLOR	ω	ε	B	C	G Calc.
1.	colorless to very pale yellow	1.694 (2)	1.701 (2)	.007	3.52 (2)	-
2.	"	1.62	1.64	-	-	-
3.	"	1.630	1.636	.006	-	-
4.	pink	1.653 (2)	1.661 (2)	.008	3.457	3.471
5.	bright orange or pinkish brown	1.658	1.664	.006	-	-
6.	honey-yellow	1.662	1.675	.013	3.32	-
7.	greenish-gray, reddish-gray, dark-gray	1.678 (2)	1.684 (2)	.006	3.46	-
8.	yellow to reddish brown	1.680	1.685	.005	-	-
9.	clear pale yellow	1.680	1.685	.005	3.586	-
10.	red, orange, gray or yellow	1.680	1.690	.010	3.5	-
11.	colorless to very pale yellow	1.685 (1)	1.688 (1)	.003	-	-
12.	bright orange or pinkish brown	1.691	1.705	.014	-	-
13.	clear pale yellow	1.695	1.705	.010	3.695	3.702
14.	orange red	1.696 (2)	-	-	3.50 (1)	-
15.	"	1.702	1.715	.013	-	-
16.	colorless	1.709	1.718	.009	-	-
17.		1.713	1.719	.006	-	-

1. Zaïre (this study). 2. Modubwe, Kivu, Zaïre (van Wambecke 1971). 3. Polar Urals, U.S.S.R. (Mel'nikova et al. 1975). 4. Kangankunde Hill, Nyasaland (McKie 1962). 5. Eastern Sayan, Siberia (Somina & Bulakh 1966). 6. Turkestan Ridge, U.S.S.R. (Nikolaeva et al. 1971). 7. Donets basin, U.S.S.R. (Kuznetsov et al. 1974). 8. South Australia (Whittle 1954). 9. Minas Gerais, Brazil (Hussak & Prior 1900). 10. Bondoukou region, Ivory Coast (Casanova et al. 1970). 11. Bodaybo, Siberia (Aleksandrov et al. 1975). 12. Eastern Sayan, Siberia (Somina & Bulakh 1966). 13. Klein Spitzkopje, S.W. Africa (Ramdohr & Thilo 1940). 14. Normandy, France (Devismes et al. 1968). 15. Northern Verkhoyansk, Siberia (Aplonov & Petrova 1965). 16 and 17. Ural koivinite and florencite (Frank-Kamenetskii et al. (1953). B: birefringence; C: specific gravity.

powder-diffraction data of the florencite from Zaïre and Diamantina were determined by a least-squares analysis of the data using the digital computer program written by Appleman & Evans (1973). The data are shown in Table 6 and compared with other data available from the literature.

The data from the literature (Tables 2–6) do not always refer to the same florencite crystals or even to the same occurrences. This is unfortunate, particularly for the Nd-rich florencite, as it would be interesting to compare its optical data and X-ray powder pattern with those of the Ce- and La-rich equivalents.

ORIGIN OF THE ZAIRIAN FLORENCITE

Because the Mwashya Group in the Shituru deposit has been intensely chloritized, all the detrital feldspars have disappeared; only ghosts of silicified plagioclases remain visible in the basic volcanic rocks. This recrystallization has been tentatively attributed to an episode of hydrothermal alteration that may have been associated with the copper mineralization (Lefebvre 1974). The transformation of chlorite into an interstratified clay mineral indicates that the florencite–clay assemblage is a late phenomenon relative to the copper mineralization and

that it is probably post-tectonic, if the euhedral monazite found in the matrix of the tectonic breccia is proven to be associated with florencite. In this case, parallels may be drawn between the florencite and monazite crystallization of Shituru and the monazite veins of the post-tectonic hydrothermal uranium deposits of Shinkolobwe and Swambo.

Milton & Bastron (1971) gave an interesting explanation for the origin of the anomalous Nd-rich florencite from Sausalito by assuming that it was related to the weathering process. Perhaps a similar interpretation can be invoked for the origin of the florencite from Zaïre, as weathering processes are extremely intense in the African copperbelt. There, weathering is generally favored by the late tectonic fractures and huge breccias that form channels for meteoric water; as mentioned above, the florencite and monazite found in Shituru are in close proximity to the brecciated axial plane of the Shituru anticline. According to such interpretation, Ce more than La and Nd is capable of assuming a tetravalent state in preference to a trivalent state (Krumholz 1964). Such transition is favored under conditions of Eh and pH normally found in weathering environments (Robinson et al. 1958, Ronov et al. 1967). In the oxidized state, Ce is less soluble and will

TABLE 5. POWDER X-RAY DATA FOR FLORENCITE FROM ZAIRE AND OTHER REPORTED LOCALITIES

$d_{meas.}$	1. I	hkl	$d_{meas.}$	2. I	hkl	$d_{meas.}$	3. I	$d_{meas.}$	4. I	$d_{meas.}$	5. I	$d_{meas.}$	6. I
-			-			-		-		8 Å	7	-	
5.67 Å	90	101	5.68 Å	90	101	5.63 Å	90	5.71 Å	70	5.7	5	5.70 Å	3
-			-			-		4.91	30	-		-	
3.49	70	110	3.51	70	110	3.48	70	3.50	70	3.48	5	3.48	3
-			3.23	10	np	-		-		3.23	5	3.23	2
3.37	10	104	-			3.37	10	-		-		-	
2.93	100	113	2.94	100	113	2.93	100	2.95	100	2.923	10	2.93	1
2.86	20	015	2.85	20	015	2.83	20	2.84	10	-		-	
2.743	20	np	2.718	20	006	2.71	40	2.746	10	2.709	2	2.70	1
			2.423	30	024	2.42	50	2.439	10	2.428	2	2.42	2
-			-			-		-		2.387	4	-	
2.208	10	122	2.254	10	211	2.28	20	2.259	10	2.201	2	2.21	4
2.171	80	107	2.181	65b	107	2.16	80	2.198	70	2.165	5	2.17	8
-			-			-		-		-		2.09	1
-			1.983	35	214	1.99	20	-		-		1.992	1
1.884	70	303	1.884	60	303	1.885	80	1.890	50	1.897	2	1.888	8
1.743	70	220	1.743	45	220	1.741	70	1.745	30	1.738	6	1.746	6
-			1.678	10	208	1.683	10	-		-		-	
-			-			1.661	10	-		1.667	5	-	
-			-			1.622	20	-		1.637	5	-	
1.601	70	nc	1.619	20b	306	1.600	40	-		-		-	
1.487	20	042	1.487	20	042	1.486	50	-		-		1.487	2
1.467	20	226	1.467	20	226	1.461	50	-		1.464	2	1.465	3
1.435	20	01.11	1.434	20	01.11	1.428	60	-		1.430	3	1.434	6
1.418	10	404	1.419	15	404	1.413	10	-		-		-	
-			-			1.384	10	-		-		-	
1.358	10	137	1.355	10	00.12	1.358	20	-		-		1.360	1
-			1.343	10	309	1.342	20	-		-		1.343	1
1.334	10	np	-			-		-		-		-	
1.313	10	324	1.321	10	410	1.320	20b	-		-		-	
1.281	50	413	1.282	25	413	1.280	50	-		1.278	7	1.286	6
-			1.262	10	11.12	-		-		-		-	
1.190	70	327	1.187	20	416	1.190	60	-		1.189	7	1.193	4
-			1.163	20	330	1.164	50	-		-		1.166	2
-			-			1.108	40	-		-		1.109	1
-			-			1.097	50	-		-		1.098	4

1. Zaïre (This study).
2. Diamantina (This study).
3. Diamantina. (A.S.T.M. No. 8-143).
4. Kangankunde Hill, Nyasaland (McKie 1962).
5. Ural, U.S.S.R. (Frank-Kamenetskii et al. 1953).
6. Bodaybo, Siberia (Aleksandrov et al. 1975).
np - index not permitted by given space group.
nc - line not accounted for by the proposed unit cell.

not migrate with the other rare-earths. This would explain the Ce-rich monazites found at Shituru. The La-rich florencite would then be the result of the solution and subsequent deposition in the proximate siltstones of the rare-earth elements other than tetravalent Ce, together with the P and Al.

To conclude, the monazite of the Shituru deposit may be related to a post-tectonic, hydrothermal event. Florencite may have been deposited simultaneously or redeposited under supergene conditions after the withdrawal, from the breccia zone, of all the rare earths and only some of the cerium.

TABLE 6. UNIT-CELL DIMENSIONS OF FLORENCITE FROM ZAIRE AND OTHER LOCALITIES

	1.	2.	3.	4.	5.	6.	7.	8.
a (Å)	6.987 (2)	6.979 (4)	6.971	6.960 (5)	6.75	6.971 (4)	6.978 (1)	7.01
c (Å)	16.248 (6)	16.25 (1)	16.42	16.34 (4)	16.52	16.42 (13)	16.39 (2)	16.23
c/a	2.325	2.328	2.355	2.35	2.45	2.35	2.35	2.32

1. Zaïre (This study).   2. Diamantina (This study).
3. Diamantina (A.S.T.M. No. 8-143).
5. Klein Spitzkopje, S.W. Africa (Frank-   4. Ural, U.S.S.R. (Frank-Kamenetskii et al. 1953).
   Kamenetskii et al. 1953).   6 and 7. Kangankunde Hill, Nyasaland (McKie 1962).
8. Amherst, Virginia (Mitchell & Geitgey 1968).

REFERENCES

ALEKSANDROV, A.L., OLOVYASHNIKOV, V.M. & POTO-ROCHENKO, A.N. (1975): Florencite from the Bodaybo gold-ore field as an indicator of hydrothermal processes. Dokl. Acad. Sci. USSR, Earth Sci. Sect. 224, 110-112.

APLONOV, V.S. & PETROVA, N.V. (1965): New data on mineralogy of rare earths in northern Verkhoyansk area. Uch. Zap. Nauch.-Issled. Inst. Geol. Arktiki, Reg. Geol., 155-161 (in Russ.).

APPLEMAN, D.E. & EVANS, H.T., Jr. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. U.S. Geol. Surv. Comp. Contr. 20.

BAIN, D.C. (1970): Plumbogummite-group minerals from Mull and Morven. Mineral. Mag. 37, 934-938.

CAHEN, L. (1974): Geological background to the copper-bearing strata of southern Shaba (Zaïre). In Gisements Stratiformes et Provinces Cuprifères (P. Bartholomé, ed.), Soc. Géol. Belg. Vol. Cent., 55-77.

CASANOVA, R., LOUP, G. & BROCHE, J. (1970): Découverte de florencite en Côte d'Ivoire. Ann. Univ. Abidjan, Ser. C 6, 5-7.

DAGENHART, T.V., JR. & MADDOX, G.L. (1977): The history and mineralogy of a Revolutionary War period iron mine, North Garden, Virginia. Rocks Minerals 52, 360-366.

DERRIKS, J.J. & OOSTERBOSCH, R. (1958): Swambo and Kalongwe deposits compared to Shinkolobwe: contribution to the study of Katanga uranium. In Geology of Uranium and Thorium. Proc. U. N. Int. Conf. Peaceful Uses Atomic Energy, 2nd, Geneva 2, 663-695.

DEVISMES, P., GUIGUES, J., LAURENT, Y. & PARFENOFF, A. (1968): Première découverte de florencite en France. Soc. franç. Minéral. Crist. Bull. 91, 500-502.

FAZEKAS, V., KOSA, L. & SELMECZI, B. (1975): Rare earth mineralization in the crystalline schists of the Sopron Mountains. Foldt. Kozl. 105, 297-308 (in Hung.; see also Chem. Abstr. 85, 49363).

FRANK-KAMENETSKIĬ, V.A., KOMKOV, A.I. & NARDOV, V.V. (1953): X-ray data on florencite and koivinite. Zap. Vses. Mineral. Obshchest. 82, 297-301 (in Russ.).

GAPON, A.E. (1965): Accessory florencite. Mineral. Sb. L'vovsk. Gos. Univ. 19(1), 105-110 (in Russ.; see also Chem. Abstr. 64, 19209f).

GARSON, M.S. (1958): Investigations of carbonatites and ring structures. Nyasaland Protectorate Geol. Surv. Bull. 1957, 7-11.

GASPARRINI, C. (1980): The role of the ore microscope and electron microprobe in the mining industry. Can. Mining Metall. Bull. 73(817), 73-85.

HUSSAK, E. & PRIOR, G. (1900): On florencite, a new hydrated phosphate of aluminum and cerium earths, from Brazil. *Mineral. Mag.* **12**, 244-248.

JAMES, T.C. (1958): Carbonatite investigation: progress report. *Rec. Geol. Surv. Tanganyika* **6**, 45.

KING, D. (1952): Examination of rare-earth pegmatite near Wiperaminga Hill, Old Boolcoomata station. *S. Aust. Dep. Mines Mining Rev.* **97**, 93-94.

KRUMHOLZ, P. (1964): Solution chemistry. *In* Progress in the Science and Technology of the Rare Earths 1 (L. Eyring, ed.), Macmillan, New York.

KUKHARENKO, A.A. (1951): Comment on A.N. Labuntsov's report on "Florencite crystals". *Zap. Vses. Mineral. Obshchest.* **80**, 238 (in Russ.).

KUZNETSOV, YU. A., KUZNETSOVA, S.V., MEL'NIK, M.A. & SIDENKO, D.G. (1974): Florencite, an accessory mineral of gold in the Bobrikovo ore deposit in the Donbas. *Dokl. Acad. Sci. USSR Earth Sci. Sect.* **210**, 144-145.

KUZNETSOVA, S.V., KUZNETSOV, YU, A., KORNIENKO, T.G. & SIDENKO, D.G. (1972): Florencite from the Donets Basin. *Dopov. Akad. Nauk Ukr. RSR, Ser. B* **34**, 316-319 (in Ukr.).

LABUNTSOV, A.N. (1950): Florencite crystals. *Trudy Mineral. Muzeya Akad. Nauk SSSR* **2**, 135-136 (in Russ.).

LEFEBVRE, J.-J. (1974): Minéralisations cupro-cobaltifères associées aux horizons pyroclastiques situés dans le faisceau supérieur de la série de Roan, à Shituru, Shaba, Zaïre. *In* Gisements Stratiformes et Provinces Cuprifères (P. Bartholomé, ed.), *Soc. Géol. Belg. Vol. Cent.*, 103-122.

———— (1978): Le groupe de Mwashya, mégacyclothème terminal du Roan (Shaba, Zaïre, sud-oriental). I. Approche lithostratigraphique et étude de l'environnement sédimentaire. *Soc. Géol. Belg. Ann.* **101**, 209-225.

McKIE, D. (1962): Goyazite and florencite from two African carbonatites. *Mineral. Mag.* **33**, 281-297.

MEL'NIKOVA, E.M., KOKAREV, G.N. & KNYAZEVA, D.N. (1975): Florencite from hydrothermal metasomatites of the polar Urals region. *Zap. Vses. Mineral. Obshchest.* **104**, 341-343 (in Russ.; see also *Mineral. Abstr.* **27**, 179).

MILTON, D.J. & BASTRON, H. (1971): Churchite and florencite–(Nd) from Sausalito, California. *Mineral. Record* **2**, 166-168.

MITCHELL, R.S. & GEITGEY, R.P. (1968): Barian florencite, weinschenkite, and rhabdophane from a perrierite-bearing pegmatite in Amherst County, Virginia. *Southeastern Geol.* **9**, 143-150.

NIKOLAEVA, E.P., GERTMAN, P.L. ZHDANOVA, ZH.N. & ELIZOV, I.N. (1971): Florencite from the northern slope of Turkestan ridge. *Zap. Uzb. Otd. Vses. Mineral. Obshchest.* **24**, 124-127 (in Russ.; see also *Chem. Abstr.* **77**, 37409f).

RAMDOHR, P. & THILO, E. (1940): Stiepelmannit, ein neues Mineral der Hamlinitgruppe mit Yttrium und seltenen Erden. *Zbl. Mineral. (Abt. A)*, 1-8.

RAO, A.B. & DA CUNHA E SILVA, J. (1968): Fosfatos dos pegmatitos brasileiros. *J. Mineral. Recife, Ed. Espl.* **6**, 99-121 (see also *Mineral. Abstr.* **22**, 226).

ROBINSON, W.O., BASTRON, H. & MURATA, K.J. (1958): Biogeochemistry of the rare earth elements with particular reference to hickory trees. *Geochim. Cosmochim. Acta* **14**, 55-67.

RONOV, A.B., BALASHOV, YU. A. & MIGDISOV, A.A. (1967): Geochemistry of the rare earths in the sedimentary cycle. *Geochem. Int.*, 1-17.

RUCKLIDGE, J.C. & GASPARRINI, E. (1969): EMPADR VII. Specifications of a computer programme for processing electron microprobe analytical data. *Dep. Geol., Univ. Toronto.*

SEMENOV, E.I. & BARINSKII, R.L. (1958): The composition characteristics of the rare earths in minerals *Geochem.*, 398-419.

SMITH, W.C. (1953): Carbonatites of the Chilwa series of southern Nyasaland. *Brit. Mus. (Nat. Hist.), Bull. Mineral.* **1**(4), 97-119.

SOMINA, M.YA. & BULAKH, A.G. (1966): Florencite from the carbonatites of eastern Sayan and the chemical constitution of the crandallite group. *Zap. Vses. Mineral. Obshchest.* **95**, 537-550 (in Russ.; see also *Mineral. Abstr.* **18**, 204).

STATHAM, P.J. (1975): *Quantitative X-Ray Energy Spectrometry: the Application of a Si(Li) Detector to Electron Microprobe Analysis.* Ph.D. thesis, Univ. Cambridge, England.

TAYLOR, S.R. (1964): Abundance of chemical elements in the continental crust – a new table. *Geochim. Cosmochim. Acta* **28**, 1273-1285.

THEUNISSEN, K. & MARTIN, H. (1969): Découverte d'un phosphate alumineux des terres rares dans un coticule de Vielsalm. *Soc. Géol. Belg. Ann.* **92**, 173-176.

THOREAU, J., BRECKPOT, R. & VAES, J.F. (1936): La monazite de Shinkolobwe (Katanga). *Acad. Roy. Belg. Bull.* **22**, 1111-1122.

TRACE, R.D. (1960): Significance of an unusual mineral occurrence at Hicks Dome, Hardin County, Illinois. *U.S. Geol. Surv. Prof. Pap.* **400-B**, 63-64.

TRUEB, L.F. & DE WYS, E.C. (1971): Carbon from Ubangi – a microstructural study. *Amer. Mineral.* **56**, 1252-1268.

VAN WAMBEKE, L. (1971): The problem of cation deficiencies in some phosphates due to alteration processes. *Amer. Mineral.* **56**, 1366-1384.

WHITTLE, A.W.G. (1954): The radioactive minerals of South Australia and their petrogenetic significance. *J. Geol. Soc. Aust.* **2**, 21-45.