

Goyazite and florencite from two African carbonatites.

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Summary. Florencite with ω 1.653, ϵ 1.661, G 3.457, a 6.971 ± 0.004 Å, c 16.42 ± 0.13 Å, and rhombohedral unit-cell contents $\text{Sr}_{0.42}\text{Ce}_{0.52}\text{Ca}_{0.14}\text{Al}_{2.83}(\text{PO}_4)_{1.77}(\text{SO}_4)_{0.10}\text{F}_{0.41}(\text{OH})_{5.24}(\text{H}_2\text{O})_{0.85}$ occurs in the Kangankunde carbonatite in Nyasaland, and goyazite with G 3.388, a 6.982 ± 0.001 Å, c 16.54 ± 0.02 Å, and rhombohedral unit-cell contents $\text{Ba}_{0.08}\text{Sr}_{0.50}\text{Ce}_{0.41}\text{Ca}_{0.08}\text{Al}_{2.78}(\text{PO}_4)_{1.62}(\text{SO}_4)_{0.19}\text{F}_{0.30}(\text{OH})_{5.30}(\text{H}_2\text{O})_{1.18}$ on the Wigu carbonatite in Tanganyika. Hydrothermal decomposition experiments in the Wigu material indicate stability below $535 \pm 10^\circ \text{C}$ at $p_{\text{H}_2\text{O}}$ 200 bars and $565 \pm 10^\circ \text{C}$ at $p_{\text{H}_2\text{O}}$ 2500 bars; both minerals exhibit endothermic peaks at 630°C in differential thermal analyses. The crystal chemistry of the goyazite series is discussed in the light of the two new analyses and of newly determined unit-cell dimensions for four other members of the goyazite series. Goyazite, florencite, and gorceixite appear to have crystallized during late-stage replacement processes or under supergene conditions in carbonatites.

MINERALS of the goyazite or plumbogummite isostructural series of rhombohedral phosphates are known to occur in some six carbonatite complexes, Kangankunde, Nkalonje, and Tundulu in Nyasaland, Mbeya (Panda Hill) and Wigu in Tanganyika, and Mrima in Kenya. Florencite was tentatively identified in a pyrochlore-synchysite-apatite-quartz sövite from Tundulu by Campbell Smith (1953); it was subsequently found to be of widespread occurrence at Kangankunde and to be present in sövite at Nkalonje (Garson, 1957). A mineral apparently between florencite and goyazite in composition was later identified by its optical properties and X-ray powder pattern in apatite-bastnäsite sövite from Nathace Hill, Tundulu, by Garson (unpublished Ph.D. thesis, 1961). Florencite was tentatively identified in monazite-blende-pyrite-baryte-dolomite rock from the Wigu carbonatite in 1956 (McKie in James, 1958). Gorceixite has been described, with an analysis of impure material, from Mrima by Coetzee and Edwards (1959), and a more detailed analysis has been made on cleaner material by Pickup (unpublished).

It is the purpose of this paper to describe the minerals originally identified as florencite from Kangankunde and Wigu, to relate their composition and physical properties to those of the goyazite series as

a whole, and to consider the paragenesis of such minerals in carbonatites. This study has developed from investigations begun at the Mineral Resources Division of the Overseas Geological Surveys, the British Museum (Natural History), and the Geological Surveys of Nyasaland and of Tanganyika; and I must at the outset express my indebtedness especially to Mr. T. Deans, Dr. W. Campbell Smith, and Dr. M. S. Garson for their generosity in making specimens and information available to me. The provision of two new chemical analyses and the gift of analysed specimens of gorceixite, described some years ago by Mr. E. H. Beard, by the Mineral Resources Division are most gratefully acknowledged.

The carbonatite complex at Kangankunde Hill, Nyasaland, is one of the intrusions of the Chilwa Alkaline Province, described originally by Dixey, Campbell Smith, and Bisset (1937). It has subsequently been the subject of detailed study by Garson and Campbell Smith (Geol. Surv. Nyasaland, Memoir II, in preparation). Goyazite- or florencite-bearing ankeritic carbonatites occur at a number of localities in the 'central mobilized area'. The analysed strontian florencite occurs as small pink rhombohedra associated with green and colourless monazite in an ankerite-strontianite rock with accessory baryte, blende, quartz, and apatite. The carbonatite is very variable in composition, with ankerite or strontianite locally dominant.

The Wigu Hill carbonatite lies at $7^{\circ} 26' S.$, $37^{\circ} 34' E.$ near the village of Kisaki, about 40 miles south of Morogoro in the Eastern Province of Tanganyika. No detailed description has yet appeared; brief mention occurs in James (1958), and an account of the Wigu carbonatite is in preparation by McKie and James. Cerian goyazite occurs as a very fine-grained aggregate intergrown with quartz and barite and forming pink and white hexagonal prismatic pseudomorphs associated with green and colourless monazite, blende, and pyrite in a dolomitic carbonatite.

Both Kangankunde and Wigu are notable among African carbonatites for their concentration of rare earths, principally in bastnäsite and monazite, which are always associated more or less closely with baryte, strontianite, and blende. Members of the goyazite series have not, however, been found at the better known rare-earth rich carbonatite at Mountain Pass, California (Olson, Shawe, Pray, and Sharp, 1954).

Chemical composition. Two new chemical analyses of goyazite and florencite from the Wigu and Kangankunde carbonatites have been made by Mr. R. Pickup of the Mineral Resources Division, Overseas Geological Surveys, and are set down in table I.

The minerals were prepared for analysis by solution of the carbonate

TABLE I. Chemical analyses of goyazite and florencite.

	1.	2.	3.	4.	2a.	3a.
Ln ₂ O ₃ ...	—	14.1	17.6	32.0	Ln ³⁺ 0.41	0.52
CaO ...	—	0.9	1.6	—	Ca ²⁺ 0.08	0.14
SrO ...	22.4	10.9	9.0	—	Sr ²⁺ 0.50	0.42
BaO ...	—	1.7	0.1	—	Ba ²⁺ 0.05	—
Al ₂ O ₃ ...	33.1	29.8	29.8	29.8	Al ³⁺ 2.78	2.83
P ₂ O ₅ ...	30.8	24.1	26.0	27.7	PO ₄ ³⁻ 1.62	1.77
SO ₃ ...	—	3.2	1.7	—	SO ₄ ²⁻ 0.19	0.10
F ...	—	1.2	1.6	—	F ⁻ 0.30	0.41
H ₂ O+ ...	13.7	14.5	12.9	10.5	OH ⁻ 5.30	5.24
SiO ₂ ...	—	0.3	—	—	H ₂ O 1.18	0.85
	100.0	100.7	100.3	100.0		
less O ≡ F ...		0.5	0.7			
		100.2	99.6			

1. Goyazite end-member SrAl₃(PO₄)₂(OH)₅ · H₂O.
2. Cerian goyazite, Wigu Hill, Tanganyika. Analyst: R. Pickup.
3. Strontian florencite, Kangankunde Hill, Nyasaland. Analyst: R. Pickup.
4. Florencite end-member CeAl₃(PO₄)₂(OH)₆.
- 2a. Atomic ratios to 14 (O,OH,F) calculated from col. 2 neglecting SiO₂ content.
- 3a. Atomic ratios to 14 (O,OH,F) calculated from col. 3.

matrix in *N* HCl at room temperature, followed by centrifugal separation from quartz, monazite, and baryte in Clerici's solution. It proved impossible to free the very fine-grained Wigu material completely from a quartz-baryte intergrowth; the strongest lines of quartz and baryte were just observable on a diffractometer chart of the specimen submitted for analysis. The SiO₂ content of 0.3 % is therefore assumed to represent quartz, but no estimate of the baryte content of the specimen can be made; if all the BaO found and an equivalent amount of SO₃ are deducted for baryte, no very significant alteration of the Wigu analysis results. In each case just under 1 g of material was available for analysis. In table I total rare-earth figures include thoria as ThO₂; SO₃ and F values are approximate minima; Fe₂O₃ is less than 0.1 %; and TiO₂ was below the limit of detection in each case. H₂O⁺ was determined as loss on ignition at 1000° C.

Both minerals lie essentially between goyazite, SrAl₃(PO₄)₂(OH)₅ · H₂O, and florencite, CeAl₃(PO₄)₂(OH)₆, in composition, with some substitution of SO₄²⁻ for PO₄³⁻ (with corresponding adjustment of OH⁻ for H₂O) and F⁻ for OH⁻. In the last two columns of table I the analyses are recalculated in atomic proportions to 14 anions (O,OH,F); the rhombohedral unit-cell in the goyazite series is presumed to contain 14 anions

(this point will be reverted to later). Using the abbreviations Pg = plumbogummite, Gx = gorceixite, Gz = goyazite, Cn = crandallite, Fc = florencite for the members¹ of the goyazite series, the Wigu mineral can be described as $Cn_8Fc_{39}Gz_{48}Gx_5$ and that from Kangankunde as $Cn_{13}Fc_{48}Gz_{39}$, and are thus respectively a cerian goyazite and a strontianite florencite, though quite close to one another in the goyazite-florencite series.

TABLE II. Proportions of rare earth oxides in goyazite and florencite, with comparative data.

	1.	2.	3.	4.	5.
La_2O_3	30	27.2	39.7	35.8	30.7
CeO_2	50	47.17	41.65	34.34	52.0
Pr_6O_{11}	4	5.15	4.26	4.75	4.5
Nd_2O_3	15	14.22	11.11	14.90	12.3
Sm_2O_3	$\left\{ \begin{array}{l} < 1 \\ > 0.5 \end{array} \right.$	1.57	1.39	2.83	nil
R_2O_3	nil	4.63	1.89	7.30	nil

Analyses are expressed in weight per cent of rare earth oxide fraction.

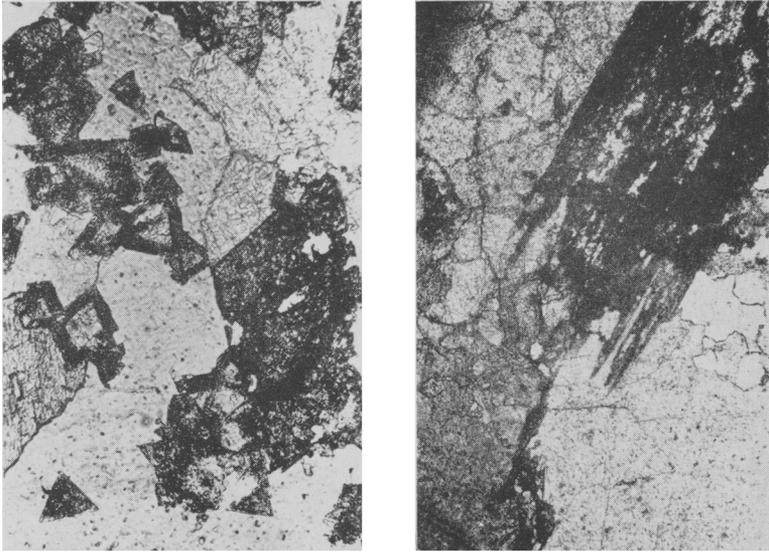
R_2O_3 = heavy lanthanon oxides Eu_2O_3 to Lu_2O_3 , Y_2O_3 , and ThO_2 .

1. Goyazite and florencite. Semi-quantitative spectrographic analysis by Dr. J. R. Butler. The Kangankunde and Wigu specimens are closely similar.
2. Monazite separated from monazite-dolomite-strontianite-carbonatite, Kangankunde. Analysis by Johnson Matthey & Co. Ltd. R_2O_3 is Eu_2O_3 0.10, Dy_2O_3 1.52, Ho_2O_3 1.02, Er_2O_3 1.39, Yb_2O_3 0.46, ThO_2 0.14 (Deans, 1959).
3. Dolomite-bastnäsite-carbonatite with some monazite and goyazite, Wigu. Analysis by Johnson Matthey & Co. Ltd. R_2O_3 is Eu_2O_3 0.10, Dy_2O_3 0.59, Ho_2O_3 0.50, Er_2O_3 0.25, Yb_2O_3 0.25, ThO_2 0.2 (Deans, 1959).
4. Monazite-gorceixite-bearing carbonatite (weathered), Mrima, Kenya. Analysis by Johnson Matthey & Co. Ltd. R_2O_3 is Eu_2O_3 0.40, Dy_2O_3 2.32, Ho_2O_3 1.01, Er_2O_3 1.26, Yb_2O_3 1.31, ThO_2 1.0 (Deans, 1959).
5. Gorceixite from lower Eocene marl, Bashi, Alabama (Murata *et al.*, 1957).

Semi-quantitative spectrographic determinations of the individual rare earths in the Wigu and Kangankunde goyazite and florencite have very kindly been made for me by Dr. J. R. Butler. The proportions in the two specimens are closely similar and approximate to the weight percentages of oxides shown in col. 1 of table II. Yttrium was not detectable in either oxide mixture and the heavy lanthanons are not dissimilar to those in the associated monazite at Kangankunde (col. 2). The goyazite-bearing carbonatite from Wigu (col. 3) has a fairly low content of heavy lanthanons and a markedly higher content of La,

¹ Deltaite, formerly thought to be member of the series, has recently been shown by Elburty and Greenberg (1960) to be a mixture of crandallite and hydroxyapatite.

which must be attributed to enrichment of La in bastnäsite relative to goyazite and monazite; Murata, Rose, Carron, and Glass (1957) record La_2O_3 contents of 25.7 %, 29.6 %, and 42.1 % in bastnäsite from the



FIGS. 1 and 2: FIG. 1 (left). Strontian florencite rhombohedra in a matrix of ankerite and strontianite. Kangankunde Hill, Nyasaland. Plane polarized light, $\times 100$. FIG. 2 (right). Fine-grained cerian goyazite (dark) intergrown with quartz and baryte in a dolomitic matrix. Wigu Hill, Tanganyika. Plane polarized light, $\times 20$.

Mountain Pass carbonatite. The proportions of rare earths in gorceixite-bearing carbonatite from Mrima (col. 4) are in contrast: the content of heavy lanthanons is higher and the proportion of Ce relatively low. All the data of table II display the predominance of the lightest lanthanons, recognized as a characteristic of alkalic parageneses by Goldschmidt *et al.* (1933). The rare earth distribution in gorceixite from a sedimentary paragenesis (col. 5) is similar to that in goyazite and florencite.

Physical properties. Florencite occurs at Kangankunde as pink rhombohedra about 0.01 cm long (fig. 1). The plane angle of the rhombohedral faces was measured on the microscope stage as 66° . The habit is therefore $\{01\bar{1}1\}$, with plane angle $62\frac{1}{2}^\circ$ in terms of the X-ray cell, rather than the other recorded habit $\{01\bar{1}2\}$, which is pseudocubic. The crystals are uniaxial positive, with ω 1.653 ± 0.002 , ϵ 1.661 ± 0.002 ; the

extraordinary vibration direction lies in the acute angle of the rhombohedral faces. For a crystal lying on a rhombohedral face ϵ' 1.660 ± 0.002 . The crystals have clear rims surrounding a mosaic, or inclusion rich, core. The density¹ of the rhombohedra is 3.457, in good agreement with the calculated density of 3.471.

Pink pitted rhombohedra with similar properties to those in the fresh rock occur in some of the *terra rossa* soils at Kangankunde.

Goyazite occurs at Wigu in pink and white striated aggregates (fig. 2), which are too fine grained for optical work except for the recognition of the largest grains as rhombohedra of similar shape to those from Kangankunde. The absence of line broadening on oscillation photographs of the aggregates indicates a grain size in the range 1 to 0.01 μ . The density of the analysed material is 3.38₆, in good agreement with the calculated density of 3.392.

X-ray crystallography. Oscillation photographs taken with Cu- $K\alpha$ radiation show that the Laue symmetry of florencite from Kangankunde is $R\bar{3}m$; glide planes are absent, and the space group is therefore $R\bar{3}m$, $R3m$, or $R32$. Measurement of high angle reflections on the zero layer of oscillation photographs gives dimensions a 6.98 ± 0.05 Å (from $\xi(8\bar{1}\bar{7}0)$ on a triad axis photograph) and c 16.42 ± 0.05 Å (from $\xi(0.0.0.18)$ on a diad axis photograph) for the triple-hexagonal unit-cell. The unit-cell dimensions of a rhombohedron extracted from the rock with cold 1:1 HCl are sensibly equal to those of a crystal picked out of a thin-section. All florencite reflections are multiple and streaked along θ -curves; some additional sharp reflections, due probably to baryte, are always observed.

Oscillation photographs of florencite crystals from soil at Kangankunde correspond to those of material from fresh rock, but always exhibit more pronounced streaking and multiplicity of reflections, due presumably to incipient alteration.

The material from Wigu is too fine grained for single crystal X-ray work. Rough unit-cell dimensions, a 7 Å, c 17 Å, were derived from electron diffraction patterns.

Use of the unit-cell dimensions obtained from single crystals enabled the powder pattern of Kangankunde florencite, and by analogy that of the Wigu goyazite, to be indexed. Indexed powder data derived

¹ Densities were determined by gradual dilution of Clerici's solution until the grains remained suspended on centrifuging for 10 min. at 3000 r.p.m. and measurement of the loss in weight of a mercury-in-glass mass totally immersed in the Clerici's solution in the centrifuge tube supported on a bridge.

from diffractometer charts taken with Cu- $K\alpha$ radiation are set down in table III. The spacings $d_{03\bar{3}3}$ and $d_{22\bar{4}0}$ are known accurately from charts prepared from mounts with an internal quartz standard; other d -spacings have been corrected by extrapolation.

TABLE III. X-ray powder data for goyazite and florencite from diffractometer charts taken with Cu- $K\alpha$ radiation at $d\theta/dt=1/3$ degree per minute.

hkl	Wigu		Kangankunde	
				d (Å)	I .	d (Å)	I .
10 $\bar{1}$ 1	5.71	vs	5.71	vs
10 $\bar{1}$ 2			4.91	m
11 $\bar{2}$ 0	3.50	vs	3.50	vs
11 $\bar{2}$ 3	2.95	vvs	2.95	vvs
20 $\bar{2}$ 2	2.84	w	2.84	w
0006	2.75	wB	2.746	w
02 $\bar{2}$ 4	2.443	w	2.439	w
2131			2.259	w
10 $\bar{1}$ 7	}	2.204	vs	2.198	vs
12 $\bar{3}$ 2							
11 $\bar{2}$ 6			2.146	w
3030			2.013	w
03 $\bar{3}$ 3	1.893	ms	1.890	ms
2240	1.745	m	1.745	m

Accurate unit-cell dimensions have been obtained by measurement of the separation of the 22 $\bar{4}$ 0 and 03 $\bar{3}$ 3 reflections from the 11 $\bar{2}$ 2 reflection of quartz at $\theta(\text{Cu-}K\alpha) = 25.093^\circ$ on diffractometer charts prepared from mounts with an internal quartz standard. The diffractometer was run 6 times over each set of peaks and the mean value of $d_{22\bar{4}0}$ and of $d_{03\bar{3}3}$ obtained. The value of a is given directly by $d_{22\bar{4}0} = a/4$; c can be obtained from $d_{03\bar{3}3} = a.c. (9a^2 + 12c^2)^{-\frac{1}{2}}$ using the previously determined value of a . The analysed material from Wigu has a 6.982 \pm 0.001 Å, c 16.54 \pm 0.02 Å. The analysed material from Kangankunde has a 6.971 \pm 0.004 Å, c 16.42 \pm 0.13 Å; another specimen from Kangankunde has a 6.978 \pm 0.001 Å, c 16.39 \pm 0.02 Å. The errors quoted are derived from the standard deviations of the mean of the six measurements of $\theta_{22\bar{4}0}$ and $\theta_{03\bar{3}3}$.

Stability. Differential thermal analyses have very kindly been made for me by Dr. R. C. Mackenzie.¹ Florencite from Kangankunde exhibits a strong endothermic peak at 628° C and goyazite from Wigu a double endothermic peak at 636° C and 655° C. The runs were made in air on

¹ The Macaulay Institute for Soil Research, Aberdeen.

30-mg samples sandwich packed with 133 mg of inert kaolinite. No comparative data are available for members of the goyazite series.

A preliminary study of the stability of strontian florencite under hydrothermal conditions has been made on a pure concentrate from Kangankunde. The experiments were conducted in sealed gold capsules containing florencite and water. Any run in which the capsule lost weight was rejected. Temperature control was within $\pm 2^\circ$, and the temperatures measured were accurate to $\pm 5^\circ$. The products at the end of each run were identified by diffractometry. The results are set down in table IV and plotted on fig. 3.

TABLE IV. Hydrothermal experiments on strontian florencite.

$p_{\text{H}_2\text{O}}$ (bars)	T ($^\circ\text{C}$)	Duration of run (days)	Phases present at end of run	$p_{\text{H}_2\text{O}}$ (bars)	T ($^\circ\text{C}$)	Duration of run (days)	Phases present at end of run
200	525	2	Fe	1000	600	2	D
200	550	5	Fe + D	1500	600	2	D
1000	525	2	Fe	2500	550	2	Fe
1000	550	2	Fe	2500	575	5	Fe + D
1000	575	3	Fe + D	2500	700	2	D

Abbreviations: Fe strontian florencite; D decomposition products only.

Strontian florencite remains stable in the presence of water up to $535 \pm 10^\circ \text{C}$ at $p_{\text{H}_2\text{O}}$ 200 bars and up to $565 \pm 10^\circ \text{C}$ at $p_{\text{H}_2\text{O}}$ 2500 bars. But since all runs were of short duration it is possible that equilibrium was not achieved; the line plotted on fig. 3 would then lie at temperatures too high by an amount related to the kinetics of the decomposition. No synthetic experiments have been made. The steepness of the decomposition curve compared with the equilibrium curves for simple dehydration reactions suggests that the decomposition product may include a hydrous phase. The decomposition product, which is the same over the whole pressure range, has not proved to be identifiable from its diffractometer chart; it probably contains more than one phase.

Crystal chemistry of the goyazite¹ series. The goyazite series has long been recognized (Schaller, 1911; Hendricks, 1937; Gossner, 1937) to be isostructural with alunite, $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, the crystal structure of which was determined by Hendricks (1937).² Pabst (1947) used the

¹ Following Fisher (1958), who rightly objects to Palache, Berman, and Frondel's (1951, p. 831) use of the term 'plumbogummite series'. It was called the hamlinite series until hamlinite was shown to be goyazite.

² Dr. C. H. Kelsey has pointed out to me that Hendricks unconventionally used left-handed axes in his (0001) projection of the structure, his fig. 1.

alunite structure to determine the atomic coordinates in the isomorphous sulphate-phosphates svanbergite, $\text{SrAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$, and woodhouseite, $\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$. No structure analysis has been made

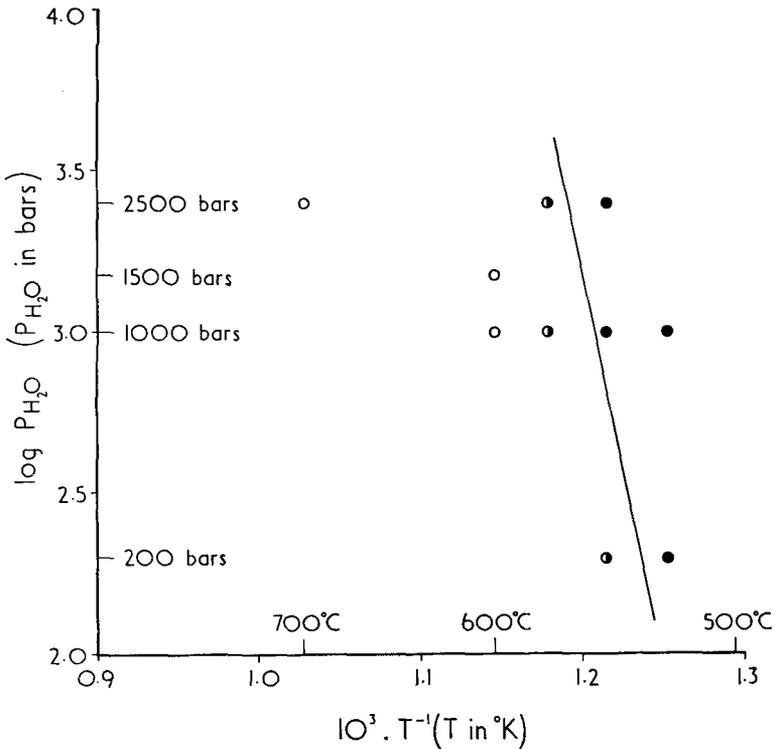


Fig. 3. Hydrothermal stability of strontian florencite. Open circles: decomposition product only. Shaded circles: partial decomposition. Solid circles: florencite persists.

of any of the phosphates of the goyazite series, but it is clear from their composition and unit-cell dimensions that they are indeed isostructural with alunite; it is therefore valid to discuss ionic substitution in the goyazite group in terms of the alunite structure.

Although alunite has a rhombohedral lattice¹ it is convenient to consider the atomic coordinates in terms of hexagonal axes. The triple

¹ Hendricks (1937) observed a pyroelectric effect and assigned alunite to the space group R3m, but Pabst (1947) pointed out that Hendricks's structure was consistent with the centro-symmetrical space group R $\bar{3}$ m.

TABLE V. Contents of the rhombohedral unit-cell, density, unit-cell dimensions, and refractive indices in the goyazite series.

	1.	2.	3.	4.	5.	6.
Ba ²⁺	—	—	0.05	0.25	0.35	0.54
Sr ²⁺	—	0.42	0.50	—	0.23	—
Ce ³⁺	0.90	0.52	0.41	0.15	—	0.06
Ca ²⁺	0.05	0.14	0.08	0.29	0.15	0.18
Zr ⁴⁺	0.02	—	—	—	—	—
Mg ²⁺	—	—	—	—	—	0.01
Fe ³⁺	—	—	—	0.29	0.17	0.06
Ti ⁴⁺	—	—	—	—	0.04	0.02
Al ³⁺	3.05	2.83	2.78	2.98	2.46	2.79
SiO ₄ ⁴⁻	0.02	—	—	0.08	—	0.44
PO ₄ ³⁻	1.92	1.77	1.62	1.43	1.95	1.47
SO ₄ ²⁻	—	0.10	0.19	0.09	—	0.06
F ⁻	—	0.41	0.30	—	—	0.05
OH ⁻	6.20	5.24	5.30	6.52	3.68	3.89
H ₂ O	0.04	0.85	1.18	1.08	2.52	2.18
ΣX	0.97	1.08	1.04	0.69	0.73	0.79
ΣY	3.05	2.83	2.78	3.27	2.67	2.87
Σ(ZO ₄)	1.92	1.87	1.81	1.60	1.95	1.97
Σ(F, OH, H ₂ O)	6.24	6.50	6.78	7.60	6.20	6.12
Formal composition	Cn ₁₃ F ₆ Gz ₉₉	Cn ₁₃ F ₆ Ca ₈ Gz ₉₉	Cn ₉ F ₆ Gz ₉₉ Gx ₆	Cn ₄₂ F ₆ Gz ₃₆ Gx ₃₆	Cn ₂₀ Gz ₃₂ Gx ₄₈	Cn ₂₄ F ₆ Gz ₆₉ X ₆₉

	1.	2.	3.	4.	5.	6.
mean $r(X)$ (Å)	...	1.12	1.17	1.20	1.27	1.31
G(calc.)	...	3.702	3.392	3.162	3.053	3.153
G(obs.)	...	3.695	3.386	2.96	—	3.07
a (Å)	...	6.949 ± 0.009	6.982 ± 0.001	6.999 ± 0.003	7.022 ± 0.002	7.028 ± 0.004
c (Å)	...	16.233 ± 0.002	16.54 ± 0.02	16.54 ± 0.11	17.03 ± 0.06	17.03 ± 0.19
ω	...	1.695	—	—	—	—
ϵ	...	1.705	—	—	—	—
grain size	...	0.1 cm ±	0.1 μ ±	0.1 μ ±	0.1 μ ±	0.1 μ ±

1. Florencite (Stiepelmannite), Klein Spitzkopje, Usakos, South-West Africa (Ramdohr and Thilo, 1940; Ygberg, 1945). Unit-cell dimensions on specimen B.M. 1952.17.

2. Strontian florencite, Kangankunde Hill, Nyasaland. Analyst R. Pickup.

3. Cerian goyazite, Wigu Hill, Tanganyika. Analyst R. Pickup.

4. Gorceixite, Bonsa River, near Dompim, Gold Coast (Junner and James, 1947). Analyst W. H. Bennett. Unit-cell dimensions on specimen L.O. 4, Overseas Geological Surveys.

5. Gorceixite, Mrima Hill, Kenya. Analyst R. Pickup. Unit-cell dimensions on analysed material.

6. Gorceixite, Oiyi No. 1 Pan Plant, Sierra Leone (Anon., 1941). Analyst W. H. Bennett. Unit-cell dimensions on specimen L.O. 120, Overseas Geological Surveys.

Analyses are listed in order of increasing mean $r(X)$. Cations are listed in order of decreasing radius. Formal composition is expressed in terms of the symbols given on p. 284.

hexagonal unit-cell of alunite, a 6.96 Å, c 17.35 Å, has K^+ at centres of symmetry on triad axes at 0 0 0, $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{3}$, and $\frac{2}{3}$ $\frac{1}{3}$ $\frac{2}{3}$, such that each K^+ is coordinated to six oxygen atoms of two sulphate tetrahedra disposed on either side and to six hydroxyl groups, three above and three below. Al^{3+} , with which we are less concerned here, is coordinated to four hydroxyl groups and to two oxygen atoms of different sulphate tetrahedra. Each sulphate tetrahedron has its sulphur atom and one oxygen atom on a triad axis; such oxygen atoms are hydrogen-bonded to three hydroxyl groups. Hendricks observed that several kinds of replacement were possible in the alunite structure, which may be given the general formula $X^{[12]}Y_3^{[6]}(ZO_4)_2(OH)_{6-n}(H_2O)_n$ for the contents of the rhombohedral unit-cell, where the substitution of OH^- by H_2O is statistical so that symmetry is not lost.

The unit-cell dimensions of four analysed members of the goyazite series in addition to the Wigu and Kangankunde goyazite and florencite have been newly determined and are set down in Table V. The determinations for specimens 3, 5, and 6 were made by diffractometry according to the procedure described in a previous paragraph. For specimen 1 a different technique was used because only a few crystals were available. In this case a good single crystal was selected, coated with gold *in vacuo*, and set up successively to oscillate about the triad and a diad axis. Oscillation ranges were chosen so that the position of the high θ reflections 1780 and 0.0.0.18 could be accurately interpolated between Au powder lines, thus eliminating errors due to film shrinkage and poor fit of the cylindrical film to the wall of the cassette in the back reflection region.

The contents of the rhombohedral unit-cell, listed in table V for the six specimens studied, have been calculated on the assumption that the unit-cell contains 14 oxygen and fluorine atoms; that $\Sigma(O,F) = 14$ is essential for the alunite structure. The published analyses have been accepted as given by the authors without subtraction of possible impurities to give a better fit to the general formula $XY_3(ZO_4)_2(OH)_{6-n}(H_2O)_n$, although some of the analyses almost certainly refer to material that was not quite pure. Separations of the order of difficulty involved here are not likely to have been achieved much before the last decade.

The rhombohedral unit-cell contents listed in table V show an acceptable fit to the general formula. The large cation X in twelve-fold coordination lies in the radius¹ range 0.70 to 1.42 Å, if the small content

¹ The radii used are those of Ahrens (1952) increased by 6% for twelve-fold coordination.

of Mg in the Sierra Leone gorceixite and of Zr in the Klein Spitzkopje florencite are not due to impurities, or in the range 1.05 to 1.42 Å if only the major constituents are considered. The alunite structure, as Hendricks (1937) observed, is tolerant of an unusually wide variation in the radius of the X cation. ΣX is equal to or rather less than unity, the deficiency being statistical since no loss of symmetry is observed. The dominant six-fold coordinated Y cation in each specimen is Al^{3+} . ΣY is equal to or rather less than three, except in specimen 4, which also has the highest value for $\Sigma(F, OH, H_2O)$ and worst agreement between observed and calculated density. The very fine-grained gorceixite (grain size 1 to 0.01 μ) of specimen 4, a pebble from a diamondiferous gravel, was apparently not separated from possible, though undetermined, impurities before analysis. The small four-fold coordinated Z cations have a sum in each case rather less than two; specimen 4 is again anomalous. The sum of anionic groups not involved in ZO_4 tetrahedra exceeds the value of six of the general formula and ranges from 6.12 to 6.78 (excluding specimen 4), balancing low values of $\Sigma(ZO_4)$. It would appear then that there can be a statistical deficiency in the occupation of tetrahedral sites by Z cations, the neutrality of the structure being maintained by the introduction of extra protons into the structure.

The data of table V lend no support to the contention of Milton, Axelrod, Carron, and MacNeil (1958) that gorceixite approximates to the formula $BaAl_5(PO_4)_2(OH)_{11}$. It is inconceivable that a rhombohedral phosphate with 19 oxygen atoms in its unit-cell could possess the alunite structure. Both the analyses of gorceixite from Dale Co., Alabama, given by Milton *et al.* were corrected for large amounts of impurity, 17.82% in one and 32.99% in the other. In the absence of unit-cell dimensions, either the corrections for impurities or the identification of gorceixite must be questioned.

The dimensions of the triple hexagonal unit-cell of the six specimens studied are listed in table V and plotted against the mean radius r of the large twelve-fold coordinated cation X in fig. 4. In calculating the mean radius departures of ΣX from unity have been ignored. It is clear from fig. 4 that the values of c lie close to a straight line of slope 4.3 and that the slope of a with respect to r is approximately only 0.40. The structure therefore responds to change in mean radius, over the range 1.12 to 1.31 Å, of the three X cations, situated at 0 0 0, $\frac{1}{3} \frac{2}{3} \frac{1}{3}$, $\frac{2}{3} \frac{1}{3} \frac{2}{3}$, by change in unit-cell dimensions such that $dc/dr = 2.15$ diameters and $da/dr = 0.20$ diameters of the X cation. That the observed dimensional variation is just over $\frac{2}{3}$ of its maximum possible value, 3 diameters, in

the c direction and only $\frac{1}{5}$ of the maximum in the a direction indicates that variation in size of the X cations is to a considerable extent taken up by readjustment of the Al-O-P framework in such a manner that Al-O-P bonds rotate to minimize atomic displacements, especially in the a -direction.

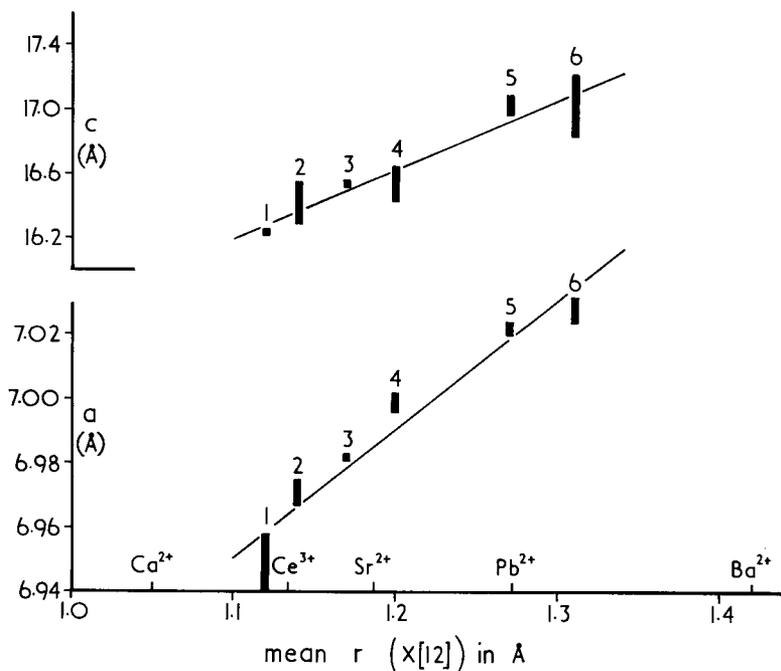


FIG. 4. Plot of triple hexagonal unit-cell dimensions in the goyazite series against mean radius of cations on twelve-fold coordinated sites. The numbering corresponds to that of the columns of table V. The size of the plotted points represents the error of the measurements. The radii of the principal X cations are indicated by their symbols.

It must be noted that lower values of dc/dr and of da/dr apply to the alunite series (Hendricks, 1937; Moss, 1958), probably because the radius of Na^+ is rather small for twelve-fold coordination to oxygen.

The anomalous a -dimension of specimen 4 can be attributed to the greater extent of the substitution of Fe^{3+} for Al^{3+} than in the other specimens studied. Correspondingly the jarosites have a larger and c smaller than the corresponding members of the alunite series.

Paragenesis. Most carbonatite complexes contain only trivial amounts of the rare earth elements. The exceptions are Mountain Pass in California, the Petrovsko-Gnutovo fluorite-carbonate vein in the Azov Sea region of Russia (Kuzmenko, 1940), Mrima in Kenya, Wigu in Tanganyika, Nkombwa in Northern Rhodesia, and Kangankunde in Nyasaland. At Mountain Pass the rare earths are present as bastnäsite, parisite, and monazite, while the Petrovsko-Gnutovo dyke is rich in parisite; from neither has any member of the goyazite series been recorded. At Nkombwa there is a rather restricted development of monazite-bastnäsite mineralization.

Coetzee and Edwards (1959) consider that the abundant gorceixite, associated with baryte and monazite, at Mrima was formed during weathering processes, the phosphate being derived by solution of apatite, the aluminium possibly being introduced from sources external to the carbonatite, and the barium being derived from solution of sövite and precipitated from ground-water solutions as gorceixite after complete precipitation of sulphate as baryte. It would seem likely, however, that the source of aluminium was solution of the feldspars and micas of xenoliths and marginal sövites. The ground-water solutions may well have acquired their barium content by solution of large amounts of carbonate minerals containing large traces of barium, rather than by solution of accessory baryte.

At Wigu the rare earths occur as bastnäsite, monazite, and goyazite. None of the rare earth minerals appears to belong, even in part, to the primary crystallization of the carbonatite; all occur principally in more or less well-shaped hexagonal prismatic pseudomorphs after some unidentified mineral, possibly apatite, of which no relics remain. Goyazite in very fine-grained intergrowth with minor amounts of baryte and quartz constitutes the smallest and least euhedral type of the pseudomorphs, which are enclosed in a calcite-dolomite matrix. The phosphate of the goyazite may have been derived from the original mineral of the pseudomorphs, but strontium, rare earths, and aluminium have apparently been introduced by ascending late-stage solutions percolating through the already crystallized carbonatite. In support of this hypothesis of the introduction of strontium are the occasional narrow celestine veins found throughout the Wigu carbonatite. No precise information about the physical conditions of goyazite crystallization has yet been obtained at Wigu, but it would seem likely that the temperature at which the late-stage processes occurred was well below the upper stability limit of the mineral at $500+^{\circ}\text{C}$, and it seems probable for a

variety of reasons to be detailed elsewhere that pressure was never high during the emplacement of the Wigu carbonatite at the level at which it is seen at present.

Florencite occurs only in the 'central mobilized area' at Kangankunde, where it may be presumed to have formed at a late stage in the active history of the carbonatite. It is intimately associated with bastnäsite and euhedral monazite, the only other rare earth minerals known at Kangankunde. The relative coarseness and the euhedral nature of the florencite rhombohedra at Kangankunde distinguish this occurrence from those of other members of the goyazite series at Wigu and Mrima. Rare-earth-bearing pseudomorphs after an unknown hexagonal mineral are here too a prominent feature of the rare-earth-bearing zones of the complex. Again no critical data are available concerning the physico-chemical conditions of florencite crystallization, but processes similar to those suggested for the Wigu occurrence may well have operated here.

Goyazite, florencite, and gorceixite appear then to have crystallized in carbonatite complexes during late-stage processes at temperatures considerably lower than the limiting temperature of $500+^{\circ}\text{C}$ for goyazite and florencite and possibly at relatively low pressures. Such conditions are consistent with Fisher's (1958) recognition of the Ca, Sr, and Ce members of the goyazite series as supergene hydrous phosphates.

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