Fluocerite and its alteration products from the Afu Hills, Nigeria

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ABSTRACT. Eluvial pebbles from the Afu Hills, Nigeria, are largely composed of fluocerite, $Ce_{0.50}La_{0.28}Nd_{0.11}Pr_{0.04}Th_{0.03}Ca_{0.02}F_3$, with minor monazite. The fluocerite shows two types of alteration, to bastnäsite, and to bastnäsite-(La) with cerianite. Electron microprobe analyses are given for fluocerite, monazite, bastnäsite and bastnäsite-(La). The refined cell parameters of the fluocerite are $a = 7.130 \pm 0.001$, $c = 7.298_5 \pm 0.001$ Å. Strongest lines are 3.204 Å (100), 3.65 (45), 2.059 (45), 2.010 (45) and 3.56_5 (40). Space group $P\ 6_3/mcm$, $Z = 6$, $D_{calc.} = 6.12$ g cm^{-3}, $\omega = 1.613$, $\varepsilon = 1.609$ both ± 0.002, uniaxial negative. For bastnäsite $a = 7.131 \pm 0.002$, $c = 9.786 \pm 0.004$ Å, for cerianite $a = 5.46_0 \pm 0.005$ Å.

SPECIMENS containing the rare earth minerals described in this paper were originally sent for analysis in March 1961 to the Atomic Energy Division of the Geological Survey of Great Britain by Mining and Technical Services Ltd. Optical and XRD studies by Mr J. E. T. Horne and Mr R. K. Harrison showed that they contained fluocerite with subordinate cerianite, and an XRF analysis showed predominant rare earths with minor Th, Fe and traces of Ca, Sr, and Pb.

The sender's description stated that the specimens were found 'in the course of ground sluicing over albite-pegmatites bearing tin and subsidiary columbite, on the property of United Tin Areas of Nigeria, near Odegi, Afu Hills, Nigeria'. Attempts were made to determine the exact location and possible source of the specimens, but despite the co-operation of Vectis Tin Mines Ltd. (previously United Tin Areas of Nigeria), Mackay and Schnellmann Ltd. (the consultants to United Tin), the Nigerian Mining Corporation and the Nigerian Geological Survey Department these attempts have been unsuccessful.

A detailed study of these unusual specimens has now been carried out by electron microprobe and X-ray diffraction.

Petrography

A polished thin section (G 152, Sliced Rock Collection, Institute of Geological Sciences) of a

pebble approximately 1.5 cm in diameter has been studied in detail. It consists largely of fluocerite (and its alteration products) and a small amount of monazite with a dark rusty brown limonitic vein along one side. The fluocerite occurs as prismatic crystals up to 5 mm in length with widespread alteration along cracks and the basal cleavage. It is colourless to very pale yellow, uniaxial negative with low birefringence and refractive indices $\omega = 1.613$, $\varepsilon = 1.609$, both ± 0.002 (Horne and Harrison, 1961).

The nature of the alteration of the fluocerite varies from point to point. Along the basal cleavage, fine cracks, and in some small patches, it is altered to a fine-grained (c. 1 μm) aggregate of a light yellowish-brown mineral with high birefringence, identified as bastnäsite. The fluocerite and bastnäsite are both cut by wider veins of a dark reddish-brown material that is composed of aggregates of mostly submicron crystals, which also appear brown in cross-polarized light with no discernible extinction or birefringence. These dark-brown aggregates were shown to be bastnäsite-(La) and cerianite with rare thorite.

Monazite occurs adjacent to the fluocerite and is pale yellow and traversed by numerous cracks and patches of dark-brown alteration products. The limonite vein is composed largely of goethite and quartz, an alumino-silicate, probably kaolinite and rare cassiterite.

Mineral compositions

Mineral compositions were determined using a Link Systems energy-dispersive X-ray analyser on a Geoscan electron microprobe. The techniques used are described in detail in the appendix.

Fluocerite. Six fluocerite grains were analysed; they are unzoned and show only slight variation from grain to grain. The average composition is given in Table I along with the ionic formula which shows close agreement to a stoichiometric fluoride composition. A chondrite-normalized RE diagram

TABLE I. *Electron microprobe analyses of fluocerite*

	1	2	
La	20.85	1.707	
Ce	37.25	3.027	
Pr	3.23	0.261	
Nd	8.18	0.645	5.982
Sm	0.35	0.012	
Ca	0.51	0.141	
Th	3.84	0.189	
F*	25.28		

* By difference.
1. Fluocerite, mean of seven analyses.
2. Number of ions on basis of eighteen fluorines.

(Leedly chrondite, Masuda *et al.*, 1973) is given in fig. 1 which shows the strong enrichment in *LRE*. Early analyses of fluocerite did not give determinations of individual *RE*; however, if the analysis given here is recalculated on the same basis it gives a similar composition with the ratio of Ce-group (Ce + Th) to La-group (La + Pr + Nd) approximately 4 : 3, (see Palache *et al.*, 1951, p. 49). A compilation of more recent analyses of fluocerite with individual *RE* determined is given in Table II.
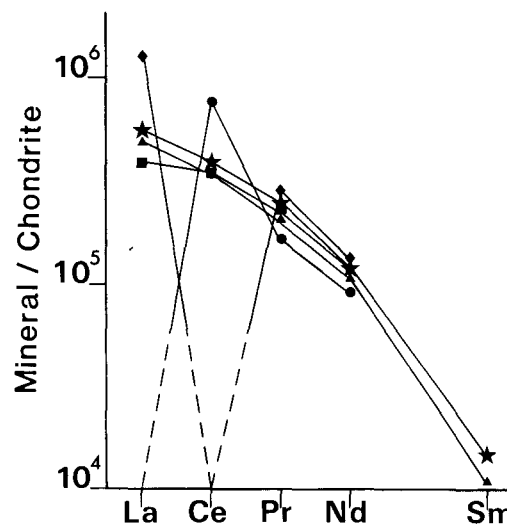
FIG. 1. Chrondrite-normalized *RE* abundances for fluocerite (stars), monazite (squares), bastnäsite (triangles), bastnäsite-(La) (diamonds) and cerianite (circles).

This shows that all fluocerites are strongly enriched in *LRE* but the proportions vary as is shown by the sum of La + Ce + Pr which varies from 70 to 96 % of the total *RE* content. The analysis with the

TABLE II. *Lanthanides in fluocerite, at %* ($\Sigma RE = 100\%$)

	1	2	3	4	5	6	7	8	9	10
La	20.3	17.9	28.5	27.3	31.5	30.1	31.2	39.1	25.0	51.5
Ce	44.0	48.3	39.4	48.4	48.0	53.4	54.5	47.2	68.0	40.1
Pr	6.5	5.7	4.9	3.2	5.7	4.6	3.1	3.2	1.3	4.4
Nd	18.2	20.7	13.9	12.3	12.8	11.4	10.1	9.3	5.1	3.7
Sm	6.5	4.0	2.3	3.1	1.4	0.5	0.8	1.2	0.6	0.2
Eu	0.1	—	—	0.5	—	—	—	—	—	—
Gd	2.6	3.0	4.2	1.9	0.4	—	0.3	—	—	0.1
Pb	—	—	—	0.4	—	—	—	—	—	—
Dy	1.2	0.4	3.1	1.0	0.1	—	—	—	—	—
Ho	—	—	—	0.6	—	—	—	—	—	—
Br	0.4	tr	1.9	0.4	0.1	—	—	—	—	—
Tm	0.2	—	—	0.3	—	—	—	—	—	—
Yb	—	—	1.8	0.3	—	—	—	—	—	—
Lu	—	—	—	0.3	—	—	—	—	—	—
La + Ce + Pr	70.8	71.9	72.8	78.9	85.2	88.1	88.8	89.5	94.3	96.0

1. Arkhangel'skaya (1970); av. of 2, metasomatic, alk. granitoids, E. Siberia.
2. Popova and Bazhenova (1976); greisen, Far Eastern USSR.
3. Feldman *et al.* (1973); granite, northern Tien-Shan.
4. Vetoshkina *et al.* (1980); amazonite pegmatite, Ploska Mt., Kola Peninsula.
5. Gurov and Gurova (1974); metasomatic, Ukraine.
6. Styles and Young; eluvial, Nigeria.
7. Heinrich and Gross (1960); granite pegmatite, Teller Co., USA.
8. Semenov and Barinskii (1958); hydrothermal alteration of granite, N. Kingiziya.
9-10. Christyakova and Kazakova (1969); hydrothermal, Kent, Kazakstan. (10) fresh, (9) altered.

TABLE III. *Electron microprobe analyses of monazite, bastnäsite, and bastnäsite-(La)*

	1	2		3	4		5	6	
La_2O_3	16.63	0.984		21.65	1.758		55.04	4.407	
Ce_2O_3	38.49	2.265		37.97	3.090		nd	—	
Pr_2O_3	3.68	0.212		3.13	0.249	6.037	4.35	0.348	6.190
Nd_2O_3	9.69	0.515	4.094	8.86	0.692		11.49	0.884	
Sm_2O_3	0.41	0.026		0.40	0.036		nd	—	
CaO	nd	—		0.65	0.212		1.72	0.551	
ThO_2	1.28	0.092		nd	—		nd	—	
P_2O_5	28.87	3.926		nd	—		nd	—	
CO_2					6.000			6.000	
F					6.000			6.000	

nd Not detected.
1. Monazite; mean of four analyses.
2. Number of ions on basis of sixteen oxygens.
3. Bastnäsite; mean of six analyses.
4. Number of ions on basis of eighteen oxygens six fluorines.
5. Bastnäsite-(La).
6. Number of ions on basis of eighteen oxygens six fluorines.

composition most enriched in *LRE* (col. 10) actually contains more La than Ce.

Monazite. The analysed monazite grains show a slight variation from grain to grain and slight zoning to more Ce-rich rims. An average analysis is given in Table III col. 1, which shows that it has a similar *RE* content to the fluocerite but is relatively depleted in La (fig. 1). It also has a much lower Th content, 1.13% compared with 3.84% in fluocerite. The textural relations suggest that the monazite and fluocerite are primary minerals and these differences in *RE* and Th represent the differing chemical affinities of the two minerals.

Bastnäsite. The light yellowish-brown bastnäsite shows only a slight variation from point to point on the thin-section and an average composition is given in Table III, col. 3. (These analyses represent aggregates of several grains as the grain size is smaller than the electron beam.) The *RE* distribution is very similar to that of fluocerite (fig. 1) although the total *RE* content is lower due to the presence of CO_2. Th was not detected (< 0.4%) and contrasts with 4% in fluocerite.

Fleischer (1978) showed that bastnäsites from different geological environments tend to show different compositions, and those described here with high La and low Nd are most like the group from alkaline rocks.

Dark-brown alteration products. Analyses of the dark-brown alteration products show a wide range of compositions varying from Ce-rich to La-rich (Table IV). The grain size is generally much smaller than the electron beam and in consequence a mixture of several mineral grains have been analysed. However, two analyses of single minerals were obtained, first of a dark-brown Ce-free bastnäsite-(La) (Table III, col. 5) and secondly of a thorite. The analyses of these mineral aggregates are plotted on a diagram of Ce *vs.* La (fig. 2) which shows that they lie on a mixing line between an La-rich phase of approximately the same composition as the analysed bastnäsite-(La) and a Ce-rich phase containing approximately 65% Ce. The mineral cerianite (CeO_2) was detected on the X-ray diffractometer charts. If it is assumed that all the La is in the bastnäsite-(La) the composition of the Ce-rich phase can be calculated. The greatest
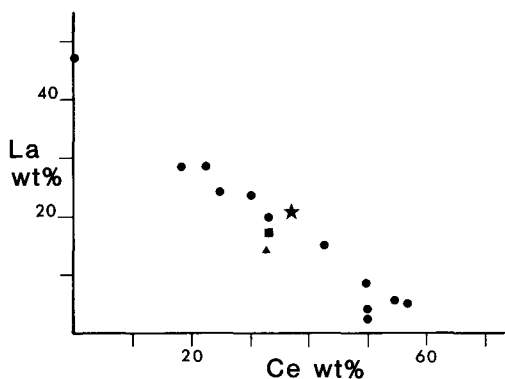

FIG. 2. La *vs.* Ce for dark-brown alteration products (circles), average fluocerite (star), average monazite (square) and average bastnäsite (triangle).
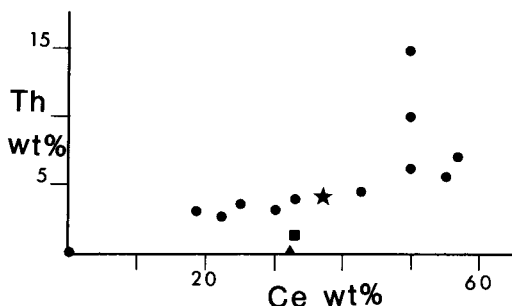
FIG. 3. Th vs. Ce for dark-brown alteration products. Symbols as fig. 2.

uncertainty in the calculation is the distribution of Th. A plot of Ce vs. Th (fig. 3) shows that, apart from two which have much higher Th, the analyses lie along a straight line. In addition, the two anomalous analyses contain high Si (Table IV, col. 5) and also lie away from the line on the Ce vs. La diagram. These results suggest that most analyses contain a Ce-rich phase with a Ce : Th ratio of approximately 8 : 1 and that two analyses also contain thorite.

A calculated composition of the Ce-rich phase, cerianite, is given in Table IV, col. 6. This is only intended as an approximation as there are several possible sources of error in the calculation including: errors in the matrix correction of the microprobe data since the detected X-rays are produced by several different phases rather than one homogeneous phase as assumed by the matrix correction program; and variation in the composition of the minerals in the aggregates, e.g. the variation in Ca shows that the La-rich aggregates have insufficient Ca to form bastnäsite-(La) of the analysed compo-

sition, whilst in contrast, the Ce-rich aggregates have excess Ca, suggesting either that Ca enters the cerianite (Ca 1.0%) or that a small amount of a Ca mineral is also present.

The survey of bastnäsite compositions (Fleischer, 1978) does not give Ce-free compositions and it is thought that this is the first reported occurrence of naturally occurring bastnäsite-(La), with a composition close to the end member.

X-ray data

The d-spacings for fluocerite, bastnäsite, and cerianite were determined from diffractometer charts taken with a Cu-$K\alpha$ radiation at room temperature (around 20 °C) and a scanning speed of $1/8°$ 2θ/min. Lead nitrate ($a = 7.8558$ Å at around 20 °C) was used as an internal standard). The powder data were provisionally indexed by comparison with published data (JCPDS Data Cards 2-529, 4-593 and 11-340) and the fluocerite and bastnäsite data were refined using the US Naval Laboratory least squares program for refining cell parameters.

The fluocerite has cell dimensions $a = 7.130 \pm 0.001$, $c = 7.298_5 \pm 0.001$ Å, space group $P6_3/mcm$, and its density corresponding to these cell dimensions and the unit-cell contents (Table I) is 6.12 g cm^{-3}. The powder data are listed in Table V. The bastnäsite was heavily contaminated with fluocerite and cerianite and it was not possible to obtain very accurate powder data since the peaks were weak and several coincided with cerianite or fluocerite peaks, but the data obtained closely match those for bastnäsite from Mountain Pass, California (Glass et al., 1958), and give cell dimensions $a = 7.131 \pm 0.002$, $c = 9.786 \pm 0.004$ Å.

TABLE IV. Electron microprobe analyses of dark brown alteration products

	1	2	3	4	5	6	7	
La$_2$O$_3$	32.83	23.16	17.36	6.65	2.70			
CeO$_2$	27.74	40.46	52.18	67.49	60.80	80.5	1.705	⎫
Pr$_2$O$_3$	3.20	2.92	3.86	1.76	1.79	2.5	0.058	⎪
Nd$_2$O$_3$	9.27	7.33	8.79	6.48	5.29	7.5	0.160	⎬ 2.054
Sm$_2$O$_3$	nd	nd	0.35	0.40	0.46			⎪
CaO	0.48	0.59	1.30	0.95	0.69			⎪
ThO$_2$	2.86	4.74	4.97	6.41	11.23	9.5	0.131	⎭
SiO$_2$	—	—	1.00	—	4.45			

nd Not detected.
1–4. Cerianite-bastnäsite-(La) mixtures.
5. Cerianite-bastnäsite-(La) mixtures with thorite.
6. Calculated cerianite composition.
7. Number of ions on basis of four oxygens.

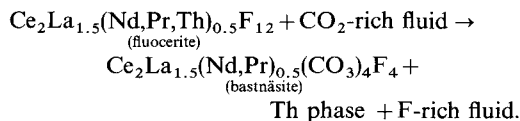TABLE V. *X-ray powder data for fluocerite from near Odegi,*
Afu Hills, Nigeria

I/I_1	$d_{obs.}$ Å	$d_{calc.}$ Å	hkl	I/I_1	$d_{obs.}$ Å	$d_{calc.}$ Å	hkl
45	3.65	3.649	002	2	1.2755	1.2751	224
40	3.56_5	3.565	110	2	1.2638	1.2641	412
100	3.204	3.203	111	2	1.2166	1.2164	006
8	2.550	2.550	112	4	1.1883	1.1884	330
2	2.223	2.223	211	8	1.1789	$\{$ 1.1788	413
45	2.059	2.058	300			1.1785	404
45	2.010	2.009_5	113	2	1.1514	1.1513	116
6	1.825	1.825	004	6	1.1299	$\{$ 1.1300	332
25	1.793	1.793	302			1.1294	225
16	1.732	1.732	221	2	1.0840	1.0839	414
3	1.624	1.624	114	6	1.0472	1.0472	306
3	1.602	1.602	222	2	1.0295	1.0292	600
12	1.437_5	$\{$ 1.4379	223	2	1.0050	1.0048	226
		1.4375	214	2	1.0006	1.0007	117
10	1.365	1.3654	304	2	0.9959	0.9958	334
6	1.350_5	1.3509	115	6	0.9902	$\{$ 0.9905	602
5	1.347	1.3475	410			0.9901	415
10	1.325	1.3251	411	4	0.9797	0.9798	521

The intensities are relative peak heights.

The cerianite peaks were broad, indicating a variable composition. The cerianite has a mean cell dimension $a = 5.46_0 \pm 0.005$ Å.
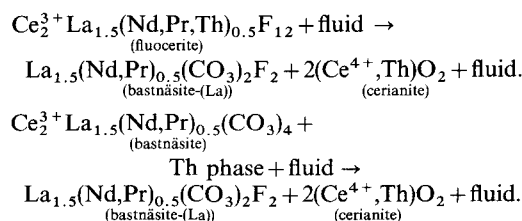
Discussion

The fluocerite–monazite pebbles show that the alteration of fluocerite takes place by two distinct processes. The first is carbonation to form the fluorocarbonate bastnäsite as is described from most of the reported occurrences of fluocerite. This involves very little mobilization of the *RE* as is shown by the very similar *RE* distribution patterns and the Ce-La diagram (fig. 1 and 2). In this particular instance the Th in the fluocerite is not incorporated in the bastnäsite and presumably forms a separate Th phase, possibly thorite or thorianite (ThO$_2$). A simplified chemical reaction is

$$Ce_2La_{1.5}(Nd,Pr,Th)_{0.5}F_{12} + CO_2\text{-rich fluid} \rightarrow$$
(fluocerite)
$$Ce_2La_{1.5}(Nd,Pr)_{0.5}(CO_3)_4F_4 +$$
(bastnäsite)
$$\text{Th phase} + \text{F-rich fluid.}$$

The second type of alteration which may occur both as a breakdown of bastnäsite and as direct alteration of fluocerite, involves the separation of Ce and La into separate mineral phases, cerianite and bastnäsite-(La). The separation of Ce and La into these separate phases is probably caused by the oxidation of Ce from Ce^{3+} in fluocerite and bastnäsite to Ce^{4+} in cerianite. This presumably indicates a different composition of the fluid

causing alteration, in this case being more oxidizing, possibly due to a lower CO_2 content.

Simplified chemical reactions are

$$Ce_2^{3+}La_{1.5}(Nd,Pr,Th)_{0.5}F_{12} + \text{fluid} \rightarrow$$
(fluocerite)
$$La_{1.5}(Nd,Pr)_{0.5}(CO_3)_2F_2 + 2(Ce^{4+},Th)O_2 + \text{fluid.}$$
(bastnäsite-(La)) (cerianite)

$$Ce_2^{3+}La_{1.5}(Nd,Pr)_{0.5}(CO_3)_4 +$$
(bastnäsite)
$$\text{Th phase} + \text{fluid} \rightarrow$$
$$La_{1.5}(Nd,Pr)_{0.5}(CO_3)_2F_2 + 2(Ce^{4+},Th)O_2 + \text{fluid.}$$
(bastnäsite-(La)) (cerianite)

The cerianites have approximately the same Ce/Th ratio as the fluocerite (fig. 3) perhaps indicating that the first reaction is more common as it does not require a separate Th phase to be recombined in exactly the same proportions which precludes mobility of chemical components during alteration.

Further evidence that Ce and La can behave differently during alteration is shown by the analyses given by Chistyakova and Kazakova (1969), Table II, cols. 9 and 10, where there is a marked change in the Ce/La ratio from 0.78 in the fresh sample to 2.75 in the altered sample. The Ce-rich altered sample is similar in composition to some of the cerianite-rich dark-brown alteration products described in this paper.

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APPENDIX

Microanalysis techniques. The microprobe analyses were made using a Link Systems energy-dispersive (ED) X-ray analyser on a Cambridge Instruments Geoscan electron microprobe. An accelerating voltage of 15 kV, a specimen current of 5×10^{-9} amps and an electron beam focused to approximately 5 μm were used throughout. The ED X-ray detector has a resolution of around 165 eV (FWHM) for Co-$K\alpha$ under the analytical conditions used

TABLE VI. *Electron microprobe analyses of glass REE3*

	1	2	3	4	5
SiO_2	26.52	0.22	27.12	0.38	27.15
Al_2O_3	30.89	0.19	31.01	0.22	30.72
CaO	24.97	0.25	25.23	0.19	25.33
La_2O_3	4.59	0.21	4.51	0.19	4.59
Ce_2O_3	4.23	0.18	3.90	0.06	4.29
Pr_2O_3	4.57	0.24	4.48	0.20	4.60
Y_2O_3	3.76	0.10	4.14	0.20	4.08
Total	99.53		100.39		

1. Average of four widely spaced analyses.
2. Standard deviation of col. 1 analyses.
3. Average of four analyses of same spot on REE3.
4. Standard deviation of col. 3 analyses.
5. Composition of REE3 given by Drake and Weill (1972).

with an input count of approximately 3.5×10^3 counts per second and a dead time around 25%. All measurements were made using a 100 sec livetime counting period.

Data processing was carried out using the Link Systems 'ZAF4 FLS +' program and calibration for RE was made using synthetic single crystals of LaB_6, CeO_2, $PrAlO_3$, $NdAlO_3$, and $SmAlO_3$. Tests have shown that the ED system can adequately deal with the overlapping spectra of the RE L lines and the transition metal K lines. The limit of detection for RE in overlapping spectra is approximately 0.35 wt. % element for the elements reported here. The detection limits for the heavier RE are slightly higher due to the less efficient excitation and it is preferable to use a higher accelerating voltage.

The glass REE3 produced by Drake and Weill (1972) was analysed using the same instrumental conditions as the minerals and the results are given in Table VI. The average of four points, widely spaced on the glass specimen, approximately 1.5 mm in diameter (col. 1), is in close agreement with the stated composition (col. 5). One point on the glass was also analysed four times to give an indication of the precision of the analyses and the results are given in col. 3. One of these four analyses has a high total, 101.9% (probably due to beam intensity drift) and this causes the standard deviations to be higher than might be expected; if the analyses are normalized to 100% before the standard deviation is calculated the RE standard deviation would be approximately 0.15. This is probably a better indication of the precision of the analysis of RE using an E.D. spectrometer.

It should also be noted that the concentrations of Y and Ce in col. 3 and col. 1 are significantly different. It has been found that the RE glasses of Drake and Weill are not homogeneous on a micro scale and that when they are analysed using a finely focused electron beam (5 μm) the concentration of RE and Y can vary by $\pm 10\%$ (relative), 0.5 wt. % oxide from the given concentrations. The bulk composition is very close to the given composition (cols. 1 and 5).