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XENOTIME FROM RAYFIELD, NORTHERN NIGERIA¹

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INTRODUCTION

In 1954, xenotime was identified by M. P. Jones² and the author in a jig concentrate submitted for examination to the Geological Survey by Amalgamated Tin Mines of Nigeria Ltd. The concentrate was obtained from the mineral dressing plant established at Rayfield (9°50'N; 8°55'E) near Jos, Northern Nigeria to work the intensely decomposed biotite-granite for primary columbite.

The geology of the Jos-Bukuru Younger Granite Complex, which includes the Rayfield-Gona biotite-granite, has been described in detail by MacLeod (1956). A briefer account was given by Jacobson *et al.*, (1958), and the economic geology of the decomposed columbite-bearing granites has also been described (Williams *et al.*, 1956). The treatment of the decomposed granite for the recovery of the associated heavy minerals has been described in a series of papers by Williams (1956, 1957, 1959).

Subsequent to the identification of the xenotime, Amalgamated Tin Mines of Nigeria produced high grade concentrates of the mineral by a combination of gravity, magnetic and high tension separation. The work described in this note was carried out on a xenotime concentrate supplied by the company.

Description of the Mineral Concentrate

A screen analysis of the concentrate gave the following result:

British Standard		
Sieve No.	Size of sieve opening, mm.	Weight %
+36	+0.422	3
-36+52	-0.422 ± 0.295	48
-52+100	-0.295 + 0.152	49
-100	-0.152	tr.

The concentrate consists of approximately 75% xenotime and 15%

¹ Published by permission of the Director, Geological Survey of Nigeria.

² Formerly on the staff of the Geological Survey of Nigeria.

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zircon; columbite, monazite, thorite, orangite, cassiterite and quartzcolumbite intergrowths make up the remaining 10%. Material for analysis and determination of optical and physical properties was separated by hand-picking under a binocular microscope.

PHYSICAL PROPERTIES

Xenotime and zircon occur in heavy mineral concentrates obtained from the columbite-rich Rayfield-Gona biotite-granite. The two tetragonal minerals can be readily distinguished by their distinctive habits. Xenotime occurs as milky white, pale yellow or buff-colored crystals showing the prism and basal plane only. The tabular prisms are commonly broken to form cube-shaped grains. Some crystals are subtranslucent, but the majority is opaque. Zircon is characterized by its bipyramidal habit; the crystals either form true bipyramids or have an extremely short prism zone (Williams *et al.*, 1956).

Intergrowths of xenotime and columbite are common, and it was noted that many of the crystals separated by hand-picking contained minute orange, brown and black inclusions. To check whether the black inclusions were due to the presence of columbite, a qualitative spectrographic analysis was made for niobium on a portion of the powdered mineral. The following sensitive niobium lines could not be detected: 3194.98, 3130.79 and 3094.18.

Refractive indices of the xenotime determined by the immersion method using sodium light are $\omega = 1.720 \ (\pm 0.005)$ and $\epsilon = 1.820 \ (\pm 0.005)$. The determined values are very similar to those given for New Zealand xenotime by Hutton (1947) viz. $\omega = 1.720$ and $\epsilon = 1.827$.

The specific gravity of the Rayfield xenotime was found to be 4.83; the mineral is moderately paramagnetic, and it accompanies columbite when passed through a magnetic separator. Monazite from the same source is weakly paramagnetic, and a good separation of monazite and xenotime can be obtained on a Frantz isodynamic separator, although there is some overlap in the magnetic behavior of the two minerals. Columbite may be separated from xenotime by the use of high-tension techniques, columbite being a good conductor whereas xenotime is a poor conductor (Jones, 1961).

METHOD OF ANALYSIS

The rare earth¹ content of the xenotime was determined by fusion of a 0.5 gm sample with potassium bifluoride followed by separation of thorium and the rare earths as the double fluorides by the method described by Rodden and Tregoning (1950). Thorium was separated from

¹ The term, rare earth, as used in this note includes yttrium.

the rare earths by the hexamine method (Ismail and Harwood, 1937).

 Fe_2O_3 , Al_2O_3 , ZrO_2 , CaO and MgO were determined by standard procedures on the filtrates from the fluoride and oxalate precipitations of the thorium and the rare earths. U_3O_8 was determined colorimetrically by the alkaline peroxide method; a chromatographic separation on a cellulose alumina column was used to remove interfering elements (Burstal and Wells, 1951; Williams, 1952). SiO₂ was determined by the conventional method and P_2O_5 gravimetrically, after separation of phosphate from the rare earths by a double fusion with potassium carbonate and water extraction of the melts.

Individual rare earths were determined on the ignited separated oxides by the optical spectrographic method of Butler (1957).

CHEMICAL COMPOSITION

Table 1 gives the chemical composition of the xenotime with the rare earths determined as a group. The reported amounts of Al_2O_3 , ZrO_2 , ThO_2 and SiO_2 are similar to those given for xenotime from Brindletown,

	1	2	3		
$(Y, Ln)_2O_3$	60.52	57.74	53.96		
Al ₂ O ₃	2.00	0.77	4.80		
Fe ₂ O ₃	0.35	0.65			
FeO	_	-	1.10		
ThO_2	0.95	tr.	2.47		
U_3O_8	0.22				
UO_2	(111)	4.13	3.17		
ZrO ₂	2.66	1.95	1.90		
CaO	tr.	0.21	0.61		
MgO	tr.	-	0.02		
MnO	tr.		1.72		
SiO ₂	2.93	3.46	4.32		
P_2O_5	29.46	30.31	25.38		
Ignition loss	0.51				
H ₂ O	·	0.57	0.20		
F		0.06			
Total	99.60	99.85	99.65		

TABLE 1. CHEMICAL COMPOSITION OF XENOTIME FROM RAVFIELD, N. NIGERIA COMPARED WITH XENOTIME FROM BRINDLETOWN, NORTH CAROLINA AND ISAKA JAPAN

1. Xenotime from Rayfield, N. Nigeria. Analyst, G. Jefford. GL. 1008.

3. Xenotime from Isaka, Japan. (Palache et al., 1951.)

^{2.} Xenotime from Brindletown, North Carolina. (Palache et al., 1951.)

North Carolina and Isaka, Japan. This supports the hypothesis (Palache *et al.*, 1951) that small amounts of substitution for phosphorus and the yttrium earths can occur.

The amounts of individual rare earths are listed in Table 2. In column 2 the analysis has been recalculated to a basis of 100% lanthanon oxides to permit comparison with the lanthanon distribution in xenotimes from the Urals and Switzerland.

Goldschmidt and Thomassen (1924) divided rare earth minerals into six types which are characterized by the relative abundance of the individual lanthanons. The lanthanon distribution for xenotime obtained by Goldschmidt and Thomassen is shown in Fig. 1. together with a plot of the lanthanon distribution in the Nigerian mineral. It will be noted that the Nigerian xenotime is relatively poor in gadolinium and rich in ytterbium.

The low gadolinium content of the Nigerian xenotime is illustrated by comparison with the values given in Table 2 for xenotime from the Urals

	Z	1	2	3	4	5
Y_2O_3	39	55.9				
La_2O_3	57	1	1	0.8	3.1	-
CeO_2	58	1	1	1.8	6.3	
Pr_6O_{11}	59	1	1	0.4	0.5	
Nd_2O_3	60	0.55	1.3	1.4	1.4	
Sm_2O_3	62	0.76	1.7	2.4	2.2	3.1
Eu_2O_3	63	1	1	0.6		
$\mathrm{Gd}_2\mathrm{O}_3$	64	1.48	3.4	13.6	7.9	14.9
$\mathrm{Tb}_4\mathrm{O}_7$	65	0.79	1.8	2.4	1.6	3.9
Dy_2O_3	66	8.25	18.9	24.3	18.9	29.0
Ho_2O_3	67	1.06	2.4	6.1	3.5	7.7
$\mathrm{Er}_2\mathrm{O}_3$	68	8.01	18.4	20.2	9.7	20.7
Tm_2O_3	69	1.86	4.3	2.6	2.2	
$\mathrm{Yb}_2\mathrm{O}_3$	70	19.3	44.2	19.2	37.7	17.8
Lu_2O_3	71	1.58	3.6	4.1	5.0	3.3
Total		99.54	100.0	99.9	100.0	100.1

TABLE 2. COMPOSITION OF RARE EARTH OXIDES SEPARATED FROM NIGERIAN XENO-TIME COMPARED WITH XENOTIMES FROM THE URALS AND SWITZERLAND

1. Nigerian xenotime. Analyst, G. Jefford.

2. Nigerian xenotime. Lanthanons calculated to a basis of 100% lanthanon oxides.

3. Xenotime from granite, Urals (Lyakhovich and Barinsky, 1961).

4. Xenotime from pegmatite, Urals (Lyakhovich and Barinsky, 1961).

5. Xenotime, St. Gothard, Switzerland. Calculated from ratios given by Vainshtein et al., (1956).

 1 Below limit of sensitivity. (Sensitivity limits are La₂O₃ 1.0%, CeO₂ 1.5%, Pr₆O₁₁ 0.3% and Eu₂O₃ 0.05%, Butler, 1957).



FIG. 1. Relationship of the distribution of Zanthanons in Nigerian xenotime (solid line) and that of the type assemblage of Goldschmidt and Thomassen (1924) (dashed line).

and Switzerland. Analyses of 11 xenotimes are listed by Vainshtein *et al.*, (1956) in terms of the ratios of individual rare earths to erbium. Calculation of the gadolinium contents on a basis of 100% lanthanon oxides gives values ranging from 6.4 to 14.9% which are appreciably higher than the determined value of 3.4% for the Nigerian mineral.

 Dy_2O_3 and Er_2O_3 values are 18.9 and 18.4% respectively, on a 100% lanthanon oxide basis. These values fall within the ranges reported for other xenotimes. Ytterbium is high, but similar proportions have been found in xenotimes from pegmatites in the Urals and Norway (Lyakhovich and Barinsky, 1961; Vainshtein *et al.*, 1956).

The small amount of light lanthanons (La, Ce, Pr and Eu could not be detected by the method of analysis used) in the xenotime is in accord with the usual lanthanon distribution.

The yttrium content of the Nigerian mineral appears to be relatively low. Values for yttrium calculated from the Y/Er ratios for nine xenotimes given by Vainshtein *et al.*, $(1956)^1$ range from 66 to 76% in com-

¹ It is not clear from the paper whether the ratios quoted refer to oxides or metals, and it has been assumed that oxide ratios are inferred. If the ratios refer to the metals, the error introduced is not sufficient to effect the comparison with the yttrium value of the Nigerian mineral.

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parison to a value of 55.9% for the Nigerian xenotime (100% rare earth oxide basis).

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CRYSTAL-OPTIC STUDY OF SECONDARY OVERGROWTH IN QUARTZ

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Sandstones in which silica forms the cementing material commonly exhibit secondary overgrowth, in optical continuity, on detrital quartz grains (Pettijohn 1957). A line of inclusions and/or a precementation limonitic coating usually marks the detrital boundary. Juxtaposition of secondary rims separately overgrown on several adjacent nuclei produces a sort of interlocking fabric. A conspicuous tendency shown by sandstones having a considerable proportion of silica cement is the formation of idiomorphic facets on the reconstituted grains (Fig. 1).

When a quartz grain is placed in a chemically identical solution, it begins to enlarge, itself forming a sort of seed crystal. A secondary rim may be formed continuously as a single shell or may be formed in a series of successive shells. Figure 2 shows a detrital grain (d) in the center and a portion of the outer rim with well marked idiomorphic facets at the boundary and a few faint lines (marked by dusty inclusions) parallel to the latter. This feature may be indicative of growth in a series of succes-



FIG. 1. (left) Photomicrograph showing idiomorphic facets in secondarily enlarged detrital quartz grains; crossed nicols, ×100.

FIG. 2. (right) Photomicrograph showing a detrical grain (d) and a portion of the outer rim with well marked idiomorphic facets at the boundary and a few faint lines parallel to the latter; crossed nicols, $\times 200$.