X-RAY FLUORESCENCE AS APPLIED
TO CYRTOLITE

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ABSTRACT

Quantitative analyses of five samples of cyrtolite were made using x-ray fluorescence, and hafnium-zirconium ratios based on these analyses are given. Microscopic, autoradiographic, and x-ray diffraction procedures were coupled with the results of the x-ray fluorescence analyses, and from the collective findings of these four techniques it was concluded that not all cyrtolites can be used for age determinations.

INTRODUCTION

X-ray fluorescence provides a rapid, comparatively simple technique for the analysis of a number of elements hard to determine by conventional wet chemical methods. It is nondestructive and may be relied upon for quantitative or semiquantitative determinations. Through the selection of suitable internal standards considerable refinement is possible.

In view of the current interest in and the forthcoming importance of rare earths, it would seem worthwhile to investigate the possibility of applying the method of x-ray fluorescence to the analysis of complex rare earth minerals, particularly since precise wet analytical techniques are so difficult.

A preliminary investigation of the rare earth mineral cyrtolite has been made to see if x-ray fluorescence is capable of providing a satisfactory procedure, from the point of view of the mineralogist, for the quantitative analysis of complex rare earth mixtures.

X-ray fluorescence curves for cyrtolite samples from five localities have been obtained, and the per cents of elements present have been calculated using three different internal standards. Hafnium-zirconium ratios based on these percentages are given for Spruce Pine, N. C. (C-1), Branchville, Conn. (C-2), Hybla, Ontario (C-3), Buffalo, Colo. (C-4), and Bedford, N. Y. (C-5). These localities are believed to furnish representative examples of cyrtolite.

EQUIPMENT

A basic North American Philips x-ray unit with a Philips electronic control and x-ray spectrographic attachment were used. A stabilized line current from the electronic control is fed into the basic x-ray unit producing 35KV at 27MA for operation of a Machlett tungsten x-ray tube. Uncollimated x-rays from the tube bombard the sample which is held stationary at a slight angle below the tube. The fluorescent x-rays produced are collimated to and diffracted by the cleavage planes of a

rotating lithium fluoride crystal ($d = 2.014$). Thus each wavelength is diffracted at a specific angle in accordance with Bragg's law, detected by a Geiger-Muller counter, passed into a scaling circuit, and then to a Brown recorder.

NATURE OF CYRTOLITE

Cyrtolite, first noted at Bedford, N. Y., by Luquer (1904), is a zircon which contains uranium, thorium, and rare earths as well as the usual zircon constituents, zirconium, hafnium, silicon, and oxygen. It may range from crystalline to amorphous, and optically, the degree of amorphousness is manifested by degree of isotropization. A single specimen exhibits a range of crystalline structure as shown by isotropic areas which grade into less isotropic areas, and finally into areas showing birefringence.

Since cyrtolites range from crystalline to amorphous, it is assumed that they originally possessed a definite crystalline structure which subsequently has been completely or partially destroyed. Cyrtolite, therefore, falls into the category of metamict substances.

The isotropization or metamictization of cyrtolite has been attributed to various causes. Broegger (1893) suggested that the cause of molecular rearrangement might be due to the complex nature of the cyrtolite molecule which was stable at P-T conditions under which it was formed, but which becomes unstable at later P-T conditions. Part of this instability might be due to the overcrowded nature of the molecule at lower P-T conditions, and part to the eight-fold coordination of Zr in cyrtolite (Machatschki, 1941), since Zr has an ionic radius which is near the limit of ranges associated with eight- or six-fold coordination. All metamict minerals contain either U or Th or both, therefore Hamberg (1914) suggested that the cause of metamictization was α-bombardment from within the mineral itself. The metamictization of cyrtolite is generally attributed to this latter reason, particularly since cyrtolite has a weakly ionic structure which would be readily susceptible to changes in state of ionization. To me it would seem that alteration must play some role as most metamict minerals contain rare earths as well as U and Th.

DESCRIPTION OF CYRTOLITE SAMPLES ANALYZED

The cyrtolite samples analyzed range in specific gravity from 3.09 to 3.57. Hand specimens of all the samples are dark reddish brown with the exception of the one from Branchville which is blackish brown. With the exception of the Branchville sample which is entirely massive, the specimens all show typical zircon-like prisms. Towards the interior of the specimen the prisms grade into massive cyrtolite.

Sample Preparation

The samples used in this study were ground to 200–300 mesh. The ground portions were thoroughly mixed in the mortar, poured through a small funnel onto a piece of paper, and quartered to insure an even distribution of the various grains.

A cylindrical plastic sample holder 1.5 mm. deep with an inside diameter of 1.2 cm. and an outside diameter of 1.8 cm., containing 0.35 to 0.45 g. of sample was used in each run. The powder is placed in the sample holder and is compacted slightly by moving a glass slide over the top of the plastic holder. This method produces approximately the same amount of compaction in each sample.

Preliminary Analysis

Calibration Curve

Before any samples were analyzed a calibration curve was obtained by running the empty aluminum-lucite sample holder, thus determining the effect of the tube on any given run. For this and all succeeding runs the scaler was set at 8, the multiplier at 1.0, and the time constant at 8. All runs were done at the rate of $\frac{1}{2}°$ per minute.

Peak Heights

Inasmuch as this study was intended to investigate the speed with which a rare earth mineral could be analyzed as well as the degrees of accuracy and reproducibility possible, peak height measurement rather than quanta counting was used. Peak heights were corrected for background in the following manner. The unit was allowed to warm up for fifteen minutes before beginning an actual run. The background used for correction purposes was that which was recorded at 14°, the position at which each run was started. This background is subtracted from the recorded peak heights thus giving corrected peak heights (PH^c).

After making several blank runs over a period of one to two weeks, it was found that the peak heights of the elements in the calibration curve were fairly constant (± 2 units*). When actual runs are made, however, the peak heights of elements caused by the x-ray tube may vary as much as ± 10 units due to absorption effects of the elements in the sample to be determined.

Qualitative Determinations

Five samples of cyrtolite from various localities were scanned to determine qualitatively the elements present. All of the samples contained

* One unit equals 0.1 inch on the charts used.

Zr, Hf, Fe, Y, U, and Th, and three of the samples contained various rare earths. The peak heights of iron (PH^{cc}) were corrected for tube contribution as well as for background. This was done by subtracting the peak heights of iron on the calibration curve from the peak height of iron corrected for background.

QUANTITATIVE DETERMINATIONS

Choice of Internal Standard

The elements found in the five samples of cyrtolite analyzed range from U (92) to Fe (26). To make a complete quantitative analysis it is necessary to use more than one internal standard, since the prime requirement

TABLE 1

	Atomic No.	Element	Standard
Group I	92	U	
	90	Th	
	83		Bi
	73		Ta
	72	Hf	
	71	Lu	
Group II	70	Yb	
	68	Er	
	67	Ho	
	66	Dy	
	41		Cb
Group III	40	Zr	
	39	Y	
	26	Fe	

for an element chosen as a standard is that its mass absorption coefficient be as close as possible to the mass absorption coefficient of the element to be determined and preferably should be higher. Elements of lower atomic number than the unknown will absorb fluorescent radiation strongly in the region of wavelengths immediately shorter than their K-absorption edge.

The elements found in the five samples of cyrtolite have been divided into three groups, and an internal standard has been selected for each group (Table 1).

Bi (83) was chosen as standard for Group I, since its atomic number is the closest practicable to 92 and 90. Ta (73) was used as internal standard for Group II, and Cb (41) as standard for Group III.

The strong peaks ($K\alpha_1$ or $L\alpha_1$) of the three elements used as internal standards are not obscured by the peaks of the other elements in the sample.

Procedure

Since the matrix of the samples examined is fairly homogeneous, no synthetic mixtures were prepared in order to obtain intensity-percentage calibration curves. The procedure used is as follows. Five per cent by weight of each of the elements chosen as a standard was added to the powdered cyrtolite, the total weight of the mixture remaining constant at 0.45 g. The standard elements were in the form of a 200–300 mesh metallic powder (SP), thus corresponding to the mesh of the powdered cyrtolite.

The mixtures were then subjected to primary tungsten radiation, and the fluorescent radiation was picked up and recorded as described in an earlier section. The elements were identified by the Bragg angles of their wavelengths, and corrected peak heights (PH^c and PH^{cc}) were measured. Table 2 is given as an illustration.

TABLE 2. STANDARDIZED CYRTOLITE, BEDFORD, N. Y. C-5

2θ	Series	Element	Atomic No.	PH^c		PH^{cc}	
				Run 1	Run 2	Run 1	Run 2
20.07	$K\beta_1$	Zr	40	51.0	58.2		
20.57	$L\beta_1$	U	92	11.2	13.0		
S* 21.40	$K\alpha_1$	Cb	41	32.1	41.8		
22.57	$K\alpha_1$	Zr	40	200.0	255.0		
23.81	$K\alpha_1$	Y	39	28.2	32.0		
26.15	$L\alpha_1$	U	92	16.6	18.2		
27.48	$L\alpha_1$	Th	90	33.0	38.0		
S 32.97	$L\alpha_1$	Bi	83	12.0	13.0		
34.05	$L\gamma_1$	Hf	72	9.0	10.0		
38.45	$L\beta_2$	Hf	72	27.8	27.4		
39.25	$L\beta_3$	Hf	72	9.0	9.0		
39.90	$L\beta_1$	Hf	72	19.0	21.0		
S 44.40	$L\alpha_1$	Ta	73	28.7	30.0		
45.90	$L\alpha_1$	Hf	72	69.5	78.0		
47.40	$L\alpha_1$	Lu	71	6.0	6.4		
51.75	$K\beta_1$	Fe	26	27.4	32.0	22.4	26.0
52.60	$L\alpha_1$	Er	68	6.5	7.0		
54.60	$L\alpha_1$	Ho	67	1.1	1.4		
56.70	$L\alpha_1$	Dy	66	11.1	11.0		
57.49	$K\alpha_1$	Fe	26	127.0	151.5	106.5	133.0

* S represents lines of the internal standards.

The corrected peak height or intensity in the case of each of the standard elements was caused by 5% of the element. Percentages of the unknown elements were calculated as follows:

$$\frac{PH_s^c}{\%S} = \frac{PH_u^c}{\%U}$$

$$\%U = \frac{(PH_u^c)(\%S)}{PH_s^c}$$

where

PH_u^c = corrected peak height of unknown element (PH^{cc} is used in the case of iron)
PH_s^c = corrected peak height of standard
$\%S$ = per cent standard element
$\%U$ = per cent of unknown element.

Two runs were made on each sample. The percentages found for each run along with the deviations between runs are given in Table 3.

Discussion of Percentages

The most accurate percentages given are those obtained when the atomic number of the standard element is one higher than that of the unknown element. Hf and Zr most nearly approximate this condition.

In Group II the accuracy of the percentages decreases from Hf to Dy (Table 4).

The percentages obtained for U and Th (Group I) are least accurate of all. This is because the atomic number of the element used as internal standard is not only some distance from 92 and 90, but also is below. The error in this case is due to two factors.

(1) Bi absorbs much less of the total fluorescence radiation than do U and Th, since its mass absorption coefficient is lower.

(2) Since the atomic number of Bi is lower than U and Th, Bi will absorb much of the fluorescence radiation produced by U and Th thus reducing their peak heights or intensity, and increasing its own peak height due to the additional secondary radiation produced by the additional absorption.

All of the total percentages calculated are less than 100%. This is because elements such as Si, O, P, H, which are present in cyrtolite have such long wavelengths that they are totally absorbed by the air surrounding the sample, and hence were not detected.

Although minute flakes of galena were observed microscopically, no lead was detected by fluorescence analysis. The average amount of lead present in the Bedford cyrtolite is 0.37% (Muench, 1931). Due to strong absorption by U, Th, and Bi, the emission lines of such a small quantity of lead are not likely to be detected.

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TABLE 3. PER CENT OF ELEMENTS IN CYRTOLITE

	C-1 Spruce Pine			C-2 Branchville			C-3 Hybla			C-4 Buffalo			C-5 Bedford		
	Run 1	Run 2	D*	Run 1	Run 2	D	Run 1	Run 2	D	Run 1	Run 2	D	Run 1	Run 2	D
Zr	23.41	22.61	±0.80	32.70	33.02	±0.32	27.94	27.06	±0.88	29.01	29.72	±0.71	31.15	30.26	±0.27
Hf	12.50	12.77	±0.27	13.88	13.52	±0.36	13.05	12.12	±0.93	11.99	11.44	±0.55	12.22	13.00	±0.78
Fe	12.94	13.21	±0.27	3.74	3.98	±0.24	17.95	18.62	±0.67	18.58	19.45	±0.87	16.58	15.90	±0.68
U	4.56	4.61	±0.05	15.40	15.64	±0.24	5.26	6.15	±0.89	3.08	3.31	±0.23	6.19	7.05	±0.86
Th	8.14	9.00	±0.86	3.99	3.99	±0.00	7.63	8.69	±0.86	6.80	7.08	±0.28	13.74	14.60	±0.86
Y	4.55	4.42	±0.13	1.82	2.01	±0.19	4.08	3.97	±0.11	3.88	3.91	±0.03	4.39	3.83	±0.56
Yb	3.93	3.34	±0.59	—	—	—	—	—	—	—	—	—	—	—	—
Er	0.12	0.14	±0.02	—	—	—	1.37	1.25	±0.12	2.51	2.37	±0.14	1.10	1.21	±0.11
Dy	—	—	—	—	—	—	—	—	—	2.24	1.85	±0.39	1.88	1.89	±0.01
Lu	—	—	—	—	—	—	—	—	—	2.00	1.78	±0.22	1.02	1.10	±0.08
Ho	—	—	—	—	—	—	—	—	—	0.59	0.47	±0.12	0.19	0.24	±0.05
							Total Per Cent Calculated								
	70.15	70.10	±0.05	71.53	72.16	±0.63	77.28	77.86	±0.58	80.68	81.38	±0.70	88.46	89.08	±0.62

* Deviation.

In his analysis of Bedford cyrtolite by wet chemical techniques Muench (1931) found that the average amount of uranium present was 7.29%. The average amount detected by fluorescence analysis is 6.62%. Using wet chemical methods Muench found only traces of thorium, whereas the average amount of Th detected by x-ray fluorescence analysis is 14.17%. This large deviation may be attributed either to sample difference or the complexity of the analytical chemistry of thorium.

TABLE 4

	Atomic No.	Element	Standard	
	73		Ta	
	72	Hf		
	71	Lu		
Group II	70	Yb		decreasing
	68	Er		accuracy
	67	Ho		
	66	Dy		

In Group III the accuracy of the percentages decreases from Zr to Fe (Table 5).

TABLE 5

	Atomic No.	Element	Standard	
	41		Cb	
	40	Zr		decreasing
Group III	39	Y		accuracy
	26	Fe		

The amounts of uranium from the highest percentage to the lowest is C-2, C-5, C-3, C-1, C-4. The amount of thorium from the highest percentage to the lowest is C-5, C-1, C-3, C-4, C-2. The amount of uranium and thorium in the same order is C-5, C-2, C-3, C-1, C-4. None of these orders would be expected to be the same as order of increasing overall crystallinity (C-1, C-2, C-3, C-5, C-4) since any attempted correlation would have to involve the age of the mineral as well. It is interesting to note, however, that the total amount of U and Th arranged in decreasing order bears resemblance to the amount of alteration arranged in decreasing order (C-5, C-2, C-1, C-3, C-4). This suggests that at least some of the U and Th in cyrtolite is secondary.

TABLE 6

Average	Ratios Hf/Zr
C-1	0.548
C-2	0.416
C-3	0.457
C-4	0.399
C-5	0.411

HAFNIUM-ZIRCONIUM RATIOS

Hafnium-zirconium ratios have been calculated on the basis of the percentages listed in Table 3. Average ratios are given in Table 6. All of these ratios agree with published hafnium-zirconium ratios for cyrtolite (Fleischer, 1955).

DISCUSSION OF CYRTOLITE

The samples were examined microscopically in thin section, and in all the slides two features were striking. (1.) Some parts of the mineral are more isotropized than other parts. In four of the slides (C-5, C-1, C-3, C-2) the isotropic areas grade outward into birefringent areas in a zonal fashion. In slide C-4 some of the isotropic areas bear definite resemblance to exsolution lamellae, and other areas are blotchy and irregular. (2.) All of the specimens have undergone alteration to a greater or lesser degree as shown by veinlets containing quartz, sericite, hematite, and uraninite (Kerr, 1935). Arranged in order of decreasing amount of alteration they are C-5, C-2, C-1, C-3, C-4.

X-ray powder photographs were taken to attempt to determine the overall crystallinity of the samples. The term "overall crystallinity" is used because different areas of the same specimen exhibit different degrees of crystallinity. Arranged in order of decreasing overall crystallinity they are C-1, C-2, C-3, C-5, C-4.

Autoradiograms were made from polished sections. These are shown in Figs. 1–5.* Three observations appear justified concerning the autoradiograms.

1. The radioactivity is not evenly distributed throughout the entire mineral as it would be if all the U and Th had been placed there in the original crystallization of the mineral.

2. There are centers of radioactivity which are much more intense than the other radioactive areas. In C-1 and particularly C-2 they occur as
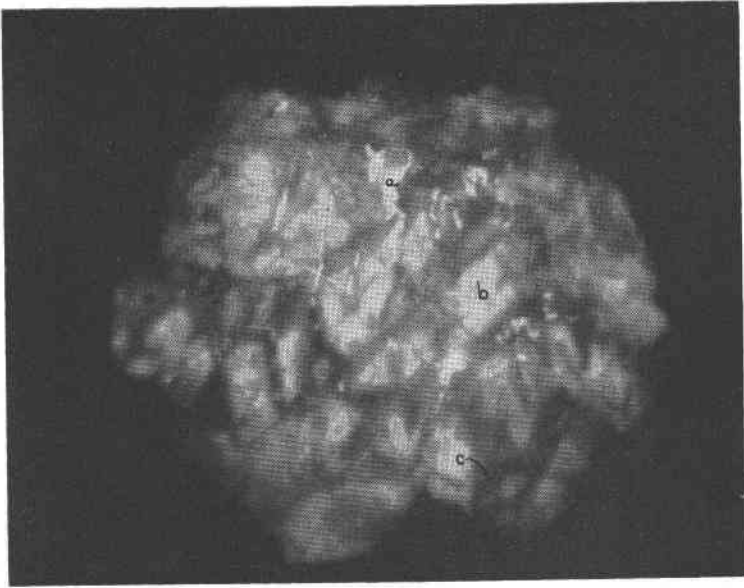
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* Enlargement is about ten times.

FIG. 1. Streaks due to uraninite (*a*) stand out in higher intensity superimposed on a ground-mass of irregularly radioactive cyrtolite (*b*). Also areas of non-radioactivity (*c*).
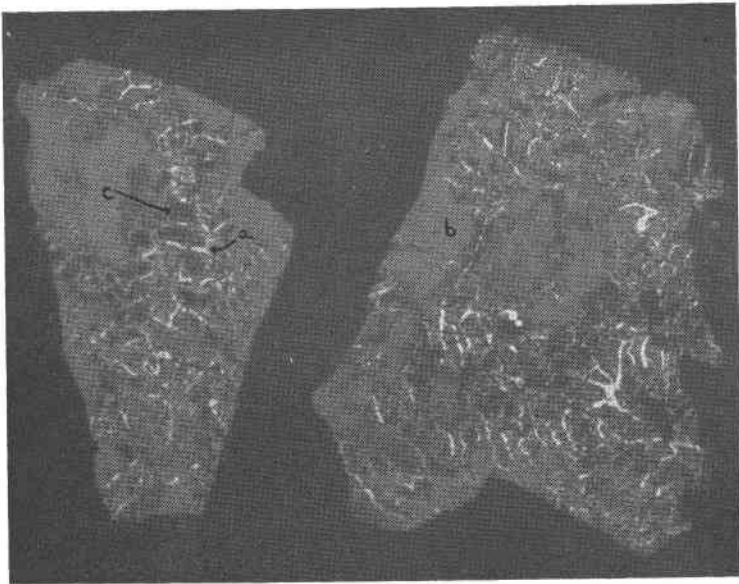

FIG. 2. Veinlets of uraninite (*a*) stand out in higher intensity dissecting a groundmass of fairly regularly radioactive cyrtolite (*b*). Areas of non-radioactivity (*c*).
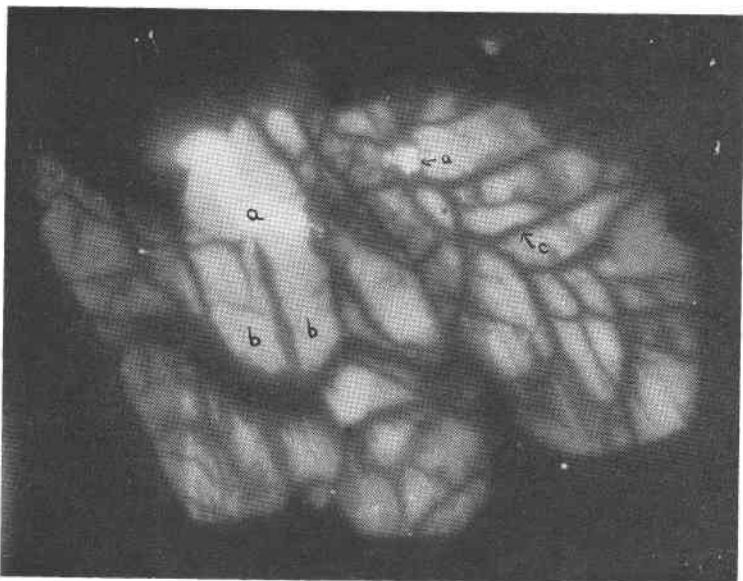
Fig. 3. Many non-radioactive veinlets (c) dissecting a groundmass of fairly homogeneous cyrtolite (b). Two centers of radioactivity (a) are much more intense than the overall radioactive cyrtolite background.
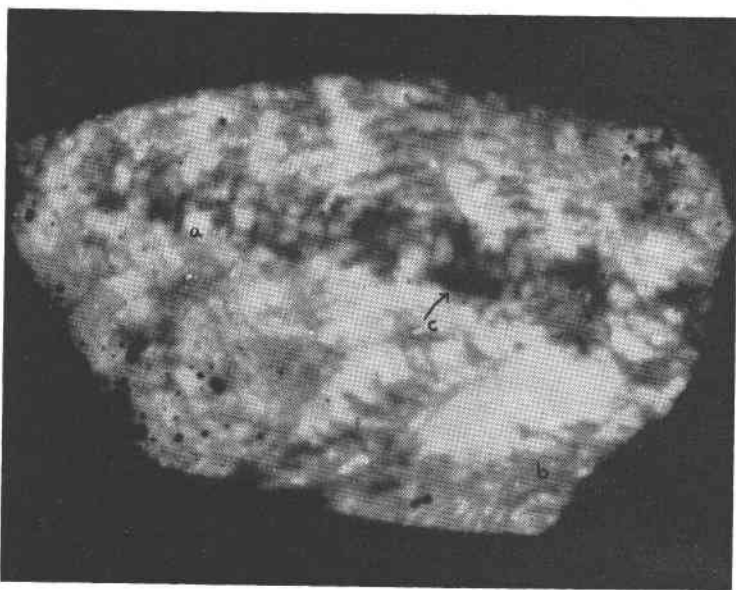

Fig. 4. This shows the non-homogeneous nature of the radioactivity, some areas being completely nonradioactive (c), some being moderately radioactive (b), and some being strongly radioactive (a).
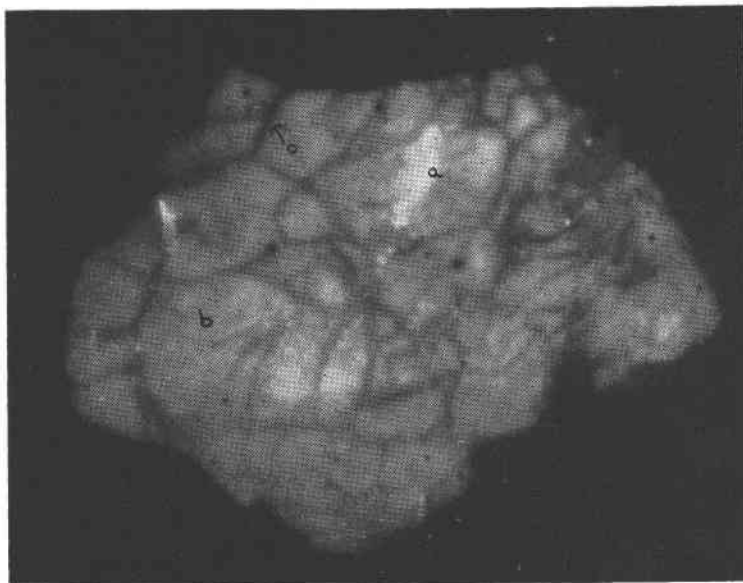
FIG. 5. Non-radioactive veinlets (*c*) dissecting a fairly regularly radioactive ground-mass of cyrtolite (*b*). Also several centers of radioactivity (*a*) are much more intense than the general cyrtolite background.

vein fillings. This too suggests that some of the uranium and thorium might have been metasomatically emplaced at a time later than the original crystallization.

3. There are regions of non-radioactivity concentrated for the most part in distinct veins which cut the groundmass.

CONCLUSIONS AND SUGGESTIONS

In view of the evidence cited above, it seems justifiable to suggest that cyrtolites may fall into one of the following three categories.

1. Cyrtolite in which all of the α-emitters (U, Th, and possibly Sm^{152}) have been placed in the structure during the original crystallization of the mineral. In this case, if the intrinsic stability of all cyrtolites can be regarded as a constant, which it probably is not, the amount of destruction of the crystal lattice is a function of the total amount of α-emitters present and the age of the mineral. The amount of lattice destruction can be measured by thermal analysis, and if the total amount of α-emitters present can be determined, the age of the mineral can be calculated (Holland and Kulp, 1950).

2. Cyrtolite in which all of the α-emitters have been introduced secondarily. In this case, metamictization might occur, but the degree of metamictization would not represent the true age of the mineral.

3. Cyrtolite in which part of the α-emitters have been placed in the structure during the original crystallization, and part by secondary introduction. In this case also, the degree of metamictization is not a function of the true age of the mineral.

This means that not all cyrtolites can be used for age determination. A possible way of selecting cyrtolites for age determination would be to take autoradiograms of thin slices of cyrtolite to see if the radiation effects are homogeneous. If there are any homogeneous areas at all, it might be possible to hand pick these areas and do age determinations on them disregarding the non-homogeneous areas.

The method of x-ray fluorescence seems perfectly applicable to a mineralogical study of cyrtolite and could be used in the study of other rare earth minerals. The degree of accuracy obtainable is, to a large extent, dependent upon the availability of the most suitable internal standard. Greater accuracy can be attained by using quanta counting instead of peak height measurement, but this process is very time consuming. Elements with low atomic numbers can be accurately determined if a helium chamber and pulse height discrimination are used.

Acknowledgments

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