A STUDY OF SOME RADIOACTIVE MINERALS BY X-RAY DIFFRACTION; WITH SPECIAL REFERENCE TO THE OXIDES CONTAINING COLUMBIUM, TANTALUM, AND TITANIUM

by

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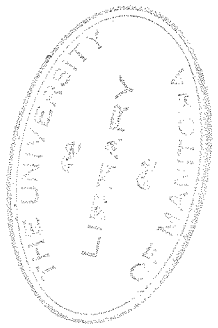

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CHAPTER I

INTRODUCTION

While working in Ottawa at the radioactivity laboratory of the Mineralogy Section of the Geological Survey of Canada during the summer of 1948, the author became interested in radioactive minerals, on which much X-ray diffraction work remains to be done. Dr. H. V. Ellsworth (Mineralogist, Geological Survey of Canada) kindly donated a representative collection of these minerals, mostly from Canadian localities, many of which he has analysed chemically (Ellsworth, 1932). Other specimens of radioactive minerals were obtained from the Mineralogical Museum of the Department of Geology, University of Manitoba.

The most important radioactive constituents of the radioactive minerals are uranium and thorium. Despite their high atomic weights, these two elements are usually present in relatively small percentages, and commonly range from 0 to 15% by weight; notable exceptions are uraninite and thorianite which contain roughly 80% of these elements. Often associated with the uranium and thorium are variable amounts of the rare-earth elements (cerium, lanthanum, "diodymium", erbium, etc.) and the closely-related element yttrium. The radioactive minerals which contain these rare-earth elements often exhibit a unique property: the presence of crystal faces with the absence of regular atomic

arrangement. Such minerals are termed "metamict".

Certain oxides constitute the largest group of radioactive minerals; some silicates and a considerable number of phosphates, arsenates, vanadates, and sulphates make up most of the remainder. The present study deals mainly with some of the oxides, although X-ray powder pictures of a number of the other minerals were taken.

In the recently published Seventh Edition of Dana's System of Mineralogy (Palache, Berman, & Frondel, 1944), the natural oxides have been divided into five groups, the following two of which include most of the radioactive oxide minerals:

1. Oxides containing uranium, thorium, and zirconium.
2. Multiple oxides containing columbium, tantalum, and titanium.

The first of these groups includes uraninite UO_2, thorianite ThO_2, baddeleyite ZrO_2, and the hydrated decomposition products of uraninite. Work on this group was confined to the uraninite-thorianite series which includes such varieties as pitchblende and bröggerite.

The second group consists of multiple oxides of the type $A_mB_nO_{(m+n)}$; where m:n varies from 1:1 to 1:2, and A = rare-earths, U, Th, Fe^2, Na, Mn, and Zr; B = Cb, Ta, Ti, Sn, W?, Zr?, Fe^3?. The crystal systems in which members of this group crystallize vary from isometric (microlite-pyrochlore series) to possibly monoclinic (arizonite). This

group affords many examples of metamict minerals.

> "The crystallography of these multiple oxides is only imperfectly known because they are nearly all noncrystalline pseudomorphs of the original minerals, that is, they are metamict . . . . When they are heated they revert, presumably, to the original structure (emitting a glow, due to recrystallization), but the crystalline units are tiny and not oriented with respect to the original external faces. The change in structure after ignition can readily be detected under the microscope or by X-ray diffraction pictures." (Palache, Berman, & Frondel, 1944, p. 745).

Because of the cryptocrystalline character of these metamict minerals after heating, single-crystal X-ray pictures of them have not been obtained, and for many of the metamict minerals of this group only the morphological axial elements, and not the unit cell dimensions, are known.

The present research was concerned principally with obtaining the unit cell dimensions and space-group of minerals which are metamict. To this end, after some preliminary work had been done on the uraninite-thorianite series, a study of the metamict oxides was undertaken commencing with the microlite-pyrochlore series. This group was chosen for the initial work for two reasons: firstly, the minerals of this series crystallize in the cubic system; and secondly, microlite often occurs only partially metamict. The remainder of the work was devoted to a study of the euxenite-polycrase series.

CHAPTER II

EXPERIMENTAL METHODS

In the course of studying these minerals a variety of techniques was used. These included various X-ray diffraction methods, specific gravity determinations, heating experiments, and graphical analyses of the X-ray evidence. Each of these is discussed briefly below.

X-ray Powder Methods. A complete description of X-ray powder diffraction methods may be obtained from a variety of standard texts such as Bragg & Bragg (1925) and Bunn (1945). It is sufficient to say here that an X-ray powder picture of a substance is obtained when a beam of monochromatic X-rays is passed through a suitably prepared specimen of the powdered material, and the diffracted rays are recorded on a strip of film held in a cylindrical shape concentric with the specimen. The diffracted rays which are conical in shape appear on the film as a series of arcs of varying intensity as shown by figures 1 to 11. The position of each line is proportional to the spacing of the set (or sets) of planes contributing to it, and the intensity of each line is determined principally by the kind and arrangement of the constituent atoms of the crystal. Hence, in the great majority of cases, every crystalline compound will give its own characteristic powder pattern. For this reason, X-ray powder diffraction is a very useful method of

mineral identification.

In recording the powder pattern, both the intensity and the spacing of each line are used. In conformity with present-day practise, all intensities given in this report have been visually estimated using a scale in which the strongest line on each film is arbitrarily assigned the value 10. It is customary to record the spacings of the lattice planes contributing to the lines, rather than the line positions on the film, since the latter vary with the wavelength of the X-rays and with the diameter of the camera used. The powder cameras used during this investigation are of a diameter (57.3 mm) such that a distance of 1 mm. on the film is equal to a glancing angle θ of 1°, and the glancing angle is readily converted to the spacing d of the corresponding lattice planes by a solution of the Bragg equation, $d = \lambda/2\sin\theta$, where λ is the wavelength of the X-rays used. A set of lattice spacing tables (Forman, 1947) for copper $K\alpha_1$ radiation, based on the above equation, were used to convert the glancing angles to lattice spacings, and all results are given in kX units ($CuK\alpha_1 = 1.5374$ kX).

Since the positions of the lines on an X-ray powder picture give only the spacings of the contributing sets of planes and not their crystallographic orientation, the dimensions of the unit cell and the possible space-groups can not be readily obtained from powder pictures except where the substance in question crystallizes in one of the

higher symmetry systems. Procedures for using powder pictures to obtain this information are discussed below under Graphical Methods.

Single-Crystal X-ray Methods. The dimensions of the unit cell and the space-group are usually determined by means of single-crystal X-ray photographs. These are obtained by rotating, about a crystallographic axis, a single small crystal of the substance within a beam of monochromatic X-rays. The diffracted beams from the various planes are recorded on a cylindrical sheet of film which may or may not be moved inconjunction with the rotation of the specimen, according to the results desired. A complete description of single-crystal methods will be found in any of the standard texts on the subject such as those cited above.

Graphical Methods. In order to obtain the unit cell dimensions and, if possible, the space-group of a crystalline substance from its powder picture, graphical methods may sometimes be used for indexing powder patterns. These methods are based on the fact that the spacing of any set of lattice planes within a crystal depends upon a limited number of variables. For an isometric crystal, the simplest case, the spacing d of any set of planes, (hkl), is determined by one cell dimension a_o; in a tetragonal crystal, by two cell dimensions, a_o and c_o; and so on with increasing complexity until, in a triclinic crystal, it is determined

by a_o, b_o, c_o, α, β, and γ. Thus for the isometric system a "cubic crystal analyser" may be constructed, showing the variation of d with a_o for a series of hkl's. Then, by plotting the spacings obtained from the powder picture of an isometric substance on a strip of paper (using the same scale as used in constructing the analyser) one can, by comparing this set of spacings with those on the analyser, find a position such that each point on the strip is matched by a line on the analyser. From this are obtained the indices of the lines on the powder pattern and the length of the unit cell edge. From the systematic extinctions in the pattern thus obtained it is possible to deduce the type of lattice and often the possible space-groups.

This method becomes more complicated as the number of variables increases, and it is not usually feasible for systems other than the isometric, tetragonal, and hexagonal. A more complete description of this method may be found in Bunn (1945, pp. 132 and 379).

An extension of this method was used in studying euxenite which is orthorhombic. In this case, the axial ratio obtained from morphological measurements was assumed to be correct, and d was plotted against b_o, with a_o and c_o being determined by the axial ratio. The details of this method and its application are described later on page 30.

Heating Experiments. To obtain X-ray powder pictures of metamict minerals, it was sufficient, in most cases, to

heat the specimens for about a minute in the flame of a Tyrrel burner (temperatures up to 1000°C). In studying euxenite, however, several heating experiments were carried out in order to study the effects of the temperature and duration of heating on the X-ray powder pattern. For this purpose an electric furnace was used for heating, and a chromel-alumel thermocouple attached to a Hoskins thermo-electric pyrometer was used to measure the temperature. Considerable fluctuation of the temperature occurred since the furnace was hand-controlled and many of the heating experiments extended over considerable periods of time. The temperatures quoted are considered accurate within ± 25°C.

Specific Gravity Determinations. In conjunction with the heating experiments, specific gravities of some euxenites were determined in order to study the effect of heating on the density of the mineral. These determinations were made on small fragments using a Berman density balance.

CHAPTER III

REVIEW OF THE LITERATURE ON THE METAMICT STATE

In view of the close association of the metamict state and radioactivity in minerals, a review of the most important papers on metamict minerals is presented here.

W. C. Brögger (1893) introduced the term "metamict" to designate those amorphous minerals which originate out of originally crystalline material by "secondary molecular rearrangement". Examples of these minerals are orthite, gadolinite, samarskite, euxenite, polycrase, polymignite, pyrochlore, fergusonite, thorite, zircon, etc. He noted that these minerals possess complicated "molecules", and he believed that the inferior stability of such molecules is probably the reason for the rearrangement. He also pointed out that metamict minerals always have a higher water content than the unaltered minerals and suggested that the change might be due to this.

O. Mügge (1922) compared the characteristics of these minerals with those of natural (silicate) glasses, and put forward the theory that metamict minerals are the result of the break down of the original structure under the influence of radioactivity. He observed that most metamict minerals have a considerable degree of radioactivity, and that some pleochroic halos have a zone between the coloured halo and the radioactive nucleus in which the original material

appears to have been broken down to an amorphous condition.

Goldschmidt (1924), however, holds that radioactivity plays a very minor part, if any, in the transformation. He believes the necessary conditions for bringing about the metamict condition are:

> "A. The constituent original crystal lattice must be a weak ionic lattice in order to permit the transformation and eventual hydrolysis.
> B. The lattice must contain one or more types of ions which are particularily susceptible to valence change, such as especially the ions of the rare earths.
> C. In many cases it may be necessary in addition that relatively strong rays act on the crystal, either rays from radioactive materials which are contained in the crystal itself or radioactive rays from outside the crystal.
>
> Condition A alone is not sufficient to bring about the metamict condition (thorveitite, many thalenites), likewise condition B (monazite and xenotime), nor condition C (bröggerite, thorianite, and monazite)". (V. M. Goldschmidt, 1924, p. 59, trans.)

L. Vegard (1927) attributed the metamict condition of xenotime to its crystallization under high pressure. He found that the structure of xenotime is similar to that of zircon but the atoms of xenotime would have to suffer a certain "accomodation" and therefore it probably crystallized under great pressure. At normal pressures the structure would be unstable and the mineral would readily change to the metamict state.

A. Faessler (1942) investigated the regaining of crystalline structure by gadolinite on heating. He found that the change takes place suddenly at about 800°C with a brilliant glow but also takes place slowly at lower temperatures. He beleived that the transformation to the

metamict state is probably due to ∝ radiation from radioactive substances. He also suggested that minerals with extensive isomorphous replacement are less stable, and liable to the change-over.

As well as the above review, a search was made through Strukturbericht, Mineralogical Abstracts, and Dana's System of Mineralogy (Seventh Edition, volume 1), for previous X-ray work on the particular minerals studied. Information obtained from this survey is given later when the minerals concerned are discussed.

CHAPTER IV

URANINITE-THORIANITE SERIES

This series includes, as well as uraninite and thorianite, pitchblende (massive or colloform uraninite), bröggerite (a thorian uraninite with some rare-earth metals), and cleveite and nivenite (rare-earth bearing uraninites). Other names applied to minerals of this series are nasturan (pitchblende) and ulrichite (uraninite) (Palache, Berman, & Frondel, 1944). None of these minerals is ever metamict. A complete series between uraninite, UO_2, and thorianite, ThO_2, has never been found in nature, but such a series has been produced artificially (Wells, Fairchild, & Ross, 1933).

These minerals crystallize in the hexoctahedral (normal) class of the isometric system, and have a cell edge a_o of approximately 5.47 kX for uraninite and 5.57 kX for thorianite (Goldschmidt & Thomassen, 1923).

X-ray powder pictures of nineteen specimens of this series were taken, read, and indexed using a cubic crystal analyser (see p. 7). Table I gives, for a typical uraninite, the indexed powder data which are in reasonable agreement with those published in the ASTM card index (1945). Table II gives a list of the specimens examined, the cell edge derived from powder photographs of each one, and the measured specific gravity for most of them. Several of the specimens were largely altered, and fragments suitable for

TABLE I

URANINITE -- $(U,Th)O_2$: X-RAY POWDER PATTERN

Locality: Lot 31, Range 1, Ottawa county, P.Q.

Cubic, F-lattice; $a_o = 5.457$ kX, $Z = 4$

I	θ(Cu)	d(meas)	(hkl)	d(calc)	I	θ(Cu)	d(meas)	(hkl)	d(calc)
2	12.83	3.14	(111)	3.15	3	47.05	1.050	(333)	1.050
10	14.10	3.16	(111)	3.15				(511)	
5	16.38	2.73	(002)	2.73	1	52.95	0.963	(044)	0.965
8	23.45	1.932	(022)	1.931	4	56.35	0.923	(135)	0.922
½	25.05	1.640	(113)	1.645	2	57.65	0.910	(600)	0.910
8	27.85	1.646	(113)	1.645				(442)	
2	29.23	1.574	(222)	1.575	2	63.05	0.862	(026)	0.863
1	34.30	1.364	(004)	1.364	2	67.35	0.833	(533)	0.832
3	37.95	1.250	(133)	1.252	2	69.15	0.823	(622)	0.823
3	39.10	1.219	(024)	1.220	¼	77.85	0.786	(444)	0.788
3	43.65	1.114	(224)	1.114					

TABLE II

URANINITE-THORIANITE SERIES: DENSITY AND CELL EDGE OF SPECIMENS FROM VARIOUS LOCALITIES

Mineral	Locality	Sp. gr.	a_o
Thorianite	Artificial ThO_2	9.87*	5.61*
"	Galle, Ceylon	9.43	5.564
"	Ceylon		5.552
"	Sherrer Quarry, Eastern Penn.		5.494
Uraninite	Artificial UO_2	10.95*	5.47*
"	Branchville, Conn., U.S.A.	9.73*	5.475
"	Raade, Norway (var. Bröggerite)		5.474
"	Wilberforce, Ontario	7.05	5.458
"	Lot 31, R. 1, Ottawa co., P.Q.	6.50	5.457
"	Belgian Congo		5.447
"	Besner Mine, Henvey twp., Parry Sound Dist., Ont.		5.443
"	Yancey co., N. Carolina, U.S.A.	9.55	5.438
"	Deer Park Mine, Spruce Pines, N. Carolina, U.S.A.	6.52	5.435
"	Lanark co., Ont.		5.425
"	Lot 9, R. 2, Mattawan twp., Ont.	8.64	5.422
"	Reboleira property, Portugal		5.398
Pitchblende	Various	6.5-8.5*	5.42-5.45*
"	Great Bear Lake, N.W.T.	6.43	5.464
"	Great Bear Lake, N.W.T.	6.51	5.461
"	Great Bear Lake, N.W.T.		5.450
"	Hottah Lake, N.W.T.	6.46	5.430
"	Black Lake, Sask.		5.392

* from Palache, Berman, and Frondel, 1944.

specific gravity determinations could not be obtained from them. Where the specific gravities were measured, a range of values was obtained for each sample. In all cases, the specific gravity quoted is the largest, since the variation is due to different degrees of alteration, and the unaltered mineral has the greatest specific gravity.

Figures 1 to 4 show powder photographs of four different members of this series.

Fig. 1

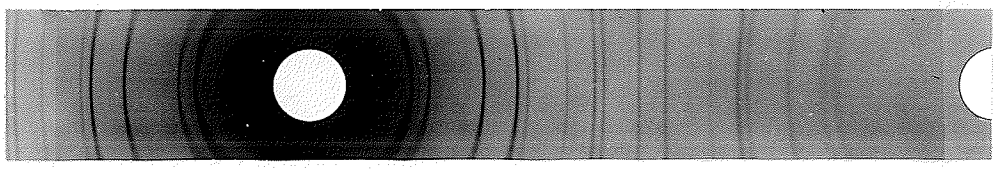


Fig. 2

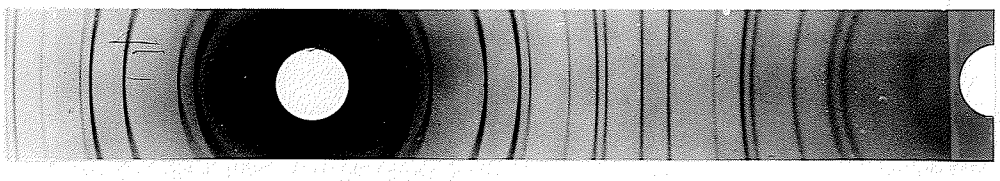


Fig. 3

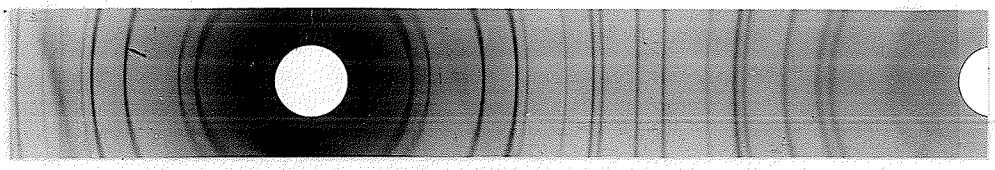
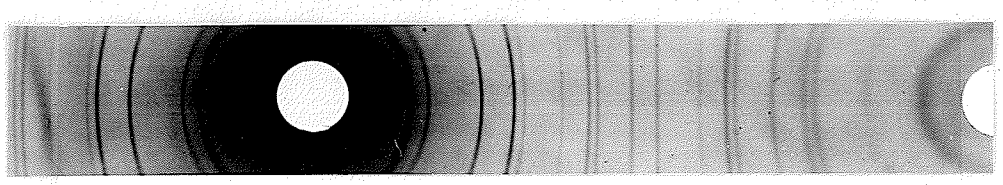


Fig. 4



Figures 1, 2, 3, 4. -- X-ray powder photographs of uraninite-thorianite series, Cu radiation, Ni filter; 1 mm. on film = $1^{o}\theta$; actual size. Figure 1. -- Pitchblende, Great Bear Lake, a_o = 5.461 kX. Figure 2. -- Uraninite, Lot 9, Range 2, Mattawan twp., Ontario, a_o = 5.422 kX. Figure 3. -- Uraninite, Branchville, Conn., U.S.A., a_o = 5.475 kX. Figure 4. -- Thorianite, Galle, Ceylon, a_o = 5.564 kX.

CHAPTER V

PYROCHLORE-MICROLITE SERIES

This series includes, as well as pyrochlore and microlite, the varieties ellsworthite, hatchettolite, and uranpyrochlor (all uranian pyrochlores), endeiolite (probably an altered pyrochlore), neotantalite (an altered microlite), marignacite (a non-metamict pyrochlore), and pyrrhite, koppite, and chalcolamprite (all evidently members of this series).

The composition of these minerals may be expressed by the formula $A_2B_2O_6(O,OH,F)$, where A = Na, Ca, K, Mg, Fe^2, Mn^2, Sb^2, Pb?, Ce, La, Di, Er, Y, Th, Zr, U; and B = Cb, Ta, Ti, Sn?, Fe^3?, W?, listed in approximate order of importance. Pyrochlore is the high-Cb end-member $(Na,Ca)_2Cb_2O_6F$, and microlite is the high-Ta end-member $(Na,Ca)_2Ta_2O_6(O,OH,F)$. There is a continuous series between the high-Cb and high-Ta members but the majority of the minerals have compositions near one end or the other. (Palache, Berman, & Frondel, 1944)

These minerals crystallize in space-group Fd3m of the hexoctahedral (normal) class of the isometric system. The cell edge a_o is about 10.35 kX for pyrochlore and 10.37 to 10.40 kX for microlite. The members of this series are almost all metamict, but this characteristic varies from slight to complete.

X-ray powder diffraction photographs were taken of

one specimen of microlite, one of pyrochlore, and two of ellsworthite. All of these were metamict and were heated and rephotographed although the microlite was only partially metamict and gave a less distinct picture without heating. The pictures obtained in this manner were read and indexed using the cubic crystal analyser. The indexed powder data for microlite (heated) from Amelia Court House, Virginia, are given in Table III. Table IV gives the cell edges of the four specimens with published specific gravities for these minerals from the same localities.

The heated microlite gave a total of fourteen extraneous lines, having an intensity of one or less, which could not be indexed or accounted for by impurities. For this reason a single-crystal treatment of microlite was undertaken to determine whether these lines belonged to the microlite pattern. Further, since a slight change in cell edge was observed after heating, this was done for both the heated and the unheated microlite. For this purpose, a small fragment of a microlite crystal which showed portions of two octahedral faces and one dodecahedral face was mounted for rotation about a [100] axis, and rotation, zero- and 1st-layer Weissenberg photographs were taken. The fragment was then heated to glowing in a bunsen flame, and the procedure repeated. The heated microlite gave much more intense spots on the film with even less exposure. Only the photographs for the heated microlite were read completely.

TABLE III

MICROLITE (HEATED) - $(Na,Ca)_2Ta_2O_6(O,OH,F)$: X-RAY POWDER PATTERN

Locality: Amelia Court House, Virginia, U.S.A.

Cubic, Fd3m; a_o = 10.403 kX, Z = 8

I	θ(Cu)	d(meas)	(hkl)	d(calc)	I	θ(Cu)	d(meas)	(hkl)	d(calc)
6	7.40	5.97	(111)	6.01	½	49.15	1.016	{(10.2.0) (862)}	1.020
¼	12.05	3.68	(022)	3.68					
½	13.55	2.97	(222)	3.00	½	49.75	1.007	{(773) (951)}	1.006
4	14.35	3.10	(113)	3.14					
10	15.00	2.97	(222)	3.00	3	50.20	1.001	(666)	1.001
3	17.38	2.57	(004)	2.60	½	52.40	0.970	(953)	0.970
1	18.85	2.38	(133)	2.39	1	55.15	0.937	{(11.1.1) (775)}	0.936
¼	21.45	2.10	(224)	2.12					
2	22.65	1.996	{(333) (511)}	2.00	2	56.75	0.919	(880)	0.919
8	24.80	1.833	(044)	1.839	2	57.75	0.909	{(11.3.1) (971) (955)}	0.909
2	26.00	1.754	(135)	1.758					
½	26.85	1.702	(244)	1.734	4	60.90	0.880	{(10.6.2) (866)}	0.879
¼	29.05	1.583	(533)	1.586					
8	29.50	1.561	(622)	1.568	3	62.45	0.867	{(12.0.0) (884)}	0.867
2	30.88	1.498	(444)	1.501					
2	31.95	1.453	{(711) (551)}	1.457	1	63.75	0.857	{(11.5.1) (777)}	0.858
2	34.70	1.350	{(731) (553)}	1.354	¼	65.25	0.846	{(12.2.2) (10.6.4)}	0.844

continued, next page

TABLE III (continued)

I	θ(Cu)	d(meas)	(hkl)	d(calc)	I	θ(Cu)	d(meas)	(hkl)	d(calc)
2	36.25	1.300	(800)	1.300	2	66.95	0.835	(11.5.3) (975)	0.835
½	37.25	1.270	(733)	1.271					
¼	38.95	1.223	(660) (822)	1.226	3	69.20	0.822	(12.4.0)	0.822
					1	69.55	0.820	(991)	0.814
¼	39.85	1.200	(555)	1.201					
3	40.15	1.192	(266)	1.193	1	75.15	0.795	(13.1.1) (11.7.1) (11.5.5) (993)	0.796
3	41.35	1.163	(840)	1.163					
1	42.45	1.139	(911) (753)	1.142	3	75.70	0.793	(10.6.6)	0.793
¼	42.95	1.128	(842)	1.135	2	78.85	0.783	(12.4.4)	0.784
½	43.85	1.110	(664)	1.109					
1	44.80	1.091	(931)	1.091	1	81.75	0.777	(13.3.1) (11.7.3) (977)	0.777
3	46.35	1.062	(844)	1.062					
1	47.35	1.045	(771) (933) (755)	1.045	½	82.45	0.775	(12.6.0) (10.8.4)	0.775

TABLE IV

PYROCHLORE-MICROLITE SERIES: DENSITY AND CELL EDGE OF SPECIMENS FROM VARIOUS LOCALITIES

Mineral	Locality	Sp.Gr.	a_o
Microlite	Various, average of 2[1]	6.33[2]	10.39[1]
Microlite (not heated)	Amelia Court House, Va.	5.656[3]	10.420
Microlite (heated)	Amelia Court House, Va.		10.403
Pyrochlore	Various, average of 4[4]	4.33[2]	10.35[4]
Pyrochlore (heated)	Brevik, Norway	4.220[3]	10.383
Ellsworthite (heated)	Hybla, Ontario	3.758[5]	10.297
Ellsworthite (heated)	Cardiff twp., Ontario	3.705[5]	10.275

[1] a_o is an average for two microlite specimens obtained from Palache, Berman, & Frondel (1944).

[2] calculated specific gravities (Palache, Berman, & Frondel, 1944).

[3] densities given in Palache, Berman, & Frondel (1944) for these minerals from the same localities.

[4] a_o is an average for four pyrochlore specimens obtained from Palache, Berman, & Frondel (1944).

[5] densities given by Ellsworth (1932) for these minerals from the same localities.

No reflections were found to explain the extra powder lines which are consequently attributed to impurities. This conclusion was substantiated by the observation that a few small black specks became visible in the microlite upon heating.

The best values of a_o for the unheated and heated microlite, obtained from the powder and single-crystal photographs, are 10.420 and 10.403 kX respectively. Although the difference between these two values is within the limit of error (approximately ± 0.2%) of the measurements, the persistently lower value for the heated specimen is readily detectable by comparing the two sets of photographs.

Figures 5, 6, and 7 reproduce the powder photographs of the heated specimens of microlite, pyrochlore, and ellsworthite.

Fig. 5

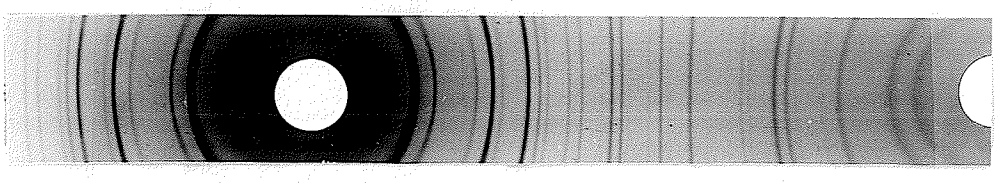


Fig. 6

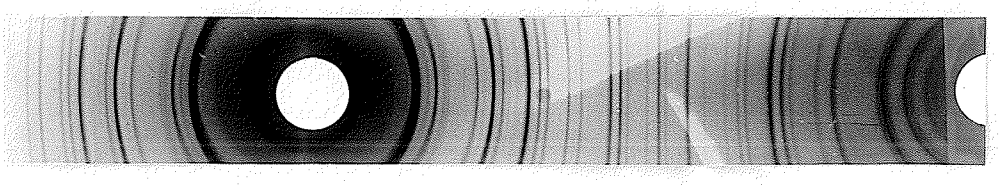
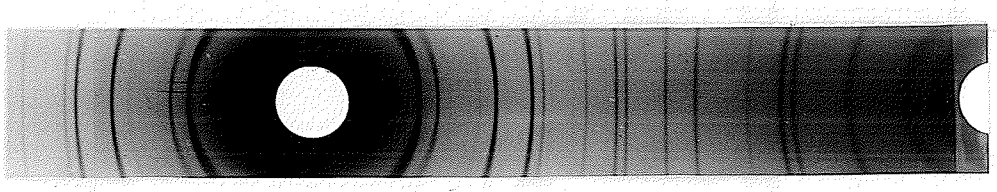


Fig. 7



Figures 5, 6, 7. -- X-ray powder photographs of pyrochlore-microlite series, Cu radiation, Ni filter; 1 mm. on film = $1^{o}\theta$; actual size. Figure 5. -- Pyrochlore, Brevik, Norway, a_o = 10.383 kX. Figure 6. -- Microlite, Amelia Court House, Va., a_o = 10.403 kX. Figure 7. -- Ellsworthite, Hybla, Ont., a_o = 10.297 kX.

CHAPTER VI

EUXENITE-POLYCRASE SERIES

As well as euxenite and polycrase, this series includes lyndochite which is a member having less than one per cent uranium (Ellsworth, 1932, p. 49), and tanteuxenite which is a high-tantalum member. The composition of these minerals may be expressed as AB_2O_6 where A = Y, Ce, Ca, U, Th; and B = Ti, Cb, Ta, and Fe^3. The high-Ti end member is polycrase and the high Cb-Ta member is euxenite.

According to morphological evidence, these minerals crystallize in the dipyramidal (normal) class of the orthorhombic system and have an axial ratio of a:b:c = 0.3789:1:0.3527 (Palache, Berman, & Frondel, 1944). They are all metamict and, to date, their unit cell dimensions and space-group have not been determined. For this reason, these minerals were selected for a more thorough X-ray investigation.

Since these minerals are metamict, they all had to be heated before they would give X-ray diffraction photographs. Although, by this means, it was easy to get powder patterns of these minerals, their orthorhombic symmetry made it difficult to deduce the cell dimensions and space-group using these alone. In an effort to determine these constants for members of this series, the following procedures appeared to offer the greatest hope of success:

1. By prolonged heating of the minerals at high temperatures to increase the size of the tiny cryptocrystalline units until they were large enough for single-crystal work. By this method, the desired information could be obtained directly.

2. To index the euxenite powder pattern by means of an analyser similar in principle to a cubic crystal analyser but using the morphological axial ratio to lower the number of variables.

3. To index the powder pattern by analogy with a similar mineral whose lattice constants are known, for instance, columbite.

The first of these methods was tried without success. The second method gave very good results, and the third method was therefore not attempted.

Experiments on Increasing the Size of the Crystalline Units.

As stated previously (page 3), the metamict minerals after heating are cryptocrystalline and thus unsuitable for single-crystal X-ray studies. It was hoped that, by prolonged heating at high temperatures, the size of the crystalline units could be increased until they became sufficiently large for this purpose. Such a process would be analogous to the annealing of metals, and it is believed that a similar action takes place in nature during thermal metamorphism.

these specimens were heated in a Tyrrel burner which gives a range of temperatures up to 1000°C. Figures 8 and 9 reproduce the identical powder patterns of two euxenites from different localities which are believed to be the "true" euxenite pattern (samples heated to 1000°C for 100 hours). Figure 10 reproduces, for comparison, one of the variable euxenite patterns which illustrates the chief difference from the true pattern -- a doubling of the strongest line.

The Euxenite Analyser. An analyser for euxenite was constructed in a manner similar to that used for a cubic crystal analyser. As mentioned previously (p. 7), the drawback to using this method on orthorhombic compounds lies in the number of variables which determine the spacings of the lattice planes. In the isometric system, the spacing d of the planes varies directly with the cell edge a_o, whereas, in the orthorhombic system, the spacing d varies with a_o, b_o, and c_o. Thus, there are too many variables to plot all of them on a two-dimensional graph. To avoid this difficulty the following method was used: assuming as correct the morphological axial ratio, a:b:c = 0.3789:1:0.3527, d was plotted against b_o for values of b_o from 7kX to 15 kX with a_o and c_o being fixed by the axial ratio. The analyser constructed by this method is shown in Figure 12.

Several attempts were made to index the lines on the first four euxenite patterns listed in Table V, but these

Fig. 8

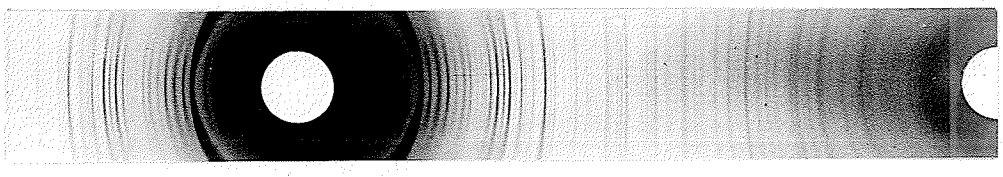


Fig. 9

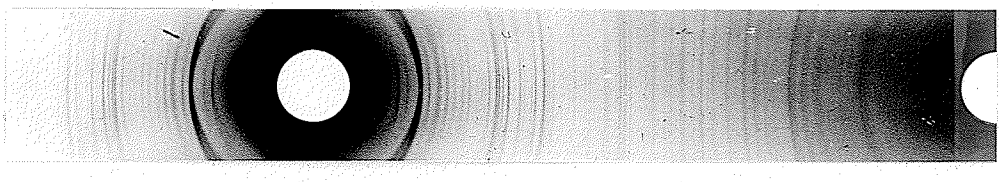


Fig. 10

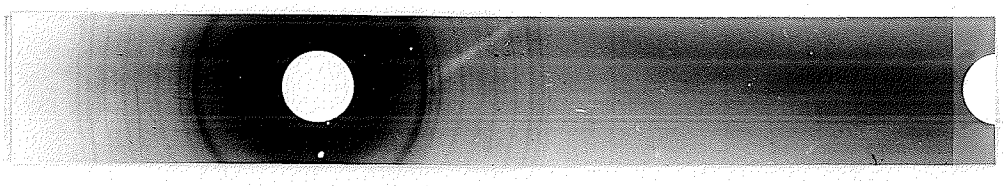
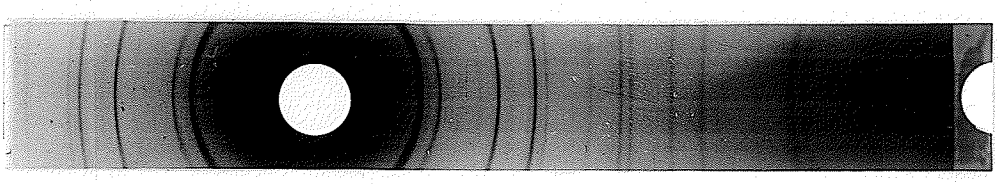


Fig. 11



Figures 8, 9, 10, 11. -- X-ray powder photographs of euxenite-polycrase series, Cu radiation, Ni filter; 1 mm. on film = $1^{\circ}\theta$; actual size. Figure 8. -- Euxenite, Mattawan twp., heated at 1000°C for 100 hours. Figure 9. -- Euxenite, Sabine twp., heated at 1000°C for 100 hours. Figure 10. -- Euxenite, Sabine twp., heated at 400°C for 5 minutes. Figure 11. -- Tanteuxenite, Bleys, West Australia, heated with Tyrrel burner.

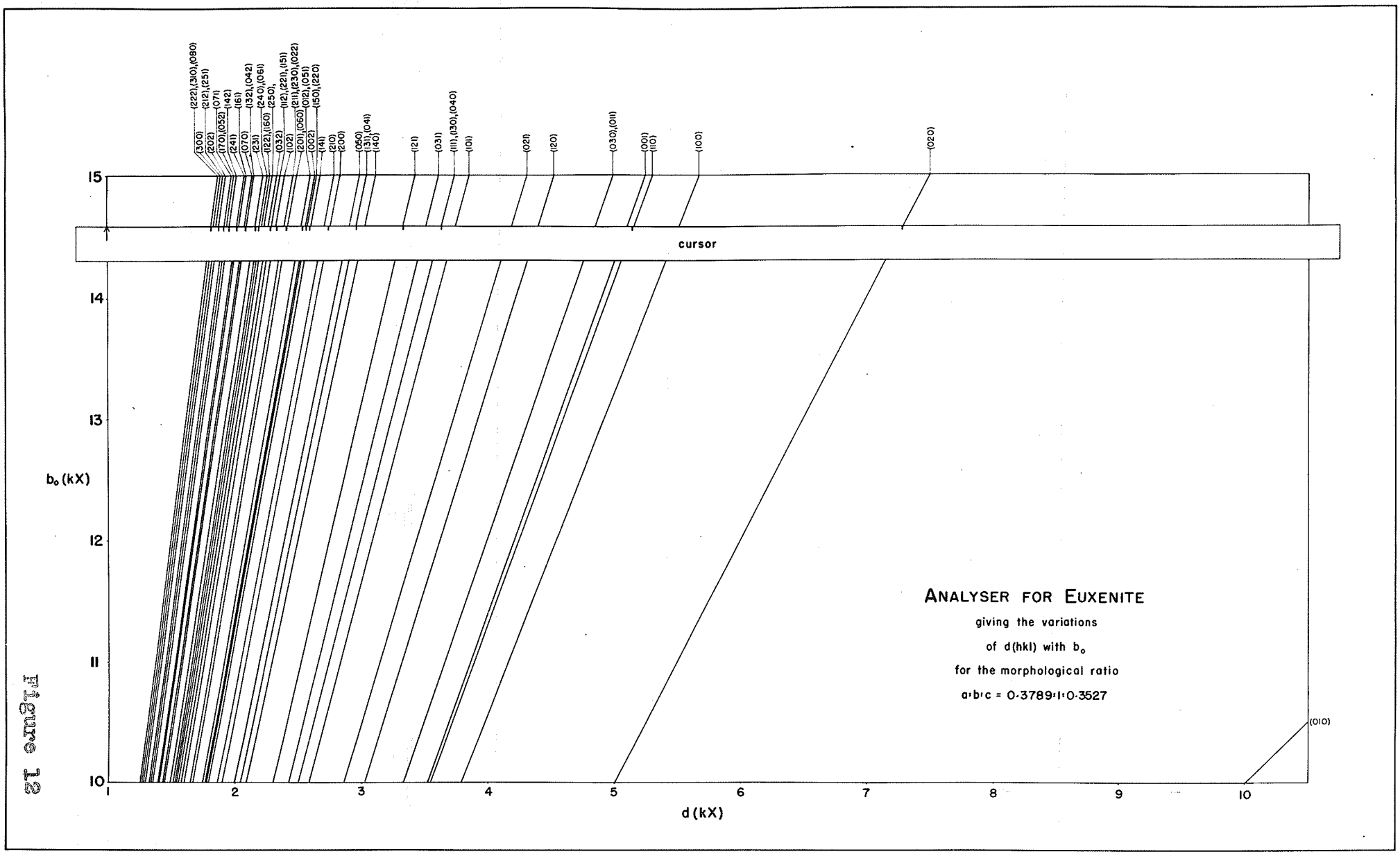

(222),(310),(080)
(212),(251)
(071)
(170),(052)
(142)
(161)
(132),(042)
(240),(061)
(250),
(122),(160)
(032)
(102)
(112),(221),(151)
(211),(230),(022)
(201),(060)
(012),(051)
(002)
(150),(220)
(141)
(210)
(200)
(050)
(131),(041)
(140)
(121)
(031)
(111),(130),(040)
(101)
(021)
(120)
(030),(011)
(001)
(110)
(100)
(020)
15
cursor
14
13
b_o (kX)
12
11
10
1
2
3
4
5
6
7
8
9
10
d (kX)
ANALYSER FOR EUXENITE
giving the variations
of d(hkl) with b_o
for the morphological ratio
a:b:c = 0·3789:1:0·3527
(010)

Figure 12

were unsuccessful, probably because these patterns were not, as described above, the true euxenite pattern.

Solution of the Euxenite Problem. As mentioned above, all the samples of euxenite from Sabine township which were heated to 1000°C gave identical powder patterns. A sample of euxenite from Mattawan township (no. 3 in Table V) was also heated to 1000°C for 100 hours, and it too gave this pattern. The powder picture from this last sample was used for further work since it is clearer in the front reflection region and shows one additional line here. The observed powder data for this sample is given in Table VI. This pattern was examined for series of lines in which the spacings of the succeeding lines are simple factors of the first line. One such series was readily found, the spacings of which are: 7.29, 3.65, 2.43, 1.821, 1.455, and 1.214 kX. This series was taken to represent the various orders of one of the pinakoidal spacings. Since the line with the spacing of 7.29 kX is the first line of the pattern, this series was assumed to be the largest of the pinakoidal spacings. In the normal orthorhombic orientation ($c < a < b$) this would be the side pinakoid. Thus we have:

d(010) = 7.29 kX	d(040) = 1.821 kX
d(020) = 3.65 kX	d(050) = 1.455 kX
d(030) = 2.43 kX	d(060) = 1.214 kX

In the orthorhombic system, the first order spacings of the pinakoids are the respective unit cell dimensions.

TABLE VI

EUXENITE (1000°C for 100 hrs.) -- X-RAY POWDER PATTERN

Locality: Lot 29, Con. 3, Mattawan twp., Nippissing Dist., Ont.

I	θ(Cu)	d	I	θ(Cu)	d	I	θ(Cu)	d	I	θ(Cu)	d
1	6.05	7.29	½	27.30	1.676	1	39.30	1.214	¼	52.35	0.971
2	8.58	5.16	3	28.08	1.633	1	39.80	1.201	½	52.75	0.966
3	12.15	3.65	½	28.48	1.612	2	40.65	1.180	1	53.15	0.961
2	13.28	3.35	1	28.65	1.603	2	41.05	1.171	1	53.35	0.958
10	15.00	2.97	½	29.10	1.581	3	41.75	1.154	2	54.90	0.940
2	16.18	2.76	1	29.55	1.559	½	42.35	1.141	¼	56.35	0.923
2	17.35	2.58	½	29.93	1.541	¼	42.85	1.130	3	57.25	0.914
½	17.63	2.54	¼	30.38	1.520	½	43.50	1.117	1	58.80	0.899
3	18.48	2.43	¼	30.85	1.499	1	43.95	1.108	¼	59.25	0.895
¼	19.05	2.36	4	31.18	1.485	1	44.45	1.098	1	59.95	0.888
1	19.53	2.30	½	31.58	1.468	½	44.90	1.089	1	60.95	0.879
1	20.50	2.20	1	31.90	1.455	¼	45.05	1.086	1	63.10	0.862
1	20.68	2.18	2	32.43	1.434	2	45.50	1.078	1	64.00	0.855
2	21.45	2.10	½	33.35	1.398	1	46.80	1.055	½	64.70	0.850
½	22.35	2.02	½	33.60	1.389	1	47.40	1.044	1	65.35	0.846
½	23.00	1.967	1	34.50	1.357	¼	48.05	1.034	2	66.70	0.837
1	23.45	1.932	2	35.20	1.334	½	48.40	1.028	½	68.15	0.828
2	24.05	1.886	1	35.95	1.309	2	48.90	1.020	1	69.85	0.819
½	24.28	1.870	1	36.55	1.291	2	49.35	1.013	2	72.35	0.807
4	24.98	1.821	½	37.20	1.271	½	49.80	1.006	½	73.45	0.802
¼	25.20	1.805	¼	37.80	1.254	1	50.65	0.994	1	74.75	0.797
3	25.80	1.766	½	38.35	1.239	1	51.35	0.984	½	78.55	0.784
4	26.55	1.720	2	39.05	1.220	½	51.75	0.979	1	80.05	0.780

From this, the b_o axial length of euxenite would be about 7.29 kX.

An effort was made to index the euxenite pattern on the euxenite analyser using this value of b_o. It was found that, although many of the lines could be indexed on this value of b_o, several of them, including the strongest line (2.97 kX), could not. Since the 7.29 kX line could be the second or higher order (0k0) reflection, a second effort was made to index the pattern using double the previous value for b_o, 14.58 kX. In this case, all but a few of the very weak lines could be indexed, and b_o was thus assumed to have approximately this value. Using the indexed spacings for different orders of the (h00) and (001) planes, the following unit cell dimensions were obtained:

$$a_o = 5.53 \text{ kX}$$

$$b_o = 14.58 \text{ kX}$$

$$c_o = 5.16 \text{ kX}$$

Derivation of the Space-Group. Using the above values for the unit cell dimensions, the spacings of all possible planes were calculated, down to a spacing of 2.00 kX. Table VII shows these planes with their calculated spacings as well as the corresponding observed spacings and intensities, and the planes which would be extinguished by each of the orthorhombic space-group extinction conditions. Using this table, the following steps were taken to derive the space-group of euxenite.

TABLE VII

EUXENITE: X-RAY POWDER DATA AND POSSIBLE EXTINCTION CONDITIONS

(hkl)	d(calc)	d(meas)	I	1	2	3	4	5	6	7	8	9	10	11	12	13	14
(010)	14.6			x	x		x	x	x	x					x		x
(020)	7.3	7.29	1														
(100)	5.54			x		x	x	x				x	x		x	x	
(110)	5.18	5.16	2		x	x		x								x	x
(001)	5.16				x	x	x	x	x		x	x		x			
(030)	4.87			x	x		x	x	x	x					x		x
(011)	4.87			x		x		x		x	x						
(120)	4.41			x		x	x	x							x	x	
(021)	4.21				x	x	x	x	x		x						
(101)	3.776			x	x	x		x					x	x			
(130)	3.656				x			x								x	x
(111)	3.656	3.65	3				x	x									
(040)	3.650																
(031)	3.540			x		x		x		x	x						
(121)	3.354	3.35	2	x	x			x									
(140)	3.048			x		x	x	x							x	x	
(131)	2.983	2.97	10				x	x									
(041)	2.980				x	x	x	x	x		x						
(050)	2.920			x	x		x	x	x	x					x		x
(200)	2.770	2.76	2														
(210)	2.721			x	x		x	x							x		x
(141)	2.624			x	x			x									
(220)	2.590																
(150)	2.583	2.58	2		x	x		x								x	x
(002)	2.580																

TABLE VII (continued)

(hkl)	d(calc)	d(meas)	I	1	2	3	4	5	6	7	8	9	10	11	12	13	14
(012)	2.541	2.54	½	x	x		x	x	x	x							
(051)	2.541			x		x		x		x	x						
(201)	2.441				x	x	x	x				x		x			
(060)	2.433	2.43	3														
(022)	2.433																
(230)	2.407			x	x		x	x							x		x
(211)	2.407			x		x		x									
(102)	2.339	2.36	¼	x		x	x	x				x	x				
(221)	2.315				x	x	x	x									
(151)	2.310	2.30	1				x	x									
(112)	2.309				x	x		x									
(032)	2.280			x	x		x	x	x	x							
(160)	2.280			x		x	x	x							x	x	
(122)	2.274			x		x	x	x									
(240)	2.207	2.20	1														
(061)	2.201				x	x	x	x	x		x						
(231)	2.182	2.18	1	x		x		x									
(132)	2.108	2.10	2		x	x		x									
(042)	2.107																
(070)	2.086			x	x		x	x	x	x					x		x
(161)	2.045			x	x			x									
(241)	2.029	2.02	½		x	x	x	x									
(250)	2.010			x	x		x	x							x		x

Continued, next page

TABLE VII (continued)

The columns headed by numbers indicate the planes whose reflections are extinguished by the following extinction conditions;

1	(hkl) present only with $h + k = 2n$.	C---
2	(hkl) present only with $k + l = 2n$.	A---
3	(hkl) present only with $h + l = 2n$.	B---
4	(hkl) present only with $h + k + l = 2n$.	I---
5	(hkl) present only with $h + k = 2n$, and $k + l = 2n$.	F---
6	(0kl) present only with $k + l = 2n$.	-n--
7	(0kl) present only with $k = 2n$.	-b--
8	(0kl) present only with $l = 2n$.	-c--
9	(h0l) present only with $h + l = 2n$.	--n-
10	(h0l) present only with $h = 2n$.	--a-
11	(h0l) present only with $l = 2n$.	--c-
12	(hk0) present only with $h + k = 2n$.	---n
13	(hk0) present only with $h = 2n$.	---a
14	(hk0) present only with $k = 2n$.	---b

(1) By inspection of columns 1 to 5 (hkl conditions), it can be shown, by the following reasoning, that none of the (hkl) extinction conditions shown are possible. If one examines the (110) and (001) spacings (the only possible spacings to give the second line on the powder pattern) it is found that all of these extinction conditions except 1 and 4 would cancel both of these planes. Therefore only these two extinction conditions are possible. Extinction condition 1 would cancel reflections from (121) which is the only possible index for the fourth line of the pattern. Therefore only condition 4 is possible. Again, extinction condition 4 would cancel the reflections from the (102) set of planes which is the only one to give the tenth line of the powder pattern. Therefore this condition is likewise impossible. These deductions are supported by consideration of other singly or doubly indexed powder lines such as (231), (012) and (051), and (241) and (250). Therefore there are no (hkl) extinction conditions and the lattice must be primitive.

Space-Group: P---

(2) By the same reasoning, the only (0kl) extinction condition which is impossible is number 7; this would cancel both (012) and (051), the only possible indices for the eighth line on the powder pattern. This leaves the following possibilities in (0kl): (i) present in all orders, (ii) present only with $k + l = 2n$, and (iii) present only with

$l = 2n$.

Space-Group: Pm--, Pn--, or Pc--

(3) For the (h0l) extinction conditions, the table shows that the line with index (102) would be cancelled by conditions 9 and 10. Therefore, the only possible (h0l) conditions are: (i) present in all orders, and (ii) present only with $l = 2n$.

Space-Group: P-m- or P-c-

(4) All the (hk0) extinction conditions are possible since none of them would cancel any of the lines which are present.

Space-Group: P--m, P--n, P--a, or P--b

Therefore, as far as can be derived <u>with certainty</u>, the space-group is: P(mnc)(mc)(mnab).

However, if the intensity effect of the structure factor (the effect of the positions of the atoms as distinct from the positions of the lattice points) is disregarded, and it is assumed that possible planes which are <u>not</u> represented by observed lines have been cancelled by the space-group extinction conditions, the number of possible space-groups can be greatly reduced.

(5) The line (021) does not appear. Therefore extinction conditions 6 or 8 must hold, since only these would extinguish the reflections from this set of planes. Thus the condition (0kl) present in all orders is no longer possible.

Space-Group: Pn-- or Pc--

(6) The line (101) does not appear. Therefore extinction condition 11 is necessary to extinguish the reflections from this set of planes.

Space-Group: P-c-

(7) The line (100) does not appear. Since conditions 9 and 10 are impossible (see 3 above), we cannot have conditions 14 or (hk0) present in all orders. Therefore either of the conditions 12 or 13 is necessary.

Space-Group: P--n or P--a

(8) Line (031) does not appear. Therefore conditions 7 or 8 are necessary. Of these, only 8 is possible (see 5 above).

Space-Group: Pc--

(9) All odd orders of (0k0) are missing. From this it can be seen that both conditions 8 and 13 cannot hold, since, if they did, these lines would not be extinguished. Since condition 8 is already necessary (see 8 above), condition 13 cannot hold. But, in the (hk0) conditions, only 12 and 13 are left (see 7 above). Then, since 13 is impossible, condition 12 remains as the sole possibility.

Space-Group: P--n

From all the above reasoning, the most probable space-group is Pccn.

Good checks for the above deductions may be found, except for the cancellation of the condition (h0l) present in all orders which is based on the absence of (101). This deduction is supported only by the absence of (201) which could be included in the line at 2.43 kX. Additional doubt

is thrown on this cancellation by the appearance of (101) and (201) as crystal forms. Thus, another probable space-group for euxenite is Pcmn.

A comparison of the two possible space-groups, Pccn and Pcmn, is given in Table VIII, along with the observed powder pattern.

Morphological Considerations. Donnay and Harker (1937) give as their modification of the Bravais law:

> "The morphological importance of a crystal face is inversely proportional to its reticular area S if the lattice is of the hexahedral mode (no centering) and the space group symmetry does not contain any screw axis or glide plane. The effect of lattice centering, screw axes, and glide planes is corrected for if the face indices are replaced, in the S formula, by the "multiple indices" of the lowest order of x-ray reflection compatible with the space group symmetry."

That is, the space-group extinction conditions apply to the order of importance of the crystal forms in exactly the same way as they do to the X-ray reflections.

The decreasing order of importance of the crystal faces, neglecting the structure factor (effect of atoms making up the motif), is the order of decreasing reticular densuty with the above correction for lattice centering, screw axes, and glide planes, when these are present in the space-group. The order of appearance of the lines on an X-ray powder pattern, again neglecting the structure factor, is the order of decreasing planar spacing with the same extinctions due to the space-group symmetry. Since the order of decreasing reticular density is identical with the

TABLE VIII

EUXENITE: POSSIBLE REFLECTIONS FOR SPACE GROUPS Pccn AND Pcmn AND POWDER DATA

Pccn	Pcmn	d(calc)	d(meas)	I
(020)	(020)	7.29	7.29	1
(110)	(110)	5.18	5.16	2
	(101)	3.78	-	
(130)	(130)	3.656		
(111)	(111)	3.656	3.65	3
(040)	(040)	3.650		
(121)	(121)	3.354	3.35	2
(131)	(131)	2.983	2.97	10
(200)	(200)	2.770	2.76	2
(141)	(141)	2.624	2.61	¼
(220)	(220)	2.590		
(150)	(150)	2.583	2.58	2
(002)	(002)	2.580		
(012)	(012)	2.541	2.54	½
	(201)	2.441		
(060)	(060)	2.433	2.43	3
(022)	(022)	2.433		
(211)	(211)	2.407	-	
(102)	(102)	2.339	2.36	¼
(221)	(221)	2.315		
(151)	(151)	2.310	2.30	1
(112)	(112)	2.309		

order of decreasing planar spacing, the order of importance of the faces observed on a crystal should be the same as the order of appearance of the lines on an X-ray powder diffraction picture of the same crystal. In applying the Donnay-Harker Law to the order of form importance, one must remember that the effect of varying conditions of crystallization is being neglected along with the effect of structure factor.

Dana's System of Mineralogy (Palache, Berman, & Frondel, 1944) gives, as the commonest crystal forms for the euxenite-polycrase series, (010), (101), (110), (111), and (100); and, as other observed forms, (001), (011), (201), (121), and (131). Since crystals are uncommon for these minerals, the above order, which is approximately that of decreasing importance, may not be too reliable. The order of appearance of the lines on an X-ray powder pattern of euxenite which would be given by the two possible space-groups deduced above are:

For Pccn: (020), (110), (130), (111), (040), (121), (131), (200), (141)[R], (220), (150), (002), (060), and (022).

For Pcmn: (020), (110), (101)[R], (130), (111), (040), (121), (131), (200), (141)[R], (220), (150), (002), (012), (201)[R], (060), and (022).

Table IX shows the theoretical order of form importance for both space-groups in comparison with the

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[R] not observed on the powder pattern.

TABLE IX

EUXENITE: COMPARISON OF THEORETICAL & ACTUAL FORM IMPORTANCE

Pccn	Pcmn	observed
(010)	(010)	(010)
(110)	(110)	(101)
	(101)[x]	(110)
(130)	(130)	
(111)	(111)	(111)
(121)	(121)	(121)[#]
(131)	(131)	(131)[#]
(100)	(100)	(100)
(141)[x]	(141)[x]	
(150)	(150)	
(001)	(001)	(001)[#]
(012)	(012)	
	(201)[x]	(201)[#]
(011)	(011)	(011)[#]

[x] not observed on powder pattern.

[#] forms whose order of importance is not given in Dana (Palache, Berman, and Frondel, 1944).

order actually observed.

In the table, the least important form, (100), of those whose order of importance is given in Dana, has been placed after (121) and (131) whose order has not been given. With this minor change, the table shows very good agreement between the actual order of importance and those orders predicted by the two space-groups, especially by Pcmn. The order given by Pccn is the same as that given by Pcmn apart from the omission of (101) and (201), both of which are observed forms. This discrepency virtually rules out Pccn as a possible space-group, leaving Pcmn as the most probable space-group for euxenite.

Recalculation of Unit Cell Dimensions. From the indexed powder pattern of euxenite, part of which appears as Table VIII, and using only those lines which index uniquely, the unit cell dimensions were recalculated. For this purpose, the equation $\frac{1}{d^2} = \frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}$ was used, which relates the spacing d of a set of planes (hkl) to the unit cell dimensions a, b, and c, for an orthorhombic lattice.

To obtain b_o = from (020) = 14.587

(231) and (241) = 14.401

(121) and (131) = 14.610

(200) and (240) = 14.489

(161) and (171) = 13.350*

(240) and (280) = 14.600

(142) and (172) = 14.237[*]

(132) and (142) = 14.775[*]

(200) and (280) = 14.573

87.260 b_o = 14.54 kX

To obtain c_o: from (131) and (132) = 5.1447

(121) and (123) = 5.0468[*]

(200) and (202) = 5.1691

(240) and (241) = 5.1875

(171) and (172) = 5.1216

(012) and b_o = 5.1576

25.7805 c_o = 5.156 kX

To obtain a_o: from (200) = 5.5188

(131) and (231) = 5.5335

(102) and (202) = 5.4572[*]

(240) and b_o = 5.5144

(132) & b_o & c_o = 5.4808

(161) & b_o & c_o = 6.2066[*]

(241) & b_o & c_o = 5.4701

(202) and c_o = 5.5346

33.0522 a_o = 5.509 kX

These values give a ratio of a:b:c = 0.3789:1:0.3546, which is in excellent agreement with the morphological value, a:b:c = 0.3789:1:0.3527.

Table X gives the powder data for euxenite indexed to d = 1.676 kX using the final best values given immediately

[*] values discarded before averaging.

TABLE X

EUXENITE - $(Y,Ca,Ce,U,Th)(Cb,Ta,Ti)_2O_6$: X-RAY POWDER PATTERN

Locality: Lot 29, Con. 3, Mattawan twp., Nippissing Dist.

Orthorhombic, Pcmn; $a_o = 5.509$, $b_o = 14.54$, $c_o = 5.156$ kX, $Z = 4$

I	θ(Cu)	d(meas)	(hkl)	d(calc)	I	θ(Cu)	d(meas)	(hkl)	d(calc)
1	6.05	7.29	(020)	7.27	¼	20.00	2.250	(032)	2.275
2	8.58	5.16	(110)	5.15				(122)	2.223
			(130)	3.64	1	20.50	2.195	(240)	2.196
3	12.15	3.65	(111)	3.64	1	20.68	2.177	(231)	2.172
			(040)	3.64	2	21.45	2.102	(132)	2.104
2	13.28	3.35	(121)	3.34	¼	21.83	2.068	(161)	2.038
10	15.00	2.97	(131)	2.97	½	22.35	2.022	(241)	2.020
2	16.18	2.759	(200)	2.755	½	23.00	1.967	(142)	1.965
¼	17.15	2.610	(141)	2.615	1	23.45	1.932	(170)	1.944
			(002)	2.578				(052)	1.929
2	17.35	2.578	(220)	2.576	2	24.05	1.886	(202)	1.882
			(150)	2.572				(222)	1.822
½	17.63	2.539	(012)	2.538				(310)	1.822
			(022)	2.430				(152)	1.821
3	18.48	2.426	(201)	2.430	4	24.98	1.821	(260)	1.819
			(060)	2.423				(171)	1.819
			(112)	2.306				(080)	1.818
1	19.53	2.300	(221)	2.305	3	25.80	1.766	(062)	1.766
			(151)	2.301					

Continued, next page

TABLE X (continued)

I	θ(Cu)	d(meas)	(hkl)	d(calc)	I	θ(Cu)	d(meas)	(hkl)	d(calc)
			(311)	1.718	¼	30.38	1.520	(280)	1.517
4	26.55	1.720	(330)	1.717	¼	30.85	1.499	(302)	1.496
			(261)	1.716				(143)	1.495
½	27.30	1.676	(242)	1.672				(312)	1.487
			(181)	1.637				(351)	1.487
3	28.08	1.633	(113)	1.630	4	31.18	1.485	(262)	1.487
			(331)	1.629				(082)	1.486
1	28.65	1.603	(123)	1.601				(191)	1.485
			(252)	1.580				(322)	1.459
½	29.10	1.581	(271)	1.579				(203)	1.458
			(341)	1.562	1	31.90	1.455	(281)	1.455
1	29.55	1.559	(133)	1.554				(0100)	1.454

Continued, next page

TABLE X (continued)

I	θ(Cu)	d	I	θ(Cu)	d	I	θ(Cu)	d
2	32.43	1.434	½	42.35	1.141	1	53.15	0.961
½	33.35	1.398	½	43.50	1.117	1	53.35	0.958
½	33.60	1.389	1	43.95	1.108	2	54.90	0.940
1	34.50	1.357	1	44.45	1.098	3	57.25	0.914
2	35.20	1.334	½	44.90	1.089	1	58.80	0.899
1	35.95	1.309	2	45.50	1.078	1	59.95	0.888
1	36.55	1.291	1	46.80	1.055	1	60.95	0.879
½	37.20	1.271	1	47.40	1.044	1	63.10	0.862
¼	37.80	1.254	½	48.40	1.028	1	64.00	0.855
½	38.35	1.239	2	48.90	1.020	½	64.70	0.850
2	39.05	1.220	1	49.35	1.013	1	65.35	0.846
1	39.30	1.214	½	49.80	1.006	2	66.70	0.837
1	39.80	1.201	1	50.65	0.994	1	69.85	0.819
2	40.65	1.180	1	51.35	0.984	2	72.35	0.807
2	41.05	1.171	½	51.75	0.979	½	74.75	0.797
3	41.75	1.154	½	52.75	0.966	1	80.05	0.780

above.

This same method, applied to the euxenite from Sabine township, Nippissing district, Ontario, gave:

$$a_o = 5.541 \text{ kX}$$

$$b_o = 14.58 \text{ kX}$$

$$c_o = 5.184 \text{ kX}$$

and a ratio of a:b:c = 0.3800:1:0.3556.

Specific Gravity Determinations. In order to study the effects of heating on the density of euxenite, the Berman microbalance was used to measure the specific gravity of several fragments of the unheated euxenite from Sabine township, Nippissing district, Ontario, and of several fragments from each sample of the same euxenite specimen which had been heated to 1000°C for varying lengths of time. The results, given in Table XI, show two significant features: first, the specific gravity varies considerably for different fragments of the same sample; and second, the specific gravity increases with heating to a maximum at about two hours, and then decreases with longer heating. Since alteration lowers the specific gravity, the highest values are considered the best , which, from Table XI are:

before heating = 4.98

after heating = 5.23

This last value is the one used in calculating Z in the next section. The results agree well with the range of values published in Dana's System of Mineralogy (Palache,

TABLE XI

EUXENITE: VARIATION IN SPECIFIC GRAVITY WITH HEAT TREATMENT

Treatment	Fragment number	Wt. of fragment	No. of readings	Specific Gravity Fragment average	Specific Gravity sample average
unheated	1	4.3 mg	1	4.808	
	2	16.6 mg	4	4.978	
	3	21.6 mg	4	4.938	
	4	16.3 mg	1	4.855	4.96
1 hr. at 1000°C	1	12.4 mg	1	5.178	
	2	17.9 mg	2	5.120	5.13
2 hrs. at 1000°C	1	18.5 mg	6	5.180	
	2	11.5 mg	2	5.232	5.21
13 hrs. at 1000°C	1	35.2 mg	5	5.020	
	2	27.2 mg	5	5.127	5.08
25 hrs. at 1000°C	1	11.7 mg	3	5.108	
	2	19.6 mg	2	4.930	
	3	10.0 mg	2	5.147	5.13
32 hrs. at 1000°C	1	12.5 mg	2	5.015	5.02
40 hrs. at 1000°C	1	26.3 mg	2	5.046	
	2	28.2 mg	2	5.074	5.06
100 hrs. at 1000°C	1	43.1 mg	2	4.975	
	2	13.5 mg	1	4.984	4.98

Berman, & Frondel, 1944):

> "G. 5.00 ± 0.10 (for Cb:Ta > 2:1, and apparently not varying markedly with varying ratio of (Cb + Ta):Ti); 5.3-5.9 (for Cb:Ta < 1:1); the G. decreases with alteration and increases after ignition."

Atoms in the Unit Cell and Calculated Density. The relationship between the density of a crystalline substance, the volume of its unit cell, and its molecular weight, is given by the formula:

$$M = \frac{V\rho}{A} = Zm$$

where: ρ = density in gms/cc.

V = volume of the unit cell in ccs. ($kX^3 \times 10^{-24}$)

A = 1.6502×10^{-24} gms. (weight of a hypothetical atom of atomic weight 1)

Z = number of empirical formula weights in the unit cell

m = empirical formula weight

M = molecular weight of the unit cell = Zm

The calculation of Z was made for the sample of heated euxenite from Sabine township, Nippissing district, Ontario, using the following data:

ρ = 5.23 (measured on the Berman microbalance).

V = $5.541 \times 14.58 \times 5.184 = 418.8 \times 10^{-24}$ ccs.

Then $M = \frac{418.8 \times 10^{-24} \times 5.23}{1.6502 \times 10^{-24}} = 1327.$

The formula for euxenite is given in Palache, Berman, & Frondel (1944) as AB_2O_6, where A = (Y,Er, etc.), (Ce, etc.),

Ca, U, Th; and B = Cb, Ta, Ti, Fe^3.

Table XII gives, for euxenite from the same locality, the analysis by Ellsworth (1932) and the number of the various types of atoms in the unit cell calculated for the above value of M. The numbers of "molecules" of each of these oxides in the unit cell (column 2) have been calculated using the relationship:

$$\text{number of molecules} = \frac{\%\text{ by analysis x M}}{\text{total \% x molecular wt. of oxide}}$$

Thus, for TiO_2, this is $\frac{22.96 \times 1327}{95.72 \times 79.9} = 3.9846$.

The numbers of atoms of each type in the unit cell (columns 3, 4, & 5) have been obtained by multiplying the values given in column 3 by the number of the particular atoms in the corresponding oxide "molecules".

From this table, it can be seen that there are 4.156 atoms of type A, 7.496 of type B, and 22.725 oxygen atoms in the unit cell. Thus the cell content of euxenite is $A_{4.16}B_{7.50}O_{22.73}$, which is approximately $A_4B_8O_{24}$. Therefore, apparently Z = 4. The value of Z for the A part of the molecule (4.16) is very close to the probable value of 4. However, since the values for the B atoms (3.75) and the oxygen atoms (3.78) check well between themselves, it seems more likely that their proportions represent the true value of Z if the density is increased to bring them to 4. The consequent error in the A part of the molecule probably arises from the calculation of the number of Y+ Er atoms in the unit cell which was done on the assumption that this

TABLE XII

EUXENITE: ANALYSIS AND CELL CONTENT

	1	2	3	4	5
TiO_2	22.96	3.9846		3.985	7.969
Fe_2O_3	2.07	0.1797		0.359	0.539
Cb_2O_5	28.62	1.4929		2.986	7.465
Ta_2O_5	2.65	0.0832		0.166	0.416
CaO	1.92	0.4748	0.475		0.475
UO_2	8.61	0.4421	0.442		0.884
UO_3	0.20	0.0097	0.010		0.019
ThO_2	3.94	0.2069	0.207		0.414
$(Y,Er)_2O_3$	24.31	1.4927	2.985		4.478
$(Ce,etc.)_2O_3$	0.44	0.0186	0.037		0.056
Totals	95.72		4.156	7.496	22.725

1 Euxenite, Sabine township, Nippissing district, Ontario - analysis, Ellsworth (1932).

2 "Molecules" in the unit cell, M = 1327.

3 Atoms of type A in the unit cell.

4 Atoms of type B in the unit cell.

5 Oxygen atoms in the unit cell.

combination is all yttrium. (It is practically impossible to separate these two elements by chemical methods). If part of this is erbium, the number of these combined atoms in the unit cell will be lower since the atomic weight of erbium (167.2) is nearly double that of yttrium (88.92). The Y:Er ratio necessary to give Z for the A part of the molecule a value of 3.75 was calculated and found to be about 2:1. That is, if one third of the yttrium-erbium atoms in the unit cell are erbium, the value of Z for the A part of the molecule will be 3.75.

The low value of Z (3.75 instead of 4) obtained by the above method is probably due to a low measured specific gravity. This is quite probable since the density of euxenite decreases with alteration and possibly is not completely regained on heating. Assuming that the measured density is too low and that the value of Z is 4, the density was calculated to be 5.58.

Tanteuxenite. During the investigation of euxenite, two X-ray powder diffraction photographs were taken of specimens labelled tanteuxenite (a high-tantalum euxenite), one from Woodstock, West Australia, and the other from Eleys, West Australia. Neither specimen showed any crystal form and both specimens had low densities (4.9) but otherwise they corresponded to the physical description of tanteuxenite as given in Dana's System of Mineralogy (Palache, Berman, & Frondel, 1944):

"Fracture subconcoidal, H 5-6. G. 5.4-5.9. Lustre resinous with brownish black color."

Both specimens were metamict but on heating gave patterns similar to that of the uraninite-thorianite series and were readily indexed using the cubic crystal analyser. The cell edge for the specimen from Woodstock is 5.11 kX, and that for the specimen from Eleys is 5.09 kX.

The powder photograph of the specimen from Eleys is shown in Figure 12 for comparison with powder photographs of euxenite. As well as the strong lines described above, this specimen also gave a considerable number of very weak lines which could not be indexed on the cubic crystal analyser.

CHAPTER VII

SUMMARY AND CONCLUSIONS

X-ray powder photographs of nineteen specimens, from different localities, of the uraninite-thorianite series (UO_2-ThO_2) were read and indexed using the cubic crystal analyser. The cell edges for thorianite ranged from 5.49 to 5.56 kX; those for uraninite from 5.40 to 5.48 kX; and those for pitchblende from 5.39 to 5.46 kX. An indexed powder pattern of uraninite is given.

X-ray powder photographs were taken of one specimen of microlite, $(Na,Ca)_2Ta_2O_6(O,OH,F)$, (partially metamict), one of pyrochlore, $(Na,Ca)_2Cb_2O_6F$, (metamict), and two of ellsworthite (metamict), a uranian pyrochlore, all isometric. The cell edge of the microlite before heating is 10.42 kX, and, after heating, 10.40 kX; that of pyrochlore (heated) is 10.38 kX; and those of the ellsworthite specimens are 10.30 and 10.28 kX. An indexed powder pattern of microlite (heated) is given.

Metamict euxenite (orthorhombic), $(Y,Ca,Ce,U,Th)(Cb,Ta,Ti)_2O_6$, defied attempts to grow single crystal units by prolonged heating. The powder pattern of the heated mineral was therefore indexed by means of a specially-constructed analyser which utilizes the morphological axial ratio. The probable space-group of euxenite was then deduced by analysis of this indexed pattern. The data thus obtained is

as follows:

Probable space group: Pcmn (or Pccn). Z = 4.

Cell dimensions:	a_o	b_o	c_o	a:b:c
Euxenite (Mattawan)	5.509	14.54	5.156	0.3789:1:0.3546
Euxenite (Sabine)	5.541	14.58	5.184	0.3800:1:0.3556

Specific Gravity: of euxenite from Sabine twp., unheated 4.98, heated 5.23. Calculated density = 5.58.

An indexed powder pattern for euxenite is given.

Two specimens labelled "tanteuxenite" (a high-Ta euxenite) gave powder patterns similar to those given by the uraninite-thorianite series, with cell edges 5.09 and 5.11 kX.

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