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A STUDY OF PYROCHLORE AND BETAFITE

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Abstract

Pyrochlore and betafite were investigated from several types of Canadian occurrences. Nine new analyses for twenty constituents and eleven analyses for eight constituents are presented. A general formula $A_{16-x}B_{16}(O, OH)_{48}(F, OH)_8$ is proposed for the pyrochlore-betafite series with x representing vacant sites in the unit cell. Differential thermal and thermogravimetric curves indicate two states of water. Betafite and thorian pyrochlore are metamict, but recrystallization can begin well below the exothermic reaction indicated on D.T.A. curves. The cell edge of ignited minerals tends to decrease as titanium and iron increase. Molecular weights derived from density-cell edge data correspond qualitatively to those calculated from analyses. Observed x-ray intensities agree with calculated values, but the role of iron is uncertain. Frequency diagrams suggest a natural division of pyrochlore and betafite at 15 per cent uranium.

INTRODUCTION

The relationship of pyrochlore and betafite has long been disputed. X-ray powder patterns of pyrochlore and ignited betafite are very similar but chemical compositions are usually quite different. Pertinent chemical work has been reported by Machatschki (1932), who showed that members of the pyrochlore series depart considerably from stoichiometry, and Rosén & Westgren (1938), who showed that vacant cationic sites are common in compounds with the pyrochlore structure. Borodin & Nazarenko (1957) maintain that this type of defect structure occurs in natural pyrochlore. Ginzburg *et al.* (1958) extended the pyrochlore series to include betafite and djalmaite with the general formula $A_{2-x}B_2X_7$. The writer's research was nearly complete before these last two publications became available. A new assessment of data independently substantiates the main conclusions of the Russian authors.

The symmetry and structure of pyrochlore have been known for some time. The space group was determined as $O_h^7 - Fd3m$ by Gaertner (1930), using x-ray diffraction and by Donnay (1941), using morphological data. Gaertner also determined the structure. It is described as the type $E8_1$ in the *Strukturbericht*.

All betafite and some pyrochlore are metamict, a state which has hindered x-ray investigation. Crystallization is known to take place with evolution of heat when the minerals are ignited. The exothermic phenomena are manifested as peaks on differential thermal curves (Kurath, 1957). Peaks that are typical for the specific mineral do not always appear (Kulp, Volchock, & Holland, 1952).

PYROCHLORE AND BETAFITE

X-ray diffraction patterns of pyrochlore and ignited betafite are similar although not identical. A structural relationship between the two minerals was proposed by Bjørlykke (1931) and Reuning (1933), but contested by Machatschki (1932). Rutile and pyrochlore lines were identified in the x-ray patterns of ignited betafite by Takubo, Ueda, & Nishimura (1951). A uraninite structure may also appear as was shown by Gasperin (1957). Furthermore, Sørum (1955) ignited metamict pyrochlore and obtained, besides pyrochlore, x-ray lines of columbite, loparite, and a new phase of uncertain composition.

DESCRIPTIONS OF SAMPLES AND OCCURRENCES

Mineral Separation

Samples of pyrochlore and betafite were separated in Ottawa at the Geological Survey of Canada and at the Mines Branch, Department of Mines and Technical Surveys. Most samples were concentrated by hand under the binocular microscope but some (H9-1-1, H9-1-4, and H9-1-HS) were concentrated on the Frantz isodynamic separator, upgraded on the Haultain superpanner, and finally handpicked under the binocular microscope. Sample H8A was passed through the Frantz isodynamic separator, and a heavy liquid concentrate (sink from diluted Clerici solution) was made by Dr. E. H. Nickel of the Division of Mineral Dressing and Process Metallurgy, Mines Branch.

Mineral association, purity, and zoning of pyrochlore and betafite grains were studied by means of thin sections, polished sections, and autoradiographs. Autoradiographs were taken on Kodak, x-ray, noscreen film.

Most sample concentrates weighed from 2 to 5 grams although five samples weighed about 1 gram and one sample (H9-4B) weighed only 0.3 gram. Lack of material limited the number and type of tests for many samples.

Sample data are listed in Table 1. Data are not included for samples H1C and H7 which had been separated previously by Dr. R. J. Traill and were given to the writer in powder form. Sample H1C is a rare thorian variety of pyrochlore from Blue River, British Columbia, while H7 is the "betafite" from the Manny zone, Molybdenum Corporation of America, Oka, Quebec (Rowe, 1955, p. 5, "betafite").

Occurrence

The geological occurrence of most deposits from which samples were taken has been previously described and only a few generalizations will be given in this paper. Occurrences are summarized and references listed

	HIA	H2	H3	H4A	H4B	H4C	H5	H6A	H6B	H6C
Origin of sample	Verity property, Blue River, B.C.	Viking Lake, Beaverlodge, Sask.	Woodcox Mine, Hybla Ont.	MacDonald I	Mine, Hybla, (Ontario	Hogan property, Wilberforce, Ont.	Basin property	y, Bancroft, (Ontario
Type of occurrence	Layered carbonate rock (pyrochlore)	Zoned granite pegmatite (betafite)	Zoned granite pegmatite (pyrochlore)	Zoned granit	e pegmatite ()	betafit e)	Calcite-fluo- rite-apatite vein (betafite)	Carbonate roc	k (ellipsoidal	body) (betafite)
Principal references	McCammon (1953, 1955). Rowe (1958, pp. 31-35)	Robinson (1955, p. 35)	Walker and Parsons (1923 b) Ellsworth (1932, pp. 209-211)	Walker and (1932, pp. 2	Parsons (1923) 00–209), Peacl	a), Ellsworth h (1950)	Satterly and Hewitt (1957, pp. 62-63)	Giblin (1955), pp. 123-132)	Satterly and	Hewitt (1957.
Diameter of largest grain or fragment	5 cm.	2.5 cm.	3 cm.	1.5 cm.	l cm.	2 mm.	2 cm.	3 cm.	2 mm.	>10 cm.
Colour	Reddish brown	Very dark brown	Dark brown	Amber	Dark brown	Black	Black	Black	Black	Dark brown
Density (gm./cc.)	4.48	3.98	4.49	3.50	3.79	4.00	4.03	4.15	3.90	4.05
Refractive	>2.00	1.96	2.0	1.84	1.91	1.945	1.96	>2.00	1.94	1.98
Crystal forms	111, 001-rare	111(?)- rare	(Anhedral)	(Anhedral)	(Anhedral)	Unidentified	111, 001	111, 001 113, 011 -rare	(Anhedral)	111, 001 113, 011 -rare
Twinning Cleavage Zoned crystals	Spinel-rare Absent Common	Absent Absent Absent	Absent 111-rare Absent	Absent Absent Absent	Absent Absent Absent	Absent Absent Absent	Absent Absent Absent	Absent Absent Absent	Absent Absent Absent	Spinel-rare Absent Absent

TABLE 1. SAMPLE DATA

TABLE 1. (Continued).* SAMPLE DATA

•	H8A	H9-1-1	H9-1-4	H9-1-HS	H9-3A	H9-3B		
Origin of sample	Bond zone, Quebec Columbium	Hull tp. Con. IX	(N1), L	ot 22. P.Q. F	Iull tp. Con. XI ((N 1), Lot 27, P.Q.	Hull tp. Con. X (N	H9-4A
Type of occurrence	Mines Ltd., Oka, P.Q. Layered car- bonate and silicate rocks	Biotite-apatite b	reccia (b	etafite)	Calcite vein (t	ætafite)	Amphibole vein	(betafite)
Principal references	(pyrochlore) Nickel (1956), Rowe (1958, pp. 65-87)			·				
Diameter of largest grain or or fragment	0.1 mm.	2 mm.	2 mm.	2 mm.	20 mm.	5 mm.	20 mm.	5 mm.
Colour Density (gm./cc.)	Reddish brown 4.33	Very dark brown 4.30	Brown 4.06	Yellowish brown 4.13	Black 4.60	Black 4.00	Yellowish brown 3.94	Black 4.12
Refractive index Crystal forms	>2.00 111	>2.00 111	> 2.00 111	>2.00 111,	>2.00 111, 011 -rare	1.97 (Anhedral)	±2.02 111 011 -rare	>2.00 111
Twinning Cleavage Zoned crystals	Spinel Absent Common	Spinel -rare Absent Absent	Absent Absent Absent	Spinel -rare Absent Rare	001 -rare Spinel-rare 111-rare Absent	Absent Absent Absent	Absent 111-rare Common	Absent Absent Common

*Data for H1C and H7 are not included. These samples were received in powdered form. H1C is a thorian pyrochlore from the Verity property, Blue River, British Columbia. H7 is the "betafite" from the Manny zone, Quebec Columbium Mines Ltd., Oka, Quebec.

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in Table 1. Further details are given in the writer's Ph.D. thesis (Hogarth, 1959).

Well-crystallized pyrochlore at Blue River, British Columbia, and Oka, Quebec, occurs in carbonate rock. The Blue River pyrochlore is found in both dolomite and calcite. Dolomite appears to have been granulated. Pyrochlore often contains columbite. At Oka pyrochlore was observed in calcite- and diopside-rich rocks. The larger grains contain abundant gangue minerals. Pyrochlore from both localities is frequently zoned with the most radioactive zone at the exterior of the crystal.

Betafite was studied from several types of occurrence. The pegmatites of Viking Lake, Saskatchewan, and Hybla, Ontario, contain unzoned and usually anhedral betafite. Betafite from calcite veins and ellipsoidal calcite bodies of the Hogan and Basin occurrences near Bancroft, Ontario, is unzoned but commonly "cubo-octahedral" in habit. Betafite in the amphibole-rich veins in Hull township, Quebec, is octahedral and sometimes zoned with a strongly radioactive rim. The associated breccias also contain betafite but here the mineral is rarely zoned.

Apatite is abundantly associated with all the pyrochlore and betafite samples except those which came from pegmatite. Magnetite is common with samples from Oka, Viking Lake, and Blue River. It occurs in small amounts in the Hogan betafite, is rare in the Hull township betafite, and was not detected in betafite from the Basin occurrence.

THE CHEMICAL COMPOSITION OF PYROCHLORE AND BETAFITE

Methods of Analysis

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The choice of analytical methods was determined principally by the quantity of sample available. In most cases the small amount of material limited the number of wet chemical determinations.

Nine samples were selected for detailed examination and were analysed in the following steps:

(1) Samples were scanned by x-ray fluorescence to $2\theta = 87^{\circ}$ with a General Electric x-ray spectrometer. Analyses were made by R. J. Traill at the Geological Survey of Canada and the writer at McGill University.

(2) Quantitative x-ray fluorescent analyses were carried out in both helium and air paths by the writer. Peak intensities were read directly from a binary scaler. Background was subtracted from each reading. Specimens to be chemically analysed were employed as standards along with previously analysed samples. In addition, synthetic ThO₂ and SrO standards were prepared.

(3) Moisture in H9-3A was measured by the writer by drying a portion with an infra-red lamp and storing in a desiccator with P_2O_5 as desiccant.

(4) Samples H1A, H2, H5, H6A, H7, H8A, H9-1-4, H9-3A, and H9-4A were sent to Ledoux and Company, Teaneck, New Jersey, for the determination of major constituents.

(5) A portion of sample H7 was dehydrated by S. Abbey at the Geological Survey of Canada and total water was determined.

(6) Portions of samples were sent to S. Courville of the Geological Survey of Canada for the determination of Na₂O (in sample H9-3A), H_2O , and F.

(7) Qualitative spectrographic analyses were made by W. H. Champ at the Geological Survey. Particular attention was paid to SiO_2 , Al_2O_3 , and MgO.

(8) MgO in sample H2 was determined spectrographically by W. O. Taylor, Ontario Department of Mines.

Analytical Data

Detailed analyses are presented in Table 2. The oxide percentages are based on moisture-free samples. Total iron is given as FeO, uranium as U_3O_8 . The symbols $\sum Ce_2O_3$ and $\sum Y_2O_3$ refer to the sums of cerium and

TABLE 2. ANALYSES OF CANADIAN PYROCHLORE AND BETAFITE

	H1A	H2	H5	H6A	H7	H8A	H9-1-4	H9-3A	H9-4A
Na ₂ O	6.80	0.42	0.64	0.33	2.88	1.46	0.31	4.04	0.58
K2O	0.1	n.d.†	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	13.76	4.44	10.64	10.94	17.11	20.32	10.59	9.1	8.70
MnO	Tr.*	0.26	0.52	0.62	1.17	0.09	0.1	0.17	0.28
FeO	0.47	7.88	3.15	3.44	1.80	2.06	2.41	2.15	1.67
MgO	Tr.	0.5	0.32	Tr.	n.d.	Tr.		Tr.	Tr.
∑Ce₂O₃	0.2	0.2	Tr.	0.2	2.2	8.87	0.3	Tr.	Tr.
∑Y₂O₃	n.d.	2.4	Tr.	Tr.	0.2	0.1	Tr.	Tr.	Tr.
ThO ₂	0.07	0.5	0.2	0.2	7.23	1.08	0.1	0.1	0.2
U_3O_8	3.51	21.10	22.24	22.79	1.83	0.59	23.11	18.95	22.10
РЬО	Tr.	0.75	1.49	1.43	0.1	0.06	2.0	3.23	2.61
SrO	0.83	0.21	0.42	0.21	0.65	0.67	2.01	0.72	0.70
BaO	Tr.	2.77	Tr.	Tr.	Tr.	Tr.	n.d.	Tr.	Tr.
Nb ₂ O ₅	60.90	18.99	32.44	31.06	40.53	48.04	33.34	50.06	41.24
Ta ₂ O ₅	6.55	3.64	0.25	3.33	3.08	2.77	1.26	0.72	0.54
ZrO ₂	Tr.	Tr.	Tr.	Tr.	1.45	1.99	Tr.	Tr.	Tr.
TiO ₂	2.07	20.65	16.93	17.50	10.4 2	8.64	15.85	6.77	13.18
SnO ₂	n.d.	n.d.	Tr.	Tr.	n.d.	n.d.	n.d.	n.d.	n.d.
F	3.75	0.46	1.23	1.35	2.17	2.30	1.91	2.18	3.06
$[H_2O^+]$	0.10	4.70	3.47	5.88	7.5	0.87	5.60	1.61	5.85
SiO ₂		4.04							
Al ₂ O ₃		0.72							
	99.1	94.6	93.9	99.3	100.3	99.9	98.9	99.8	100.7
$0 \sim F$	1.6	0.2	0.5	0.6	0.9	1.0	0.8	0.9	1.3
Total	97.5	94.4	93.4	98.7	99.4	98.9	98.1	98.9	99.4
Moisture	0.25	2.99	5.21	1.51	0.41	0.18	1.16	0.61	2.28
H ₂ O	0.35	7.55	8.50	7.30	7.9	1.05	6.70	2.20	8.00
*Tr. trace.			tn.	d. sougl	nt but no	t detect	ed.		

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yttrium group oxides respectively. Structural water $[H_2O+]$ was found by subtracting moisture from the total water (H_2O) and correcting for the weight of the dried sample. The oxygen equivalent of fluorine $(O \sim F)$ was subtracted for each sample analysed. The oxides SiO₂ and Al₂O₃ were only determined in sample H2 and probably account for much of the remaining percentage in other samples.

The analyses show a large variation of components, a feature characteristic of pyrochlore and betafite. Sample H2 is abnormally rich in yttrium and barium. With respect to a high content of titanium and iron, the mineral is similar to pyrochlore and betafite from the Tangen quarry, Norway (Palache, Berman, & Frondel, 1944, p. 804, analyses 6, 7, and 8).

Sample H7 and similar material from Oka has been called betafite. Rowe's analyses (Rowe, 1955, p. 5, and 1958, p. 80, analysis B) and those of the writer show that the mineral is high in thorium (>5 per cent), sodium (>2 per cent), and fluorine (>2 per cent) but low in uranium (<2 per cent). According to Lacroix (1922, p. 378), who named betafite, the betafite group: "doit être placé dans la systématique à côté de celui *pyrochlore* dont il se distingue surtout par sa grande richesse en urane et l'absence de proportions notables d'alkalis et de fluor."

It therefore seems appropriate that the Oka "betafite" should be renamed thorian pyrochlore. Samples H1A, H1C, H3, and H8A were also classified as pyrochlore in this study, while the other samples were tentatively classified as betafite.

Sample H9-3A contains an amount of uranium typical of betafite. However, the low percentage of water (2.20 per cent) and high percentage of Na₂O (4.04 per cent) are more characteristic of a low-uranium pyrochlore. Sodium is not recorded in any of the betafite analyses in Palache, Berman, & Frondel (1944, p. 804), nor in the Hybla ellsworthite or hatchettolite (*ibid.*, p. 750, no. 7 and 9). The high density, 4.60, is perhaps the result of a low titanium and water content.

TABLE 3. PARTIAL CHEMICAL ANALYSES*

									H9-1-		
	HIC	Н3	H4A	H4B	H4C	H6B	H6C	H9-1-1	нѕ	H9-3B	H9-4B
	1.4	2.9	3.4	3.5	3.8	4.1	3.5	4.4	2.9	5	2
ThO.	3.9	0.5	0.1	0.1	0.1	0.1	0.2	0.1	0.1	Low	Low
1102	17	14.5	18.7	18.7	18.7	20.0	22.7	23.2	23.0	22	23
PhO	Tr	1.0	0.5	0.5	1.0	0.3	1.4	1.4	2.1	2	2
5+0	0.5	0.3	0.5	0.7	0.5	0.2	0.7	0.3	1.3	0.7	0.5
Nh-O-	15	33.0	39.6	41.1	40.7	28.6	31.1	38.5	32.0	50	37
T O	-10 -9 A	12	4 4	4 2	4.0	4.0	3.7	1.6	1.2	<0.5	<0.5
TiO	10.1	11.8	13.5	14.3	14.0	17.1	17.8	17.4	18.7	6	13
н.о.		3.20	12.80	10.40	8.40	9.80	9.30	6.70			7.95
NbOs:TatOs	18.7	2.8	9.0	9.8	10.2	7.2	8.4	24	27	>100	>74

*X-ray Fluorescence by D. D. Hogarth. Total H₂O by S. C. Courville.

Table 3 presents partial analyses of other samples. The analyses must be considered as approximate only, because data were derived by x-ray fluorescence on undried samples.

The Relationship of Pyrochlore and Betafite

The main difficulty in classifying betafite with pyrochlore has been chemical composition. Ideally in pyrochlore, $8(A_2B_2O_6F)$, A represents sodium and calcium and B niobium and tantalum (Gaertner, 1930). On the other hand Madagascar betafite has a formula close to $AB_3O_{9.7}H_2O$, with A mainly uranium and calcium and B niobium and titanium (Palache, Berman, & Frondel, 1944, p. 803).

If the formula of betafite is written as $8(A_{2/3}B_2O_6H_2O).\pi H_2O$, one can consider betafite as a hydrous, uranian pyrochlore with 67 per cent of the A ions missing. Other pyrochlore structures with vacant sites in the A position* have been described by Pabst (1939), Ferrari & Cavalca (1944), and Mason & Vitaliano (1953). If pyrochlore and betafite are isostructural the general formula could be written as $A_{16-z}B_{16}(O, OH)_{48}(F,$ $OH)_8$, A representing ions with typical radii 0.9 to 1.1 Å and B ions with radii 0.65 to 0.75 Å. The ions Al^{3+} , P^{5+} , and Si^{+4} appear to be too small for the B position.

As a check on these speculations sixty-three analyses from the literature and the nine analyses in Table 2 are plotted on a triangular diagram according to their atomic contents (Fig. 1). The plots 7 and 8 represent the formulas $A_{16}B_{16}O_{48}$ and $A_{5.33}B_{16}O_{48}$ respectively. The calculations were based on the following premises:

 $A = Na, K, Ca, Mn, Mg, Fe^{+2}, \Sigma Ce, \Sigma Y, Th, U, Pb, Sr, Ba, Bi$

B = Nb, Ta, Ti, Zr, Sn, Fe⁺³, W

SiO₂, Al₂O₃, P₂O₅ were excluded.

Atomic weight of \sum Ce assumed to be 140.6,† that of \sum Y assumed 88.92. Valencies were recorded as reported in the literature except where a sample number is followed by the letters "a" and "b" in which cases iron was included in the structural positions A (as Fe⁺²) and B (as Fe⁺³) respectively. For the new analyses in Table 2, uranium was calculated as U₂O₈, however, in sample H5 and H6A oxygen was calculated directly from thermobalance data as outlined below. All calculations were based on 16.00 ions in the B position.

The compositions plotted on Fig. 1 are in accord with the proposed formula $A_{16-x}B_{16}(O, OH)_{48}(F, OH)_8$. The marked tendency for the points to lie to the right of the line $A_{16-x}B_{16}O_{48}$ can be explained by an excess of oxygen due to substitution of $(OH)^-$ for F⁻. This line generally agrees with the plotted compositions with Fe⁺² in the A position. However, if all iron is regarded as Fe⁺³ in the B position one must assume some

*In this paper A and B are used to denote both chemical groups and their respective structural positions.

Ce: La: Nd: Pr = 5:1:1:1 from x-ray fluorescent analysis of sample H8A.





FIG. 1. Diagram showing the atomic compositions of 63 previous analyses and 9 new analyses of pyrochlore and betafite.

substitution of $(OH)^{-}$ for O^{-2} since it is necessary to balance the reduced positive charge of the *B* ions.

High titanian pyrochlore and betafite are not in good agreement with the proposed pyrochlore formula when all iron is assumed to be in the B position (plotted as H2b, 1b, 2b, 3b, and 4b) but agree better when iron is assumed in the A position (as H2a, 1a, 2a, 3a, and 4a).

The series $A_{16}B_{16}O_{48}-A_{5.33}B_{16}O_{48}$ appears to be complete but most compositions are closer to $A_{16}B_{16}O_{48}$. Samples from Ambatofotsikely (No. 5) and Ambatolampikely (No. 6), formerly claimed to be of anomalous composition by Palache, Berman, & Frondel (1944, p. 805, Notes 8 and 9), fit satisfactorily into this scheme.

Combined and Excess Water

The role of water in pyrochlore and betafite is not clear. Hydroxyl is best calculated by balancing positive charges and is assumed to fill the negative sites normally occupied by O^{-2} and F^{-} .

There appears to be little relation between water determined by analysis (after subtraction of "moisture") and water necessary to balance the positive charge. Generally there is more water in the sample as $[H_2O+]$ than required in the formula. This may be due to failure to liberate all loosely bound water when the sample was dried.

Extra water (water not substituting for oxygen and fluorine as hydroxyl) does not appear to be related to the number of vacant sites in the A position of betafite— $A_{16-7}B_{16}(O, OH)_{48}(F, OH)_8$. Madagascar betafite is particularly deficient in A cations yet the Canadian mineral often contains more water by analysis. Often there is too much water to be accommodated in the structure even if we assume all iron to be in the B position. Consider sample H7. The quoted analysis suggests 13.7 molecules of water per unit cell. Only 1.94 water molecules (or 3.88 hydroxyl ions) can be located in the positions normally occupied by fluorine. The remaining 11.8 H₂O molecules cannot possibly reside in the 0.5 vacant sites of the A position.

That there are two types of water is, however, suggested by differential



FIG. 2. Reconstructed D.T.A. and T.G.A. curves of betafite (H4A) from Hybla, Ontario. The samples were fired in argon.

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thermal analysis (D.T.A.) and thermogravimetric analysis (T.G.A.) curves. Figure 2 is an example for "ellsworthite"—H4A. The endothermic peaks at 200° C and 425° C may correspond to loosely bound and combined water respectively. The 425° C peak can be correlated with a thermobalance indication occurring above 340° C. The difference in temperature can be explained by different heating rates (12 deg. C/min. for D.T.A. and 6 deg. C/min. for T.G.A.). The equilibrium curve (airignition) of Walker & Parsons (1923a, p. 15) is quite different and shows no corresponding inflection.

It is interesting to note that most of the water in ellsworthite appears to be loosely bound. The T.G.A. curve indicates a loss of 8.9 per cent water at the 340° C inflection point. If the total water is 12.80 per cent (data from analysis) at least 69.5 per cent of the water is loosely bound.

The significance of the excess water is still imperfectly understood. Canadian betafite contains numerous microscopic [fluid?] inclusions but those observed could probably not account for sufficient water. One may theorize that water is adsorbed in open spaces and is loosely held by bonds that have been disrupted through radioactive bombardment.

STRUCTURAL CRYSTALLOGRAPHY

Crystallization

Pyrochlore exhibited varying degrees of crystallinity. Sample H7 showed no x-ray reflections and H8A gave an x-ray powder photograph with only 14 broad lines. Some samples from Blue River, British Columbia, gave excellent powder patterns with α_1 and α_2 reflections clearly resolved at high angles.

X-ray photographs indicated that all betafite samples were metamict although sample H9-1-HS showed 6 weak pyrochlore lines and samples H5 and H6A each showed 5 weak pyrochlore lines.

Crystallization temperatures were investigated at McGill University using D.T.A. (air-ignition) apparatus. In order to evaluate oxidation effects some samples were tested by D.T.A. (argon ignition) and T.G.A. (air and argon ignition, Stanton thermobalance) at the Mines Branch. It was found that significant exothermic peaks could not be attributed to

oxidation. Comparison of the exothermic peaks on D.T.A. charts of pyrochlore and betafite shows that they are usually quite different. Typically, at a heating rate of 12° C per minute, pyrochlore-microlite shows a broad exothermic peak at 500-550° C (Kulp, Volchock, & Holland, 1952, Soboleva & Pudovkina, 1957, pp. 287-288, p. 294) while betafite gives a narrow peak at 670-700° C (Kerr & Holland, 1951, Orcel & Lévy, 1953).

TABLE 4. EXO	thermic Peaks o	N D.T.A.	CURVES OF	Pyrochlore <i>I</i>	and Betafite
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	Air	ignition-1	2.5 deg. C/1	min.	Argon ignition-12 deg. C/min.					
Sample	520- 570° C	660-700°C	Other peaks (°C)	Ultimate temp. (°C)	520-570°C	650-690°C	Other peaks (°C)	Ultimate temp (°C)		
H1B H1C	w	w	435 -S 465 -W	1000 890	w		425 -S	1050		
H2		w	720 -S	850			{710 -S 895 -W	1095		
H3	w	w	465 -W	850						
H4A H4B	w	s		850 1005		5		1070		
H4C	w	S S#		850 850		w	∫580 -S }	1075		
H6A	w	s	$ \begin{cases} 385 & -S \\ 715 & -W \end{cases} $	900		s	(635 -S }	1060		
H6B		S		850		S		1080		
H6C H8A	w	s W	610 -S	850 900	s	S	615 -S	1030 1070		
H9-1-1		s		850		s	:	1070		
H9-1-4 H9-1-HS		s s	{490 -W 760 -W	850 850						
H9-3A					w		380 -S	1045		
H9-3B H9-3C		s s	585 -W 425 -S	850 850						
H9-3D	s	S		900	-					
H9-3E H9-4A	S	w s		870 850				•		

*Double peak.

S, Strong or prominent peak.

W. Weak or questionable peak.

The present data are summarized in Table 4. It will be noted that the "pyrochlore peak" (520-570° C) is prominent for several betafite specimens while the "betafite peak" (660-700° C) appears in the pyrochlore curves of H1B and H8A. Furthermore, samples from the same occurrence may display very different thermal behaviour. Samples H9-3A, H9-3B, H9-3D, and H9-3E were all taken from within 2 feet, yet each gave a distinctive D.T.A. curve. Samples from the MacDonald mine show typical betafite peaks (Fig. 2) in contrast to the corresponding "ellsworthite" curves of Kerr & Holland (1951) and Kurath (1957).

X-ray diffraction tests before and after the exothermic peaks indicate a crystallization phenomena at the peak temperature. For crystalline pyrochlore the cooling curve did not show a corresponding inflection, and heating above the exothermic peak merely sharpened the x-ray

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FIG. 5. Graph illustrating the variation of the cell size of pyrochlore and betafite with the number of Ti⁴⁺ and Fe³⁺ cations in the *B* position of pyrochlore structure. The broken line indicates a trend in composition but was not positioned mathematically. Cell edges were determined from samples ignited in vacuum for 30 minutes at temperatures from 700 to 750° C.

Molecular Weight

A molecular weight was calculated after ignition using the relationship M = (DV)/(1.6602), where M is the molecular weight for the contents of the unit cell, D is the density (grams per cubic centimeter), and V the cell volume (Å).

The following data were used:

H6A—Density of sample ignited in air at 700° C for 15 minutes = 4.5Cell edge of sample ignited in air at 700° C for 15 minutes = 10.28

$$M = \frac{4.51 \times 10.28^3}{1.6602} = 2950$$

Molecular weight was also calculated from the chemical analys Calculations were based on the following premises:

(1) All water driven off but fluorine retained;

(2) Uranium present as U⁶⁺;

(3) The general formula $A_{16-x}B_{16}O_{48-y}F_{8-x}$.

The following values were obtained:

All iron as Fe⁺² in the A position; M = 3202; All iron as Fe⁺³ in the position; M = 2908.

Agreement with the value calculated from density-cell size da is surprisingly good and does not invalidate the proposed form $A_{16-z}B_{16}(O, OH)_{48}(F, OH)_8$. However, uncertainties in both types calculation preclude any generalization of the role of iron.

X-ray Diffraction Pattern

The x-ray powder pattern of the Blue River pyrochlore (H1A) similar to that of pyrochlore and microlite from other districts. T pattern of ignited Blue River pyrochlore includes all the reflections list by Arnott (1950, Table 3) for microlite from Amelia, Virginia, with t exception of 244, 842, and $10 \cdot 8 \cdot 4 - 12 \cdot 6 \cdot 0$; the latter is not in acco with the pyrochlore structure of Gaertner (1930). The x-ray patterns ignited betafite and pyrochlore from other localities were not as sha and showed fewer lines. Systematic extinctions agreed with the symmetry O_h^7 and the structure $E8_1$, and no justification could be found the relegating pyrochlore to the space groups $O_h^5 - Fm3m$, $O^8 - F432$ $T_d^2 - F\overline{4}3m$ as recommended by Ginzburg et al. (1958).

Besides pyrochlore, other phases were identified in the patterns ignited betafite. Anatase and rutile were only identified in specime from Viking Lake, Saskatchewan (H2), but x-ray diffraction phot graphs indicated that the titania was not distributed homogeneous throughout the sample. The x-ray diffraction patterns of ignited betaf from other localities showed 5 weak lines designated as a, b, c, d and (Fig. 6). These lines were sometimes markedly broader than those of t accompanying pyrochlore and were therefore thought to represent additional phase or phases. The relative intensities varied greatly b typical data are as shown in Table 5.





FIG. 7. Frequency histogram showing the uranium content of pyrochlore and betafite.

tion. Figure 7 is a frequency histogram of seventy-two minerals of the pyrochlore-betafite series.

Atoms of uranium were calculated on the basis of a pyrochlore structure. Valencies of iron were resolved as reported in the literature except for the iron-rich titanian betafites where iron was assumed to be divalent and located in the A position. Iron was also taken as divalent in the new Canadian analyses.

A bimodal distribution is apparent: frequency peaks occur at compositions with 0 to 0.5 atoms of uranium and 2.5 to 3.0 atoms of uranium per unit cell. These two peaks correspond to analyses listing approximately 0 to 5 and 15 to 20 per cent uranium respectively. Rare intermediate members indicate that, in nature, a complete series may extend from pyrochlore to betafite.

The writer would define betafite as a mineral with the pyrochlore structure and high uranium and niobium content. As pyrochlore analyses with 10 to 15 weight per cent uranium or 1.5 to 2 atoms of uranium seem to be relatively uncommon, it seems logical to restrict the name betafite to a mineral with more than 15 per cent uranium metal. Ellsworthite and hatchettolite are intermediate members and need not be retained in the mineralogical nomenclature. Parallel series would extend from titanian pyrochlore to titanian betafite and from microlite to tantalian betafite. Grouped together all could be classed as the pyrochlore group, anisodesmic by virtue of the linked B_2O_6 groups which are the essential units of the structure (Machatschki, 1932 and Byström, 1945).

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