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A THORIAN INTERMEDIATE MEMBER OF THE BRITHOLITE-APATITE SERIES

Physical and Chemical Studies

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ABSTRACT

In 1954 J. P. Girault identified as britholite an occurrence of a thorium-bearing cerian silicate apatite mineral from Oka, Quebec. The unique composition of the Oka mineral, distinguished by $P_2O_5 > SiO_2$ in contrast to other analyses of britholite where silica greatly exceeds phosphorus pentoxide, suggests that the Oka mineral is an intermediate member of a series from britholite to apatite. The values of the physical properties of the Oka mineral approximate the average of those for britholite and apatite and lend support to this theory. An appreciable amount of thorium oxide, 5.62 per cent, is present in the Oka mineral. Britholite was originally found in the Julianehaab district of South Greenland. Recently several occurrences in the U.S.S.R. have been described. The Oka mineral is clove brown, massive, and has a dull resinous luster. The measured specific gravity of a concentrate of this mineral is 3.86 and the calculated value is 3.95. The higher index of refracton ω is 1.72. The Oka mineral is hexagonal with $a = 9.48$ Å and $c = 6.96$ Å (ignited material). The possible space groups are $P6_3$ or $P6_{3/m}$.

An accurate ion exchange separation technique was developed by using Dowex 50W-X8 cation exchange resin (50–100 mesh) and was applied to the quantitative separation of rare earths from phosphates, common elements and thorium all of which are present in the Oka mineral.

The physical and chemical data thus obtained indicate that the probable formula is: $(Ca, Ce\ etc., Th, Mg, Fe, Na, Ti)_5[(P, Si, Al)O_{4}]_3(OH, F)$ which is similar to the theoretical formula proposed by Machatschki in 1939 for britholite.

INTRODUCTION

In 1954 a cerian silicate apatite mineral containing several per cent thorium was found in an ore sample from Oka, Quebec by J. P. Girault and identified as britholite. The results of the present work indicate that it is more likely an intermediate member of a series from britholite to apatite and for this reason we shall refer to the mineral hereafter as the "Oka mineral." Prior to this the only known occurrence of britholite was in Greenland but recently britholite has been discovered at several localities in the U.S.S.R. Table 1 summarizes the physical properties and partial compositions of eight known britholites and a similar rare earth calcium phosphosilicate.

The Greenland britholite was described by Winther (Winther and Böggild, 1899) as hexagonal prisms but closer examination of the crystal faces led him to believe that the mineral was truly orthorhombic and only apparently hexagonal by twinning on the 110 faces. Later workers, Hägele and Machatschki (1939) and P. Gay (1956) using x-ray diffraction meth-

TABLE 1. PHYSICAL PROPERTIES AND PARTIAL COMPOSITION OF BRITHOLITES AND A SIMILAR RARE EARTH CALCIUM PHOSPHOSILICATE

	1	2	3	4	5	6	7	8	9
Specific Gravity	4.446	4.062	4.319	—	3.95–3.92	—	—	4.405	4.08
Indices of Refraction	1.777–1.772	1.776–1.772	1.77	1.752–1.748	1.77	1.72	—	1.780–1.767	1.756±0.002 before heating 1.81 after heating.
a, Å	9.61	—	—	—	9.47±0.01	9.45±0.01	—	—	—
c, Å	7.02	—	—	—	6.95±0.01	6.91±0.01	—	—	—
SiO_2	16.71	17.28	20.10	19.85	19.03	21.93	19.02	17.94	18.1[1]
P_2O_5	6.48	3.84	—	4.86	4.51	3.96	1.87	1.85	2.6[1]
CaO	11.28	11.51	12.62	12.69	14.8	17.34	22.55	12.82	12.8[1]
Al_2O_3	—	—	0.10	0.60	—	14.91	9.45	—	0.5[1]
ThO_2	—	—	5.00	—	9.77	4.76	9.25	—	0.2[1]
$(R.E.)_2O_3$	60.54	56.96	56.70	59.36	40.89	27.58	32.32	58.04	61.3[1]

[1] Oxide per cents calculated from formula given by Bel'kova and Volkova, 1958.

1. Britholite, Julianehaab, Greenland (Winther and Böggild, 1899, specific gravity and chemical analysis; Barth and Berman, 1930, refractive indices; and Hägele and Machatschki, 1939, unit cell).
2. Britholite, Transbaikalia, U.S.S.R. (Nechaeva and Borneman-Starynkevich, 1956).
3. Britholite, Tuva, U.S.S.R. (Korkin, *et al.*, 1960).
4. Britholite, Vishnevye Gory, U.S.S.R. (Zhabin, *et al.*, 1960).
5. Britholite, Siberia, U.S.S.R. (Kudrina, *et al.*, 1961).
6., 7. Alumobritholites, Siberia, U.S.S.R. (Kudrina *et al.*, 1961).
8. Britholite, Azov Sea, U.S.S.R. (Yurk, *et al.*, 1961).
9. Rare earth calcium phosphosilicate, Kola Penninsula, U.S.S.R. (Bel'kov and Volkova, 1958).

ods have shown britholite to be hexagonal. Hägele and Machatschki considered britholite to be a member of the apatite group. From composition determined by Chr. Christensen (Winther and Böggild,1899), Hägele and Machatschki interpreted the formula to be $(Ca, Ce, Na)_5[(Si, P)O_4]_3(OH, F)$. The general formula for britholite minerals suggested by Kupriyanova and Sidorenko (1963) is similar to the latter formula, although the rare-earth minerals and Ca, Fe, etc. are divided into two groups.

Specimens of the Oka mineral were obtained from Mr. S. Bond of the Molybdenum Corporation of America. One of us (M.R.H.) prepared a purified sample, determined the physical and optical properties and carried out the *x*-ray powder diffraction analysis. The chemical analysis was performed by the second author.

The complete chemical analysis of the species is a difficult problem, particularly for the quantitative separation of the rare earths from the other elements and from each other. The precipitation of rare earths by the classical oxalate method of separation (Schoeller and Powell, 1955) is incomplete; also subsequent separations of the rare earths from thorium and from each other involve too many precipitation steps, thereby leading to small losses each time in the filtrate. To overcome these difficulties, an ion exchange separation technique, involving the use of Dowex 50W-X8 cation exchange resin and *x*-ray fluorescence analysis of the rare earth fraction, has been developed and applied to the analysis of the Oka mineral.

EXPERIMENTAL

Separation and purification. A specimen of the rock containing the Oka mineral was pulverized and sized with Tyler screens. The minus 65 plus 100 mesh (204 to 147 microns) size fraction was subjected to a series of magnetic and gravity separations to remove the gangue minerals. The presence of very faint apatite lines in the *x*-ray powder diffraction pattern of the final concentrate of the Oka mineral indicated that several per cent apatite had not been removed. It was found by grain counting that approximately one per cent of black to dark brown impurities, chiefly pyrochlore-microlite, also remained. The intimate association of impurities with the Oka mineral precluded any further mechanical separation and the investigation was carried out with this material. The unit-cell contents and the formula were calculated as if the sample were pure.

Physical and optical properties. The Oka mineral occurs in niobium deposits in the Oka complex described by Rowe (1958) as carbonate and alkaline rocks and probably post Precambrian in age, that are found in the central part of the Oka hills, Precambrian rocks rising abruptly from the plains of the St. Lawrence lowlands. Specimens of the Oka mineral are massive and contain coarse phenocrysts of magnetite and biotite (Fig. 1). Medium-to-fine-grained apatite, calcite, pyrochlore-microlite, feldspar, and quartz are also present.

The Oka mineral is clove brown in color and has a resinous luster. It is a fine-grained, anhedral mineral with uneven fracture and shows no cleavage (Fig. 2). The specific gravity of a sized concentrate of the Oka mineral was found to be 3.85 using a pycnometer and 3.86 using a Berman density balance.

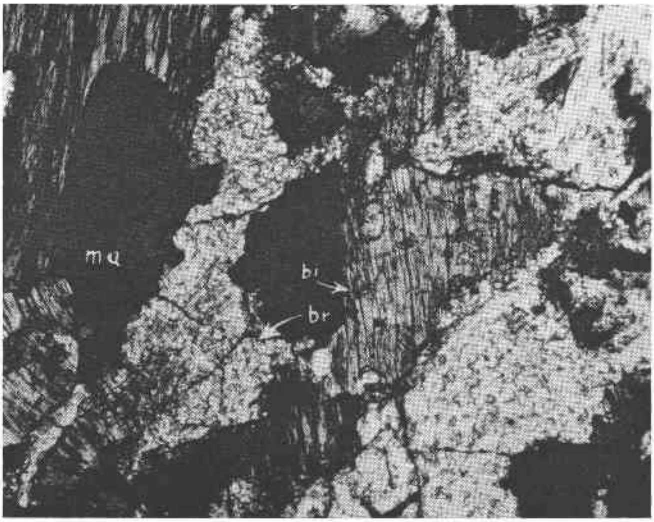

FIG. 1. Photomicrograph showing coarse phenocrysts of magnetite (ma) and biotite (bi) in the Oka mineral (br). ×50. Polars not crossed.

It was difficult to accurately determine the indices of refraction since the Oka mineral is very fine-grained and the extinction is wavy and irregular within each grain. The higher index of refraction ω was determined to be 1.72. The value for the lower index of refraction ϵ appeared to be close to the ω index of the apatite impurity and is considered of doubtful accuracy. In thin section, the Oka mineral is pale olive green and shows no pleochroism. There is no visible cleavage or parting; the relief is moderate. The interference color with crossed nicols is first order gray and the extinction is wavy. There is no indication of twinning.

X-ray powder diffraction data. Because no crystals of the Oka mineral of adequate size for single crystal analysis were found, the *x*-ray diffraction data are based entirely on powder patterns. The Oka mineral is partly metamict and no sharp reflections were observed in the x-ray diffraction patterns of unignited specimens. The few blurred lines are similar to the apatite structure but are too indistinct to be measured. The best powder pattern was obtained from a finely ground sample that had been ignited for 30 minutes at approximately 900° C. in a vacuum. Iron radiation ($\text{FeK}\alpha_1 = 1.9360$ Å) was used with a manganese filter in a 114.57 mm Debye-Scherrer camera. Proper allowance was made for film shrinkage.

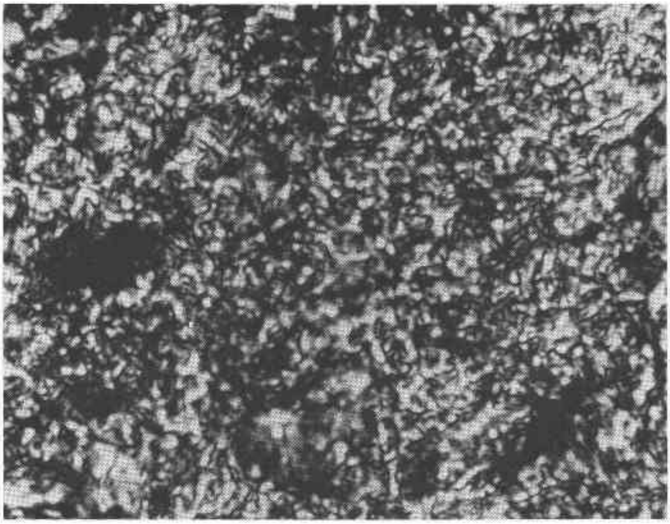

FIG. 2. Photomicrograph showing the Oka mineral highly magnified, showing the vague, irregular outlines of the grains. ×500. Polars not crossed.

The data are given in Table 2.

Eight weak reflections listed in Table 2 are considered to be apatite lines. Using the indices of the adjacent Oka mineral reflections the unit-cell dimensions were calculated giving $a = 9.38$ Å and $c = 6.89$ Å which are identical to the unit cell dimensions listed for fluorapatite in the ASTM index.

The powder pattern of the ignited Oka mineral was indexed on a Bunn Chart for hexagonal crystals having $0.1 \leq c/a \leq 0.9$. The unit-cell dimensions $a = 9.48$ Å and $c = 6.96$ Å were calculated by the method of least squares using normalized equations. The axial ratio c/a is 0.735. Using these values for a and c good agreement was obtained between measured and calculated spacings.

Considering the symmetry to be hexagonal, a systematic extinction of

0001 reflections was found which allowed l = 2n. The possible space groups are $P6_3$ or $P6_{3/m}$ which agrees with the symmetry suggested for britholite by P. Gay (1957).

CHEMICAL ANALYSIS

Because of the difficulties associated with the classical methods of analysis, as mentioned earlier, the possibility of using a cation exchange separation technique was first studied. Chung and Riley (1963) used Zeo-

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR THE OKA MINERAL HEATED $\frac{1}{2}$ HOUR IN A VACUUM

I (est.)[1]	d (meas.) Å	d (calc.) Å	hkīl	I (est.)[1]	d (meas.) Å	d (calc.) Å	hkīl
M	4.116	4.104	$20\bar{2}0$	VW	1.553	1.551	$42\bar{6}0$
M	3.927	3.918	$11\bar{2}1$	W	1.543	1.541	$33\bar{6}1$
S	3.480	3.482	0002	W	1.519	1.518	$21\bar{3}4$
M	3.211	3.205	$10\bar{1}2$	VVW	1.504[2]		
M	3.112	3.102	$21\bar{3}0$	W	1.484	1.485	$50\bar{5}2$
VS	2.836	2.834	$21\bar{3}1$	W	1.468	1.469	$30\bar{3}4$
S	2.809	2.807	$11\bar{2}2$	W	1.463	1.463	$32\bar{5}3$
M	2.730	2.736	$30\bar{3}0$	W	1.443	1.443	$51\bar{6}1$
VW	2.706[2]			VVW	1.428[2]		
VW	2.658	2.655	$20\bar{2}2$	VVW	1.419	1.418	$41\bar{5}3$
VW	2.629[2]			VVW	1.338		
W	2.273	2.277	$31\bar{4}0$	W	1.328		
VW	2.254	2.244	$22\bar{4}1$	W	1.292		
W	2.085	2.085	$11\bar{2}3$	W	1.273		
W	2.058	2.052	$40\bar{4}0$	W	1.251		
VVW	2.018	2.021	$20\bar{2}3$	W	1.236		
VVW	2.006[2]			VW	1.160		
M	1.956	1.960	$22\bar{4}2$	VW	1.149		
W	1.938[2]			VW	1.128		
W	1.906	1.906	$31\bar{4}2$	VW	1.114		
VW	1.887	1.883	$32\bar{5}0$	VW	1.103		
S	1.858	1.858	$21\bar{3}3$	VW	1.045		
W	1.840[2]			VW	1.018		
M	1.819	1.818	$32\bar{5}1$	VW	1.012		
W	1.793	1.792	$41\bar{5}0$	VW	0.9949		
M	1.772	1.772	$30\bar{3}3$	VW	0.9871		
W	1.741	1.742	0004				
VW	1.722[2]						
VVW	1.659	1.658	$22\bar{4}3$				
VVW	1.643	1.641	$50\bar{5}0$				

[1] Intensities by visual estimation; VS—Very Strong, S—Strong, M—Medium, W—Weak, VW—Very Weak, VVW—Very Very Weak.

[2] Apatite impurity.

carb 225 cation exchange resin for the separation and determination of rare earths and other constituents in monazite; they did not, however, determine phosphate in the effluent, and moreover, the flow-rate of 60 ± 10 ml per hour used by the authors was too slow to be of any practical use because 80 hours would be needed before 5.5 liters of total water and acid wash solutions would pass through the column. The applicability of the method to the analysis of the Oka mineral was investigated by means of synthetic mixtures; Dowex 50W-X8 (50–100 mesh) was used instead of Zeocarb 225.

Synthetic rare earth mixture. A synthetic solution of rare earths (cerium, lanthanum, praseodymium, neodymium, samarium, gadolinium and yttrium) was prepared by direct weighing of the individual spectrographically pure oxides and dissolution of the mixture by boiling with 30 ml of 2N sulphuric acid in a beaker tightly covered with a watch glass, to which small amounts of 30 per cent hydrogen peroxide were added from time to time. A clear solution was obtained after prolonged fuming. After cooling it was diluted with ice-cold water.

Thorium solution. Thorium solution was prepared by dissolving an accurately weighed quantity of ThO_2 in a platinum crucible by heating with 2 ml of concentrated nitric acid and 1 drop of 1:40 hydrofluoric acid. It was converted to sulfate by heating with sulphuric acid and dissolved in ice-cold water.

Other reagents. The solutions of other metal ions were prepared from their pure salts or oxides and then standardized. A solution of phosphate was prepared from disodium hydrogen phosphate and standardized by the magnesium pyrophosphate method.

Preparation of the ion exchange columns. Dowex 50W-X8 cation exchange resin of 50–100 mesh size was packed wet into an ion exchange column of 22 cm height and 1.70 cm internal diameter, supported by a plug of pyrex wool. The resin in each column was washed with 3N hydrochloric acid until no test for iron was obtained with ammonium thiocyanate, and then finally washed with water until the washings were neutral to litmus paper.

Preliminary investigation. The solutions of rare earths, thorium, phosphate (disodium salt) and other common metals were mixed in the required amount (Oka mineral composition), the pH adjusted to 1.0 with a pH meter, and the solution then passed through the cation exchange column at a flow rate of 2.5 ± 0.5 ml/min. Elution of phosphate and other

TABLE 3. SEPARATION OF PHOSPHATE FROM THE RARE EARTHS BY ION EXCHANGE

Wash Liquid	P_2O_5 taken, gm	P_2O_5 found, gm	Difference, gm
500 ml dilute HCl (pH 1.3)	0.1780	0.1780	0.0000
600 ml dilute HCl (pH 1.3)	0.1780	0.1782	+0.0002
600 ml water	0.1780	0.1770	−0.0010
1000 ml water	0.1780	0.1780	0.0000

elements was investigated as shown in Tables 3–5. Separation of the phosphate (Table 3) was achieved with either H_2O alone, or with dilute HCl (pH 1.3). However, it is preferable to use dilute HCl (pH 1.3) to guard against the possible formation of aluminum, iron and thorium phosphates on the column.

The common elements were then eluted from the columns by washing with 1N hydrochloric acid. The effects of different volumes in 1N hydrochloric acid as well as that of temperature are shown in Table 4. Two liters of 1N hydrochloric acid was thus found to be most effective.

Table 5 shows the recovery of the rare earths when the column was eluted with 3N and 4N hydrochloric acid solutions. The thorium was then washed out with 800 ml of 3.6N sulphuric acid as suggested by Chung and Riley (1963) and quantitative recovery was obtained.

The rare-earth oxide mixtures obtained from the ion-exchange columns (No. 1–3 of Table 5) were then analysed by *x*-ray fluorescence spectroscopy and the results are given in Table 6. The recovery is found to be satisfactory if 500 ml of 4N HCl is used for eluting the column.

ANALYTICAL PROCEDURE

Decomposition. A 1.0000 gm sample of the Oka mineral was placed in a platinum dish fitted with a cover, and then digested with 5 ml of concen-

TABLE 4. RECOVERY OF COMMON ELEMENTS FROM THE RESIN BY ELUTION WITH 1N HCL

1N HCl used, ml	Temperature	Fe_2O_3 in mg		TiO_2 in mg		Al_2O_3 in mg		CaO in mg		MgO in mg	
		Taken	Found	Taken	Found	Taken	Found	Taken	Found	Taken	Found
1200	Room temp.	2.08	2.08	0.977	0.972	5.00	2.443	293.79	288.89	5.31	5.26
1200	50° C	2.08	2.10	0.977	0.972	7.343	3.043	293.79	288.89	5.31	5.00
1500	Room temp.	2.08	2.08	0.977	0.977	7.343	4.043	293.79	293.79	5.31	5.31
2000	Room temp.	2.08	2.08	0.977	0.977	7.343	7.44	293.79	293.79	5.31	5.31

TABLE 5. RECOVERY OF THE RARE EARTHS FROM THE ION-EXCHANGE COLUMN

Solution Used for Eluting the Rare Earths	Total $(RE)_2O_3$ in mg		Difference, mg
	Taken[1]	Found	
1) 500 ml of 3N HCl	204.2	184.0[2]	−20.2
2) 750 ml of 3N HCl	204.2	201.1[3]	− 3.1
3) 500 ml of 4N HCl	204.2	204.4[3]	+ 0.2

[1] RE = Ce+La+Pr+Nd+Sm+Gd+Y.

[2] Precipitated as oxalate, but recovered 16.1 mg total $(RE)_2O_3$ from the filtrate.

[3] Precipitated by ammonia-ammonium sebacate method (Carron *et al.*, 1955).

trated sulfuric acid for 3 hours on a sand bath at 250° C. The mass was then cooled and dissolved and filtered through a Whatman No. 42 filter paper. The filtrate (A) was reserved and the residue was treated as follows.

Determination of silica and treatment of any undissolved residue. The paper containing the residue was first ignited at 350–400° C. and finally heated to constant weight at 1000° C. Silica was then determined by volatilization with hydrofluoric and sulfuric acids. Any unattacked residue was washed into a 250 ml beaker with hot 2N sulphuric acid and dissolved by heating on a hot plate with repeated additions of 30 per cent hydrogen peroxide. The solution was diluted with ice-cold water and mixed with filtrate A.

Ion-exchange treatment of filtrate A. The filtrate A was diluted with deionized water until a pH of 1.0 was obtained (pH meter). The solution was

TABLE 6. RECOVERY OF THE INDIVIDUAL RARE EARTHS FROM ION-EXCHANGE COLUMN

Oxide	Taken mg	Found					
		Sample 1 mg	Difference mg	Sample 2	Difference mg	Sample 3	Difference mg
CeO_2	130.28	117.39	−12.89	129.91	−0.39	131.22	+0.94
La_2O_3	39.00	34.22	− 4.78	37.40	−1.60	38.63	−0.37
Pr_2O_3	12.66	10.67	− 1.99	11.66	−1.00	11.86	−0.80
Nd_2O_3	10.62	9.75	− 0.87	10.66	+0.04	10.42	−0.20
Sm_2O_3	5.72	5.34	− 0.38	5.43	−0.29	5.72	0.00
Gd_2O_3	3.47	3.50	+ 0.03	3.02	−0.45	3.88	+0.41
Y_2O_3	2.45	3.13	+ 0.68	3.02	+0.57	2.66	+0.21

poured into a large separatory funnel clamped on the top of the ion-exchange column and allowed to drop in at such a rate that about 2.5 ±0.5 ml effluent came out through the column in one minute. The effluent was collected in a 2-liter beaker and the column was washed with 500 ml of dilute hydrochloric acid (pH 1.3). The effluent was evaporated to about 25 ml and transferred to a 400 ml beaker with water. The phosphate was then precipitated as $Mg(NH_4)PO_4$ by ammonia and magnesia mixture and phosphorus was determined as $Mg_2P_2O_7$.

The common elements were eluted from the column with 2 liters of 1N hydrochloric acid, the rare earths by 500 ml of 4N hydrochloric acid.

The thorium was eluted from the column using 800 ml of 3.6N sulfuric acid and collected in a 1-liter volumetric flask. The effluent was diluted to one liter with water and its thorium content was determined colorimetrically with thorin by the method of Chung and Riley (1963).

Analysis of 1N hydrochloric acid effluent. This effluent was evaporated to about 25 ml, transferred to a 100 ml beaker and evaporated to dryness on a steam bath. To destroy the traces of resin, the beaker was covered with a watch glass, 2–3 ml of fuming nitric acid and a few drops of 30 per cent hydrogen peroxide were added and the whole heated on the steam bath for 10–15 minutes. This operation was repeated 3 times. Finally the watch glass was raised on the top of the beaker by means of 3 bent glass hooks and the solution was evaporated to dryness on the steam bath. The beaker was again covered with the same watch glass and the salts were converted to chlorides by heating with small amounts of concentrated hydrochloric acid. When the vigorous reaction subsided, the solution was evaporated to dryness on the steam bath. The treatment with hydrochloric acid, followed by evaporation, was repeated 3 times. Finally the residue was dissolved in dilute hydrochloric acid by heating, 2 gms of solid ammonium chloride and 3 drops of concentrated nitric acid were added and the solution was heated to boiling. The hydroxides of iron, aluminum and titanium were precipitated by adding 1:1 freshly prepared ammonium hydroxide solution. The precipitate was filtered and washed with ammonium nitrate solution. The filtrate was reserved for calcium and magnesium determinations. The filter paper and the precipitate were ignited at 350–400° C. and finally heated to constant weight at 1000° C. to give the total weight of Fe_2O_3, Al_2O_3, and TiO_2. This residue was then fused with 0.5 gm potassium bisulfate at low heat, cooled and the fusion cake was dissolved in 25 ml ice-cold water. The solution was then transferred to a 50 ml flask and diluted to volume with water. Both iron and titanium were determined colorimetrically from this solution, the former by the method of Shapiro and Brannock (1962) and the latter by the method of Rigg and Wagenbauer (1961). Aluminum oxide was obtained by difference.

The filtrate from the iron, titanium and aluminum precipitation was evaporated to about 75 ml, cooled to room temperature, transferred quantitatively to a 100 ml volumetric flask, and then diluted to the mark with water. Calcium and magnesium were each determined in separate 10 ml aliquots of this solution by the EDTA titration method of Patton and Reeder (1956). However, 1 ml of 10 per cent triethanolamine was used as a complexing agent in place of potassium cyanide and hydroxylamine hydrochloride, and Metab [sodium salt of 3,3′-(bis,N,N′-di(carboxymethyl-aminomethyl)thymolsulfonphthalein indicator (Fisher Scientific Co.)] was used for titration of calcium.

Determination of the total rare-earths in 4N hydrochloric acid effluent. This effluent was evaporated to about 25 ml and quantitatively transferred to a 250 ml beaker. After evaporating to dryness on the steam bath, the resin present was destroyed by fuming nitric acid and hydrogen peroxide as described under the treatment of the 1N hydrochloric acid effluent. The cover glass on the beaker was raised with 3 bent glass hooks and the solution was evaporated on the steam bath to about 2–3 ml, then diluted to 150 ml with water; 1 gm of hydroxylamine hydrochloride was added, the solution was cooled to room temperature and the rare-earths were precipitated by ammonium hydroxide and ammonium sebacate using the method of Carron *et al.* (1955). After filtration and washing, the precipitate was ignited to constant weight in a platinum crucible at 1000° C. and the total $(RE)_2O_3$ was obtained. This was then analyzed by *x*-ray fluorescence spectroscopy to obtain the percentages of the individual rare-earth oxides.

The chemical composition of the Oka mineral is given in Table 7 and the percentages of the individual rare earths are shown in Table 8.

CONTENTS OF THE UNIT CELL

The unit cell contents of the Oka mineral were calculated from the chemical analysis on the basis of 26 (O, OH, F) per unit cell. The specific gravity calculated from the unit cell volume and contents is 3.95. The agreement with the measured value of 3.86 is considered good in view of the apatite impurity present. The results are shown in Table 9. Considering the Oka mineral to be a member of the apatite group and if $Z = 2$ the formula based on the type formula $A_5(XO_4)_3Z$ (Palache *et al.*, 1951) is:

$$(\mathrm{Ca, Ce, etc., Th, Mg, Fe, Mn, Ti})_{4.82}(\mathrm{P, Si, Al})_{2.92}\mathrm{O}_{11.90}(\mathrm{OH, F})_{1.10}.$$

TABLE 7. CHEMICAL COMPOSITION OF THE OKA MINERAL
(Analyst—J. G. Sen Gupta)

Component	Wt, %
CaO	28.84
$\sum(Ce, La, —)_2O_3$	33.43
ThO_2	5.62
MgO	0.20
Fe_2O_3	0.14
Na_2O	0.21
TiO_2	0.09
P_2O_5	16.96
SiO_2	12.28
Al_2O_3	0.47
H_2O	0.54
F	2.10
	100.88
Less $O\equiv F$	0.90
Total	99.98

DISCUSSION

The composition and physical properties of the Oka mineral deviate from those of britholites given in the literature. Phosphorus pentoxide is in excess of silica in the Oka mineral and the calcium oxide content is much higher than in britholites. The thorium oxide content of the Oka mineral is approximately one half of the highest recorded value of 9.77 per cent in a britholite from Siberia (Kudrina *et al.*, 1961). The specific gravity, refractive indices, and unit cell dimensions are all lower than

TABLE 8. *X*-RAY FLUORESCENCE ANALYSIS OF RARE EARTHS CONCENTRATE FROM THE OAK MINERAL

Oxide	Wt, %
CeO_2	15.0
La_2O_3	5.6
Nd_2O_3	8.0
Pr_2O_3	1.9
Sm_2O_3	1.5
Gd_2O_3	0.9
Y_2O_3	0.4
$(Pr, Dy)_2O_3$	0.1
Total	33.4

Table 9. Unit Cell Contents of the Oka Mineral
Number of Ions Calculated on the Basis of 26 (O, OH, F)

Ce	1.13	2.54	9.64
Nd	0.61		
La	0.44		
Pr	0.14		
Sm	0.11		
Gd	0.06		
Y	0.04		
Er, Dy	0.01		
Ca	6.54	7.10	
Th	0.28		
Mg	0.06		
Fe	0.02		
Na	0.09		
Ti	0.01		
P	3.08	5.83	
Si	2.63		
Al	0.12		
OH	0.79	26.00	
F	1.42		
O	23.79		
	41.47		

those reported for britholites. With respect to composition and physical properties, the Oka mineral is close to the midpoint between britholite and apatite (Table 10). The values given for britholite in Table 10 were obtained from the references in Table 1. The chemical analysis, refraction

Table 10. Physical Properties and Partial Compositions of Britholite, the Oka Mineral and Fluorapatite.

	Britholite (Greenland)	Oka Mineral	Fluorapatite
Specific gravity	4.446	3.86	3.203
Indices of refraction	1.777–1.772	1.72	1.6332–1.6291
a, Å	9.61	9.48	9.35
c, Å	7.02	6.96	6.87
SiO_2	16.71	12.28	—
P_2O_5	6.48	16.96	41.87
CaO	11.28	28.84	55.16
$(RE)_2O_3$	60.54	33.43	—

indices and specific gravity of the fluorapatite are from Pehrman (1939) and the unit cell dimensions from Deer *et al.* (1962).

The presence of a small proportion of apatite in the Oka mineral would not account for the differences between britholite and the Oka mineral. Therefore, it may be concluded that the Oka mineral is an intermediate member of a britholite-apatite series.

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