INVESTIGATION OF THUCHOLITE

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ABSTRACT

The rather unusual mineral thucholite contains about 50 per cent carbon, 25 per cent volatile gases, and 25 per cent ash. The ash commonly consists of thoria, rare earth oxides and uranium oxide. A purified specimen (*i.e.*, freed from contaminating uraninite) of this interesting material from Ontario, Canada, was subjected to a complete chemical analysis of the ash (including a resolution of certain individual rare earths) and two types of analyses on the volatile gas constituents.

The thoria content in this specimen was less than 1 per cent of the ash, in sharp contrast with the higher percentages which have been reported in previous samples. The rare earth fraction contained a singularly high proportion, over 50 per cent, of a single earth, yttrium oxide. The volatile matter consisted primarily of water, carbon dioxide, and methane, with lesser amounts of nitrogen, carbon monoxide, and hydrogen. The composition of such "volatiles" is shown to be a function of the particular technique employed in evolving them.

INTRODUCTION

Thucholite is a mineral of jet-black color, having a hardness of four (on Mohs scale) and a specific gravity of about 1.8.[4] The chemical composition of the mineral varies widely: it has been reported to contain 40–60 per cent carbon, 20–30 per cent absorbed volatile gases, with the remainder ash.[5] Rare earth oxides, uranium oxide and thorium oxide compose the larger percentage of the ash; smaller amounts of lead, calcium, and magnesium oxides are probably present. Although reported from several regions[4,6,7] thucholite has to the present date been found mainly in pegmatite dikes. It occurs in intimate association with the primary minerals uraninite, feldspar and mica and, according to Ellsworth, appears to be as much a primary mineral as any of these. The discovery of thucholite raises several questions which are of interest from both the chemical and the geological standpoints.

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[4] Ellsworth, Rare-element minerals of Canada, *Canadian Department of Mines, Economic Geology Series*, No. **11**, 178–85 (1932).

[5] Ellsworth, *ibid.*, 266–267.

[6] Ikawa, *J. Chem. Soc. Jap.*, **58**, 1135–1143 (1937).

[7] Spence, *Am. Mineral.*, **15**, 495–520 (1930).

TABLE 1. PROXIMATE ANALYSIS OF PARRY SOUND THUCHOLITE

Volatile gases	26.08%
H_2O (direct)	12.96
Gas by difference	13.12
Ash	28.06
Fixed carbon	45.86
Total	100.00%

TABLE 2. ULTIMATE ANALYSIS OF ASH

Water soluble	1.60%
PbO	0.20
U_3O_8	5.80
ThO_2	48.48
$(Ce, La, Dy)_2O_3$	5.45
$(Yt, Er)_2O_3$	10.95
Fe_2O_3	1.50
V_2O_5	2.25
MnO	0.02
Al_2O_3	1.45
CaO	0.50
ZrO_2	0.80
K_2O	0.15
Na_2O	0.22
P_2O_5	3.21
SiO_2	14.70
Total	97.28%

TABLE 3. VOLATILE GASES (VOLUME PER CENT)

CO_2	6.444%
CO	35.827
CH_4	1.500
H_2	44.498
N_2	3.562
A (includes all rare gases)	0.010
S_2	0.063
Cl_2	0.033
F_2	0.167
H_2O	7.857
Total	99.961%

Thucholite has never been found in intimate contact with any carbon-containing material, either in the form of limestone or organic matter. Assuming that the mineral has undergone no alteration, one apparently must accept the fact that carbon is a primary constituent of the granite magma. It appears as though the sorbed volatile gases would comprise a fair sample of the gases surrounding the magma at the time of crystallization. If one assumes that carbon is a primary constituent of the mineral, it would seem that the original composition of the neighboring uraninite should correspond to the formula UO_2. This question of the original composition of uraninite has been discussed by Ellsworth.[4]

No detailed description of thucholite was made until 1928, when H. V. Ellsworth[8] described the mineral in detail. He investigated the physical and chemical properties and, with the aid of E. S. Shepherd, was able to report on the individual volatile gases sorbed in the mineral. Table 1 lists their results from a proximate analysis of the major constituents of the mineral while Tables 2 and 3 record the detailed results from analyses performed upon the ash and the sorbed gases in the mineral.

TABLE 4. ANALYSIS OF JAPANESE THUCHOLITE

C	30%
SiO_2	20
Volatile constituents	30
Remainder (ThO_2, $R.E._2O_3$, etc.)	20
Total	100%

Since Ellsworth was unable to find a near source for the carbon, either as limestone or organic material, he concluded that thucholite was a primary mineral and that carbon must be a constituent of the original magma. H. S. Spence,[7] however, has reported a very significant occurrence of thucholite and a light oil in the same pegmatite (though at no point in intimate contact).

A mineral similar to thucholite bearing the name "carbo-cer" has been reported by Borneman-Starynkevich.[9] This mineral has approximately the same density as thucholite and upon burning, leaves 25.6% of its weight as ash. A later article by Ikawa[6] reports the presence of thucholite in a Japanese pegmatite; his analytical data are given in Table 4.

PRELIMINARY TREATMENT AND EXAMINATION

The specimen chosen for analysis was part of a suite of minerals obtained from the Besner Mine, Ontario, Canada, through Ward's Natural

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[8] Ellsworth, *Am. Mineral.*, **13**, 419–439 (1928).

[9] Borneman-Starynkevich, *Khibina Apatite*, **6**, 114–118, 270–275 (1933).

Science Establishment. Since the specimen had apparently formed in intimate association with uraninite, it was necessary to separate the two minerals. A density determination using a calibrated pycnometer on a portion of the specimen, however, gave a value of 1.86 g/cc. (taking the density of pure thucholite as 1.77 and of uraninite as 9.0, this would indicate that the specimen was 98.8% pure). The uraninite and thucholite were separated by the well known "sink and float" technique using redistilled 1,2-dibromoethane (specific gravity 2.132) as the liquid medium.

A portion of the separated and dried material was examined qualitatively with a Baird grating spectrograph. Some difficulty was experienced with cyanogen bands in the spectra (due to the large amount of carbon present), since many important lines of the rare earths lie in the region heavily covered by these bands. For this reason neither the rare earths, uranium, thorium, nor calcium can be listed as definitely present on the basis of this examination alone, though all of these are to be expected on the basis of previous work. Only the elements magnesium, silicon, aluminum, beryllium, boron, iron, and lead could be established definitely as present, with yttrium, ytterbium, uranium, thorium, erbium, cerium, neodymium, samarium, and thulium uncertain.

ANALYSES OF VOLATILE GASES

Two different techniques were applied in an effort to identify and determine the volatile sorbed gases. The first method employed a vacuum desorption technique at relatively low temperature (*ca.* 300° C.) in which the gases expelled from the heated and evacuated sample were pulled through a weighed water-collection tube and collected. The weight of water and total volume of gas at atmospheric pressure was determined for a given weight of sample. The gas was then analyzed by successive absorption by various reagents, thus yielding the "percentage-by-volume" composition. The unabsorbable residue (largely nitrogen) was examined spectroscopically in a gas-discharge tube for rare gases.

The second method employed a hot-tube (*ca.* 875° C.) technique in which the gases expelled from a strongly-heated sample were swept by a nitrogen stream through a suitable train of weighed absorbers. This procedure resulted in a "percentage-by-weight" analysis for the volatiles.

In view of the high carbon content of thucholite, it is certainly to be expected that the composition of the gases evolved by the two procedures would differ. The first procedure might be expected to yield results most justifiably interpretable as "absorbed gases" while the high-temperature method, is properly labelled an assay of the "volatile matter." The second procedure had the disadvantage of not permitting the examination of the inert gases for the possible presence of argon, helium, and other inert gases.

A. LOW-TEMPERATURE ANALYSIS OF ABSORBED GASES

Crushed samples of 50 to 120 mg. of thucholite were weighed into platinum micro-combustion boats. The samples were introduced into a Vycor test tube fitted with a ground glass connection to a conventional Toepler pump. A tared Pregl-type micro-absorption tube containing phosphorus pentoxide was located between the sample tube and pump. Samples were evacuated at room temperature to remove small amounts of superficially adsorbed gases and moisture prior to the collection of material and data for each run. During an analysis the sample was heated at 250° to 300° C. (max.) and repeatedly evacuated with the pump until no further measureable volume of gas emission could be detected. The total gases removed were collected over mercury in graduated 10 or 20 ml. tubes and their volumes measured at prevailing temperature and barometer conditions. Dried air was admitted to the P_2O_5 tube, which was then weighed as a measure of the water evolved. The sample was also reweighed at the conclusion of each analysis as a measure of the total percentage of volatile matter by weight.

Despite the fluctuations in experimental conditions between analyses (up to 50° difference in temperature and variations of two to fourteen hours in the total time of evacuation), the concordance of the results which are summarized in Table 5 indicates that data obtained by such a technique are probably as significant as those obtained by the high-temperature procedure.

TABLE 5. THUCHOLITE VOLATILES BY LOW-TEMPERATURE, VACUUM TECHNIQUE

Analysis No.	% by Wt. Volat.	Ml. Gas (STP) per mg. sample	Mg. H_2O per mg. sample
1	26.55%	0.1318	0.150
2	26.30%	0.1333	0.150
3	—	0.1300	0.153
4	26.40%	0.1325	0.151

At the conclusion of each analysis it was noted that a small yellowed area had developed at the head of the P_2O_5 tube and that the mercury surfaces in the Toepler pump and collecting vessel were faintly discolored with black scum. After oxidative dissolution, both materials were examined by suitable selective chemical tests and proved to contain sulfur. It is possible, therefore, that small amounts of either elemental sulfur or hydrogen sulfide were evolved. Chemical analyses on the mineral itself showed 1.13% sulfur and 2.84% phosphorus pentoxide.

While volumes of 8 to 18 ml. of gas were available for the analyses, it was found very convenient to employ the micro gas-analytical techniques evolved by Blacet, Leighton, *et al.*,[10] in conjunction with a horizontal micro gas buret of only 0.083 ml. total capacity. In applying these techniques small glass thimbles are inverted over mercury to serve as the reaction vessels or "gas pipets" while the absorbing reagents are successively introduced to the gas bubble as solid, essentially "dry" beads on small loops of platinum wire. The changed gas volume after each absorption is determined by returning the bubble to the capillary-tube buret. Results are obtained as rapidly and as conveniently as on the macro scale and the accuracy of the microprocedures compares favorably with conventional techniques. Replicate gas analyses could easily be made on the material from a given run when desired.

Table 6 summarizes the analytical data for the volatile gases obtained from four runs. The gas composition appears to be quite uniform under the conditions adopted. The gas sample was lost before analysis #1 could be completed. The results reported under #2 represent the averaged values from duplicate analyses on this sample. In #3 a check was also made for unsaturated hydrocarbons which were found to be absent, or present to less than 0.2 volume per cent. The unabsorbable residues (inerts) from #2 and #3 were examined qualitatively with a spectroscope at pressures of 0.01 to 0.5 mm. in a discharge tube. Several lines due to mercury (the confining liquid in the previous work) and a few weak argon lines were noted. There was no distinction from a spectrum of reduced air (atmospheric air residue with absorbable gases removed in the same fashion) produced under comparable excitation conditions. The "inert" gases from thucholite may be presumed to consist primarily of

TABLE 6. COMPOSITION OF VOLATILE GASES FROM LOW-TEMPERATURE, VACUUM PROCEDURE

Constituent	Percentages by Volume from Run:				Av. of 2, 3, & 4
	#1	#2	#3	#4	
CO_2	20.56	23.16	22.96	23.14	23.09%
O_2	0.74	1.33	1.42	1.38	1.38%
CO	17.1	17.11	17.22	17.26	17.20%
H_2	—	19.38	19.19	19.53	19.37%
CH_4	—	14.96	14.85	14.94	14.92%
inerts	—	24.00	24.36	23.75	24.04%

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[10] An excellent summary of these techniques and citations of the original references will be found in vol. II of Furman (ed.), "Scott's Standard Methods of Chemical Analysis," pp. 2537–2545, van Nostrand, ed. 2, 1939.

nitrogen with a proportion of argon comparable to that in the atmosphere and containing no *major* proportions of other rare gases.[11]

B. COMBUSTION-TUBE ASSAY OF VOLATILE MATTER

The apparatus is shown in detail in Fig. 1. About 200 mg. of the sample was ignited in a combustion boat contained in the quartz tube (*E*) at 875° C. (controlled with thermocouple). The atmosphere of purified nitrogen was prepared from tank nitrogen freed of oxygen by passage through an alkaline pyrogallol solution in (*A*) which was backed with sulfuric acid in (*B*). Traces of organic matter were removed by ignition with cupric oxide in tube (*C*) to form carbon dioxide and water, the latter being removed in the sulfuric acid bubbler and in the Ascarite plus Anhydrone absorption tube at (*D*). Water and carbon dioxide evolved from the sample were removed in the tared absorption tubes (*F*) and (*G*) which contained Anhydrone and Ascarite, respectively. Any carbon monoxide present was reacted with iodine pentoxide in tube (*H*) at 100° C., to form stoichiometric amounts of carbon dioxide and free iodine. Iodine vapor was removed from the gas stream in a bubbler (*I*) containing 10% potassium iodide solution. The resulting moisture was removed with Anhydrone in tube (*J*). The carbon dioxide (equivalent to the carbon monoxide) could then be determined in the tared Ascarite tube (*K*).

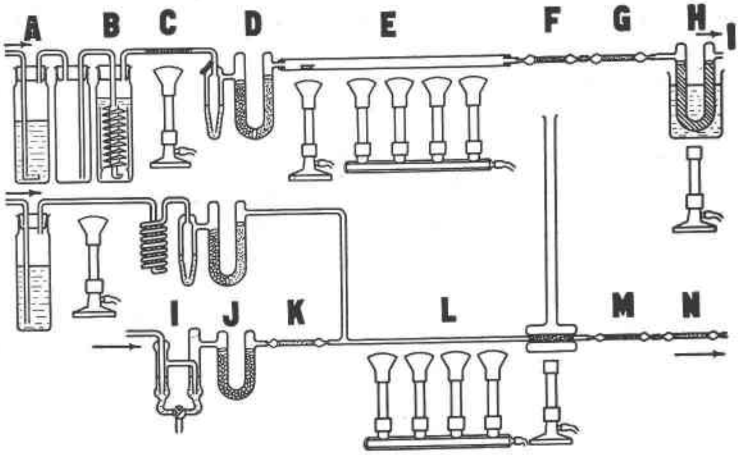

FIG. 1

At this point, a side-stream of purified oxygen gas was introduced into

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[11] These results are not necessarily conclusive as regards the absence of small amounts (yet, perhaps, greater than atmospheric) of He, Ne, etc., since the excitation potentials for these elements are much greater than for N_2 or A.

the system. The gas stream which now contained hydrogen, methane, excess nitrogen, and excess oxygen, was passed through a combustion tube (*L*) yielding water from the hydrogen and water plus carbon dioxide from the methane. These products were determined in the tared absorption tubes (*M*) and (*N*) which contained Anhydrone and Ascarite, respectively.

The surface of the ignited samples showed no visible evidence of change, indicating that little oxidation had occurred. The total percentage by weight of volatile matter found by this technique was 21.07% as the average from three runs. The higher value of 26.4% found by the low temperature, vacuum procedure seems definitely to indicate that the removal of volatile matter, even at a temperature lower by 600°, is appreciably more complete with evacuation. Such a comparison of values, however, takes no account of the possible differences in the chemical changes which may have occurred in the residual sample at 275° as compared with 875°. Table 7 records the composition of the evolved gases as determined by the high-temperature evolution technique.

TABLE 7. COMPOSITION OF VOLATILE MATTER BY HIGH-TEMPERATURE TECHNIQUE

Constituent	Percentage by Weight
CO_2	23.90%
H_2O	46.03%
CO	0.34%
CH_4	15.73%
N_2(A, S, etc.)	13.84% (by diff.)

ESTIMATION OF FREE CARBON

Weighed samples of the mineral were heated in platinum crucibles with free access of air to a final temperature of 1000° C. The weight of ash was determined after constant weight had been achieved. Since the percentage by weight of volatiles had been determined, the free carbon was calculated through the relation,

$$\%\ \text{free carbon} = 100.00 - \%\ \text{volatiles} - \%\ \text{ash}.$$

For this purpose, it seemed preferable to use the higher "% volatiles" figure which was based on Procedure "*A*." Duplicate determinations of ash gave values of 24.15% and 24.11%, averaging 24.13%. Employing the latter value with 26.42% for the volatiles, one calculates 49.45% for the free carbon.

CHEMICAL ANALYSIS OF ASH

The ash from the preceding determinations was assayed for its constituents by standard chemical procedures. These will not be detailed here,

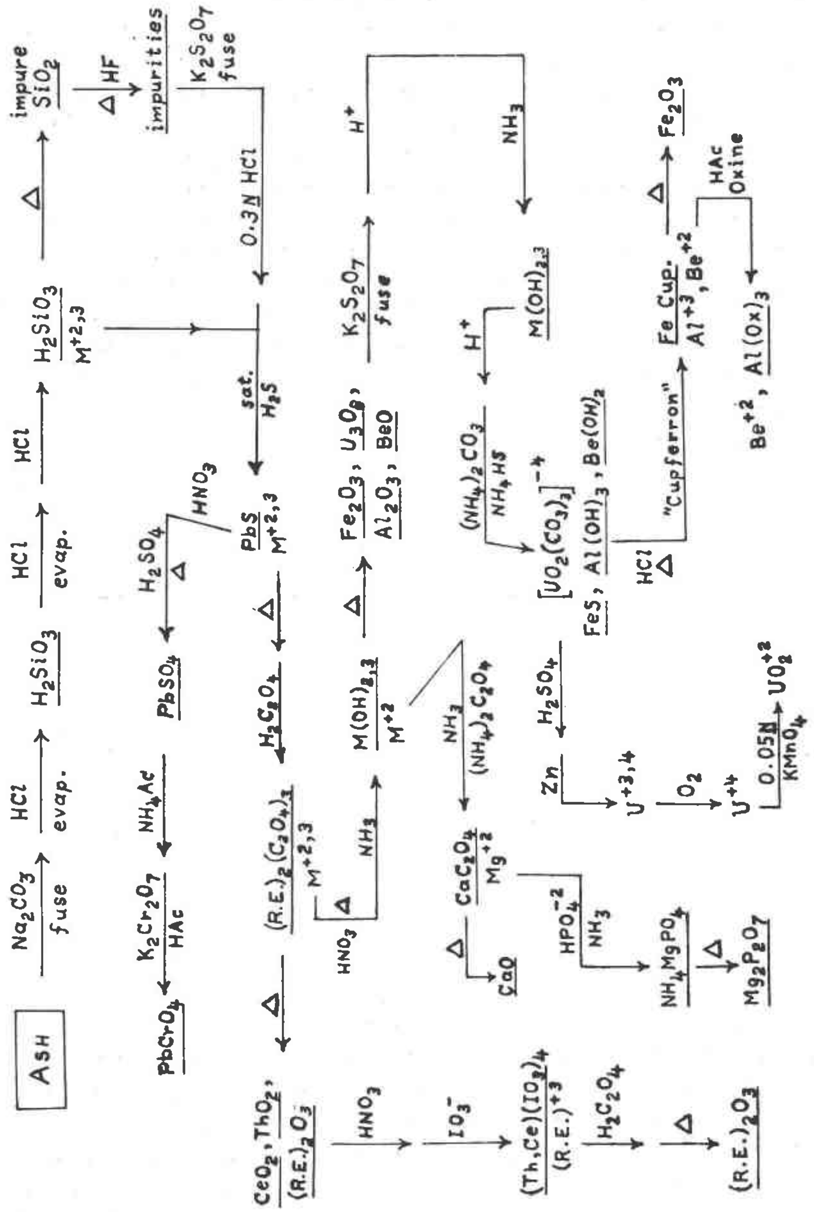

FIG. 2. Schematic flow-sheet for chemical analysis of thucholite ash.

but the separation techniques employed and the determinative forms used may be followed from a study of the diagrammatic flow-sheet given in Fig. 2. Two samples were analyzed. On one of these, the thoria and ceria were separated from the rare earth oxides by precipitation with iodate after which the rare earths were precipitated from the filtrate as oxalate and ignited to oxides; thoria and ceria were estimated by difference. The total rare earth fraction from the other analysis was later employed for the estimation of its individual rare earth content. On both samples, an R_2O_3 group consisting of U_3O_8, Fe_2O_3, Al_2O_3, and BeO was separated and weighed. The uranium, iron, and aluminum were then isolated and determined individually, but beryllia was estimated only by difference. The possible presence of phosphate may have adversely affected the accuracy of the rare earth and/or the R_2O_3 group analyses.

Data from the analyses of the ash are summarized in Table 8. Particular attention should be drawn to the very low value of thoria plus ceria found; this point will be emphasized later.

TABLE 8. SUMMARY OF CHEMICAL ANALYSIS OF ASH

	Sample 1	Sample 2	Average
SiO_2	15.63%	15.41%	15.52%
PbO	1.05	1.01	1.03
ThO_2+CeO_2	0.54	19.77	19.64
$(R.E.)_2O_3$	18.96		
U_3O_8	53.30	52.88	53.09
Al_2O_3	0.98	0.96	0.97
Fe_2O_3	0.58	0.67	0.63
BeO	0.94	1.46	1.20
CaO	5.33	5.66	5.50
MgO	1.93	1.78	1.86
Total	99.24%	99.60%	99.44%

SPECTROGRAPHIC ANALYSIS OF THE RARE EARTHS

The forty-four milligrams of earth oxides resulting from sample #2 were dissolved in 10 ml. of 6 *N* hydrochloric acid; suitable aliquots of the resulting solution were used for a qualitative and quantitative examination of the earths present. Both the 220 v. direct current arc and spark excitation were used in the qualitative examination of the spectra with the Baird grating spectrograph. Abundant yttrium and ytterbium lines were found; these two elements seemed to be the major constituents. Several lines of lutecium were found, and one line each for erbium and thorium (cyanogen bands again covered many of the available thorium lines).

On the basis of the qualitative indications, standard solutions in 6 *N* hydrochloric acid of yttrium oxide and of ytterbium oxide were prepared. The materials used in these standards had been furnished by the late B. S. Hopkins of the University of Illinois, and consisted of high purity yttria and a 96.33% ytterbia material containing 3.67% of other rare earth oxides, principally lanthanum oxide. Arc excitation at 220 v. D.C. and 8 amperes was employed using the Baird grating spectrograph and with 90 second exposures. Standard and unknown solutions were accurately dispensed into pre-arced electrodes. Yttrium lines at 3195.6, 3200.3, and 3203.3 Å were used for the preparation of three yttrium calibration curves. Ytterbium was calibrated on the 3289.4 Å line. The spectra of samples and of calibration standards were recorded consecutively on the same plates. Relative line densities were measured with a spotting microdensitometer and background corrections were applied.

In this manner, values of 2.426, 2.500, and 2.523 mg. per ml. (on 44.0 mg. of sample in 10.0 ml., total volume) of yttrium oxide were found from the three calibration curves. The average, 2.483 mg./ml., gives 56.5% yttrium oxide in the sample. The ytterbium analyses lead to a value of 15.4% ytterbium oxide. These determinations leave a residual 28.1% to be ascribed to erbium oxide, lutecium oxide, thorium oxide, or undetected substances. It should be noted that the previous analyses showed that no more than 0.54% of the ash could be thorium oxide.

DISCUSSION

Goldschmidt and Thomassen[12] have attempted to subdivide the rare earth minerals into classes and subclasses based upon the average content of individual rare earths, Table 9, and this scheme of classification has proved generally satisfactory to the present time. The present variety of thucholite, with a rare earth group consisting almost entirely of ytterbium, would be placed in *Class B*, *Subclass II*, *Type b*, a division composed of rare earth minerals containing a relatively high ratio of ytterbium in comparison to other individual rare earths.

It is interesting, however, to recall the work of Marsh[13] wherein a pitchblende was reported to contain a rare earth group with europium "at least 1000 times more abundant than in a similar mixture of earths from monazite sands, and many times more abundant than in any other known source." In view of the unusual nature of thucholite and pitchblende with respect to this rare earth content, a similarity between the

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[12] Goldschmidt and Thomassen, *Videnskapsselskapets-Skrifter, I, Matemat. natur. Klasse, Kristiania,* No. 5 (1924).

[13] Marsh, *J. Chem. Soc.*, 2387–2388 (1929).

TABLE 9. GOLDSCHMIDT-THOMASSEN CLASSIFICATION OF RARE EARTH MINERALS

Classification	Definition	Rare Earth Content (Total = 110)														
		La	Ce	Pr	Nd	61	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tú	Yb	Lu
Class A	*Complete Earth Content*															
Subclass I.	Cerium earths predominate	9	40	6	24	0	8	0	8	1	6	1?	4	0	2?	1?
Subclass II.	Yttrium earths predominate	4	20	5	20	0	10	0	15	2	10	2?	10	0.1?	7?	2?
Class B	*Selective Earth Content*															
Subclass I.	Cerium earths predominate															
Type (*a*)	Monazite type	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Type (*b*)	Orthite type	12	50	8	24	0	7	0	4	0	ca. 2					
Subclass II.	Yttrium earths predominate															
Type (*a*)	Ytter—Gadolinite type	9	40	6	24	0	8	0	8	1	6	1?	4	0	2?	1?
Type (*b*)	Thortveitite type	2	8	4	6	0	6	0	4	2?	4	1?	4	2?	60	8
Type (*c*)	Xenotime type	1	1	1	2	0	4	0	15	3	18	5?	28	3?	28	6

chemistry of europium and that of ytterbium is of significance. Of most striking importance is the fact that each of these elements may exist as a divalent ion, a property common to only a few of the rare earths. In light of the theory proposed by Ellsworth[8] that the initial composition of uraninite is UO_2, it would appear that the reducing condition within the magma at the time of crystallization might well also reduce any europium or ytterbium to the divalent state. Such a reduction might favor the concentration of the rare earth in the original uraninite. The probable origin of some pitchblendes by oxidative alteration of uraninite fits well into this general concept.

In view of the almost complete absence of thorium oxide in the thucholite specimen analyzed, it appears that a new variety of the mineral thucholite may become recognized as further work confirms this one observation. Previous analyses have never resulted in such low percentages of thorium in any thucholite specimen. Ellsworth,[8] in fact, based the first two letters of the name "thucholite" upon the relatively high content (ca. 50%) of thorium oxide in the ash which he analyzed.

SUMMARY

A relatively complete analysis of a specimen of thucholite has been made. The analysis included the determinations of the oxides in the ash as well as the quantitative spectrographic determinations of certain individual rare earths in the rare earth group.

As a result of the analysis it appears that:

(1) A new species of the mineral thucholite, containing only a trace of thorium, may become recognized.

(2) Another case has been found in which a single rare earth element makes up almost the complete rare earth content of a mineral. It may prove significant that this element, like europium in the similar instance, is capable of existing in the divalent state.

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