URANOTHORITE FROM EASTERN ONTARIO[1]

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ABSTRACT

Uranothorite is found in many deposits of the Grenville sub-province in Ontario and Quebec, and in some mines is an important ore mineral of uranium. Its occurrence, habit, and physical properties are reviewed. Analyses for eleven specimens of uranothorite are presented and variations in analyses and physical properties are discussed.

For chemical analysis, silica was separated by perchloric dehydration and lead by sulphide and sulphate precipitation. Uranium was determined by a cupferron-oxine method, thorium and rare earths via oxalate and "thorin", iron with *o*-phenanthroline, and calcium by oxalate precipitation. Water was determined by a modified Penfield method, carbon dioxide by acid evolution and total carbon by combustion, each on a separate sample.

PART I: OCCURRENCE AND DESCRIPTION (S.C.R.)

Introduction

Uranothorite was first identified and analysed in Canada by H. V. Ellsworth (1927)[4] in specimens from the MacDonald feldspar mine, near Hybla, Ontario. Since that time, it has been identified in many other deposits of the Grenville sub-province of the Canadian Shield, both in eastern Ontario and in southwestern Quebec. In the past four years uranothorite has emerged as a minor ore mineral of uranium in mines of the Bancroft-Wilberforce camp where uraninite is the principal source of uranium. Few additional data on uranothorite in Canada have been published since Ellsworth's original paper.

In the course of a field project on the mineralogy of uranium deposits in the Bancroft-Wilberforce region by one of us (S.C.R.), it became obvious that although uranothorite is an important contributor of uranium in ores of some mines, knowledge of its occurrence and composition was inadequate. This paper presents descriptions and analyses of the mineral and its occurrence as part I, and analytical methods as part II.

Occurrence

Recent descriptions of radioactive deposits in Eastern Ontario may

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[4] References for part 1 appear on page 8.

be found in Satterly & Hewitt (1955), Hewitt (1953) and Rowe (1952). Some analogous descriptions of the occurrence of uraninite in this region may be found in Robinson & Sabina (1955). Six different types of radioactive deposits are recognized in the region. Many of them are transitional one to another, but each type is represented by characteristic examples. Although uranothorite is not the dominant radioactive mineral for any one type of deposit, locally it may be the principal one.

1. Radioactive granite and syenite dykes and lenses are the result in part of replacement processes. Uranothorite as nodular grains is more abundant in the facies that are rich in pyroxene, amphibole or biotite, than in the more leucocratic, magnetite-rich facies. Uraninite is the principal radioactive mineral in both types.

2. Uraniferous metapyroxenites are thought to have been derived by metamorphism of impure limestones, and are often amphibolitic and micaceous. Many of them contain interstitial calcite or scapolite. In these bodies, uraninite is usually the main ore mineral but locally uranothorite predominates. Molybdenite is a common accessory mineral.

3. Calcite-fluorite veins appear to be introduced bodies of coarse-grained calcite and fluorite which locally contain minor amounts of apatite, albite and hornblende. It seems probable that they are equivalent to segregations of calcite and fluorite in pegmatites which have the same mineralogy, but in which calcite and fluorite are often porcelainic in texture and exhibit flow structures. In both the veins and segregations uraninite occurs as euhedral crystals. Uranothorite occurs only as traces in the veins but is found as subhedral crystals in the segregations where it is associated with titanite and marked by iron oxide staining.

4. Although most of the granite and syenite dykes of type 1 (above) are locally pegmatitic, there is also a distinct group of radioactive, partly-zoned, true pegmatites. In these, uranothorite is markedly subordinate to uraninite, particularly in the local, fine-grained, syenitic facies in which uraninite is locally abundant.

5. A distinctive group of deposits, comprising metasomatized zones in limestone are characterized by development of euhedral diopside and phlogopite in salmon-coloured calcite. In these, thorianite or thorian uraninite is the principal radioactive mineral. Despite the similarly high Th:U ratio of these minerals to that of uranothorite, the latter has been recognized in only one of these deposits.

6. Finally, betafite is the main radioactive mineral in the only carbonatite recognized in the region. Other associated minerals are apatite, amphibole and mica. Despite similarity in mineralogy to other radioactive deposits, this carbonatite does not contain uranothorite, and fluorite is present in traces only.

Uranothorite occurs as euhedral crystals in calcite, in pyroxenites and locally in feldspar associated with calcite and pyroxene. It is also found as yellow subhedral crystals developed within euhedral crystals of allanite. Euhedral crystals in a matrix of quartz and feldspar are described by Ellsworth (1927). As subhedral grains, uranothorite also occurs in a quartz and feldspar matrix cementing brecciated pyroxenite at Rockingham Mines. Undoubtedly, however, the large majority of uranothorite in Eastern Ontario occurs as rounded nodular grains in radioactive granites and syenites. Only rarely in these rocks are subhedral grains noted. Locally, masses of uranothorite cement brecciated rock and in such instances embayments and concave cusps of rock between rounded masses of uranothorite suggest replacement by uranothorite.

Uranothorite does occur in calcite and in silicified limey rocks, but it is most abundant in the normally siliceous granites and syenites, in which it is commonly disseminated as discrete grains. It is locally concentrated in sheared zones where it is more typically associated with concentrations of pyroxene than with those of quartz. Accessory minerals whose distribution is commonly similar to that of uranothorite are, uraninite, zircon, titanite, fluorite, magnetite and/or pyrite and pyrrhotite. Films or aggregates of pyrite often envelop uranothorite grains.

Description and Analyses

Euhedral grains of uranothorite are long, slender prisms of square cross-section, some of which are striated longitudinally. Typically the ends of the crystals are rounded and lack terminal faces, although Ellsworth (1927) reports termination by the basal pinacoid, and Satterly (personal communication) has recognized pyramids on crystals from one locality.

Uranothorite varies in lustre from almost sub-metallic to vitreous and sub-resinous. In colour, it varies from light yellow through red and brown to black. In some specimens a mottled red and yellow colour may be observed under a hand lens. Powdered uranothorite varies from almost white through light brown to dark grey. Under the microscope, even the best of crystals appear to be mottled due to flocculent red and black areas in basically light yellow or reddish-brown uranothorite.

Uranothorite is exceptionally brittle and slimes easily. As a result, hardness is difficult to assess but it is roughly 4 to 5. Uranothorite breaks with subconchoidal fracture, cleavage is absent, but locally fragments display platy habit. Specific gravity varies from 4.0 to 4.5 and there is some variation between fragments from the same sample. All uranothorite from the region is isotropic and the index of refraction varies from 1.66 to 1.71 with a maximum range of 0.02 within a single sample.

The magnetic susceptibility of uranothorite is uniformly less than that of allanite and hornblende and generally is less than that of uraninite. Using a Frantz Isodynamic Separator, with slope 10° and tilt 10°, 9 samples were tested. With one exception, all required more than 0.9 amp. before starting to come off, and two proved to be effectively non-magnetic. One exceptional sample showed a wide range of susceptibility, beginning to come off at 0.5 amp. Radioactivity of uranothorite, as indicated by NTA 54 Mu nuclear track plates, is roughly one quarter as great as that of average uraninite.

Miscroscopic examination reveals that all uranothorite from the region is traversed by a three-dimensional network of curving fractures. In some specimens these are observed only under magnifications of more than 200 diameters. Several specimens exhibit two separate networks, one being much more coarse-grained than the other. The width of the cracks themselves is too small to be measured and none have been observed that exceed 1 micron. Films of reddish colour and others grey to black in colour occupy these cracks and are responsible for the mottled appearance in thin section of megascopically homogeneous uranothorite. Fine-grained aggregates of pyrite and magnetite have been observed both as films in these cracks and rarely, as other inclusions in uranothorite. Despite the suspicion that uraninite might also occur as an inclusion, none has ever been identified by *x*-ray methods.

In the deposits of Eastern Ontario, most uranothorite is metamict. Specimens from two deposits, however, yielded sharp *x*-ray patterns indistinguishable from those of uranium-free thorite. A few other specimens yielded weak thorite patterns indicating that they are partly metamict. These specimens after heating gave sharp thorite patterns. Metamict uranothorites were heated for 5 minutes in a dynamic vacuum of 0.1 mm. Hg. to *circa* 1000° C. Resulting *x*-ray patterns were face-centred cubic, composed of lines that are characteristically indistinct but which correspond to those of thorianite (see Berman (1955), Pabst (1951)). A weak huttonite pattern is usually superimposed on the thorianite pattern and prolonged heating strengthens the huttonite lines at the expense of those of thorianite. In contrast to uranothorite, the few crystals of uranium-free thorite from the district, although no longer homogeneous, yield sharp thorite patterns without heating.

Before heating, metamict uranothorite often yields patterns of pyrite and/or magnetite and galena, but these patterns disappear after uranothorite is heated. Pyrite and magnetite can usually be identified under the microscope as inclusions, but galena has not been recognized. It seems likely that the galena is very fine-grained and occurs as part of the black films in some uranothorite.

The following eleven samples of uranothorite were hand picked under the binocular microscope for chemical analysis. Every care was taken that the material picked for analysis was megascopically pure as seen at a magnification of 15 diameters. It is impracticable to attempt to secure microscopically-pure material because contamination on a microscopic scale is present in the network of cracks.

1. Topspar Fluorite Mines Ltd., east wall of adit, 10 feet south of portal. Massive black uranothorite cementing fractures in pyroxene and feldspar and occurring as subhedral grains in calcite.
2. Bicroft U.M.L., Adit level, No. 2 dyke, sta. 301, massive brown to black uranothorite in pyroxene-rich part of dyke.
3. Roford Property, Monmouth Twp., Conc. XIII, lot 13, Prisms of black uranothorite in calcite segregation of a lens of pegmatite.
4. Fission Mines Ltd., eastern trenches. One cigar-shaped crystal of sub-metallic to pitchy uranothorite in calcite-fluorite segregation.
5. Kenmac Chibougamau U.M.L., No. 1 showing. Black subhedral to massive uranothorite in feldspar-calcite pod.
6. Red, massive uranothorite, same occurrence as 5.
7. Sebastopol Twp., Conc. C, lot 39. Black uranothorite in leucogranite pegmatite.
8. Silanco M. & S. L. property, Monmouth Twp., Conc. VI, lot 32. Black uranothorite in pegmatite facies of pink granite.
9. Red uranothorite from same occurrence as 8.
10. Bicroft U.M.L., 150′ level, 101 NE drift, 30′ S. of sta. 367. Yellow to brown, massive to platy uranothorite.
11. Rockingham Mines Ltd., Brudenell Twp., Conc. X, lot 24. Black subhedral uranothorite in leucogranite cementing brecciated metapyroxenite.

Discussion

There is marked variation in the physical properties of uranothorites from Eastern Ontario. The range in colour from honey yellow to black is thought to be attributable to inclusions in the microscopic reticulate fracture pattern in part, although it is possible that the colour may also be due to variation in the valence state of iron or uranium (*see* Ellsworth, 1932, pp. 205, 211). Certainly there is a tendency for black uranothorite to bleach around its margins where it is found in partly weathered deposits. Such bleached material may be transitional to the thorogummite of Frondel (1953). Equivalent variation is found in magnetic susceptibility of uranothorite which may be due to inclusions or to the valence state of iron.

Variations in specific gravity are probably attributable in part to variation in the degree of reticulate fracturing and in part to different microscopic inclusions. There is a decrease in index of refraction generally as minerals become increasingly metamict and it seems logical to suppose that the reticulate fracturing in uranothorite is associated with destruction of the originally ordered crystalline state. Certainly those specimens exhibiting maximum fracturing do have the lowest indices of refraction, due possibly, to inclusions of low index material in the fractures.

Analyses of the eleven uranothorites show satisfactory uniformity in content of the SiO_2, H_2O and, for most samples, in the total ThO_2+ U_3O_8+ total rare earth oxides. There is marked variation in content of PbO which is thought to be largely radiogenic. Ellsworth (1927) has commented on the relatively low $Pb/(U+0.38\ Th)$ ratio for uranothorite as compared with the same ratio for uraninites from the area; our work corroborates his findings. Loss of parent radon gas through the fractures could account in small part, for the relatively low content of radiogenic lead in uranothorite, but the half life of thoron, the equivalent gas in the thorium decay chain, is so short that it is unlikely to escape in significant amount. It seems more likely that the radiogenic lead being loosely bonded in the structure may have been selectively leached through the network of fractures. It is significant that galena is quite commonly detected by x-rays in metamict uranothorite; and if sulphur could find ingress to react with the lead, some of the lead may well have been removed in the process by the same channels. The iron content is fairly variable and, in part, is due to microscopic inclusions of iron oxides but lack of an x-ray pattern of any known iron compound indicates that most of the iron is probably an integral component of the mineral. Calcium, too, is likely to be a normal component of uranothorite because it is reported to substitute for uranium and thorium in other minerals, and because no calcium mineral has been found in sufficient amount to account for more than 0.7% CaO in the analyses.

Five samples were analysed for CO_2 and for free carbon. The CO_2 content in them ranges from zero to 0.54% and is probably due to traces of calcite. The non-carbonate carbon varies from 0.25% to 0.59% and is highest in black uranothorites and lowest in brown and red ones. It seems probable that this carbon may be present as microscopic films of hydrocarbon in the fractures. Traces of black included matter of low specific gravity were isolated but did not yield an x-ray powder pattern. It is interesting to find that small but significant traces of non-carbonate carbon are present, thus extending the previously known association of carbon with radioactive minerals.

Comparisons of physical measurements and chemical analyses of uranothorites from Eastern Ontario with those reported in Doelter (1918, p. 229), Ellsworth (1927), Hutton (1950) and Phair & Shimanato (1952) show good general agreement although variation in the uranium/thorium ratio is wider for Eastern Ontario samples than for those from other localities.

TABLE 1. PARTIAL ANALYSES OF URANOTHORITES

Analyst—Sydney Abbey

	1	2	3	4	5	6	7	8	9	10	11	Average
SiO_2	19.73	20.84	17.62	17.80	19.20	19.32	20.40	19.18	18.83	21.06	19.81	19.44
PbO	1.58	3.16	1.27	1.46	0.64	0.50	3.62	1.23	1.03	3.48	1.72	1.79
U_3O_8 (note)	13.94	12.31	5.78	11.32	11.72	10.83	10.73	9.00	1.68	15.09	20.73	11.19
ThO_2	46.78	43.49	57.55	49.08	51.56	48.29	49.92	52.42	58.98	39.46	40.37	48.90
Rare Earths	3.99	<0.2	1.69	1.66	<0.2	2.05	0.41	<0.2	<0.2	<0.2	<0.2	—
Fe_2O_3 (note)	0.36	2.70	3.89	3.42	3.96	2.40	2.44	2.74	3.96	2.26	0.20	2.58
CaO	5.75	3.29	2.42	2.30	2.16	2.59	2.79	2.37	3.32	3.88	5.17	3.28
H_2O	9.72	11.1	9.54		9.3	11.1	9.48	9.75	8.92	11.08	9.88	9.99
C		0.24			0.1		0.31	0.59	0.25			
CO_2		0.04			nil		0.19	0.26	0.54			
S.G.	4.33	3.98– 4.13	4.41		4.37	4.20		4.34	4.48	4.1	4.3	
n		1.655– 1.67	1.685		1.685	1.68		1.695	1.715	1.665	1.705	

NOTE: Total uranium and iron contents calculated as U_3O_8 and Fe_2O_3 respectively. The valence states of these elements were not determined (see page 9). Limited supply of sample prevented more complete analyses.

Results of this work confirm the status of uranothorite at least as a varietal name. Its occurrence as a primary mineral is in sharp contrast with that of thorogummite (Frondel, 1953), from which it is also distinguished when not metamict by its *x*-ray diffraction pattern. Uranothorite differs from thorite, in its habit of long slender prisms compared with typically tabular crystals of thorite in this locality, and in the fact that it is usually metamict whereas thorite usually is not. In two deposits 'thorites' with markedly differing uranium content have been found, one instance of which, is represented by samples 8 and 9 of Table 1. These factors suggest the possibility that uranothorite and thorite may be distinct mineral species. However, uranothorite, when not metamict, has a crystalline structure indistinguishable by *x*-ray powder diffraction patterns from thorite, and, as indicated by analyses of Table 1, there seems to be transition in composition between the two. It is concluded that uranothorite is a useful varietal name to be applied to uranium- and water-rich thorite.

Acknowledgments

It is with particular pleasure that we record our appreciation of the kindness of Dr. J. Satterly of the Ontario Department of Mines who supplied many of the best samples for analysis. Analytical results are largely dependent on the painstaking care with which samples were hand picked under the microscope by Miss N. Brown and Messrs. P. Lavergne, L. McConnell and J. Read. Miss Brown made the magnetic susceptibility tests and Miss A. P. Sabina made and interpreted the *x*-ray powder patterns. To these colleagues and to Mr. H. R. Steacy for suggestions and assistance we tender grateful acknowledgment.

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PART II. THE CHEMICAL ANALYSIS OF URANOTHORITE (S.A.)

The samples were analyzed for silica, lead, uranium, thorium, total rare earths, iron, calcium, total water, carbon dioxide and carbon. Analytical methods were selected with a view to avoiding both the large separate samples commonly used in assaying ores, and the cumulative errors inherent in the classical "complete analysis" schemes (*e.g.* Schoeller & Powell, 1955).

In the general scheme adopted (see Fig. 1) silica and lead were first separated successively from the original sample. Three aliquots were taken from the filtrate from the lead separation: one for uranium, one for thorium and rare earths, and one for iron and calcium.

Analyses for total water, carbon and carbon dioxide were done by Dr. J. A. Maxwell of the Geological Survey of Canada. Total water was determined by a modified Penfield method, carbon dioxide (presumably from carbonate) by acid decomposition of the sample, absorption and weighing. Total carbon was obtained by weighing the carbon dioxide evolved on ignition of the sample, mixed with an oxidant, in the presence of oxygen. The difference between the two carbon dioxide percentages was calculated as carbon (Maxwell, 1956).

No attempt was made to resolve the two valence states of uranium and iron. Many of the older analysts reported the two valence states of both of these elements, presumably by means of the classical hydrofluoric acid attack (Smith, 1877), in which it was assumed that hexavalent uranium and trivalent iron go into solution, while the ions in the lower valence states of both elements remain with the residue. The validity of this separation has been questioned by several authors (*e.g.* Wells 1928), who recommended decomposing the sample with sulphuric acid in a sealed tube, and determining the "reducing power" of the mineral by oxidimetric titration. This procedure is apparently still in use (Levine, 1956), but becomes less reliable in the presence of significant amounts of iron. An oxidimetric determination of uranium and iron in the same solution has also been described (Bricker & Sweetser, 1953). Application of such methods in this work would have been complicated by difficulty in obtaining a solution in which the valence ratios of uranium and iron were the same as in the original sample, by possible reactions between trivalent iron and tetravalent uranium, and by the presence of carbonaceous matter.

The reproducibility of results was within 0.2 per cent of the sample on most major constituents. Thorium and rare earths, however, may show negative errors exceeding one per cent in some cases, due mainly to solubility losses in the oxalate separation. Attempts were made to apply several different oxalate procedures (Carron *et al.*, 1955; Hagiwara, 1955; Kall & Gordon, 1953), but results were low and variable in all cases.

Decomposition of the Sample

Wherever possible, duplicate one-gram samples were taken for the general analysis. The sample was decomposed by heating with nitric acid, followed by hydrochloric. Treatment with nitric acid alone leaves a brownish residue, which was thought to contain some of the iron in the sample. Separate analyses of the nitric-soluble and -insoluble fractions of one sample showed, however, that the residue consists almost entirely of silica.

Determination of Silica

Silica was separated in the usual manner by double dehydration with perchloric acid. The residue was ignited and weighed before and after volatilization with hydrofluoric acid. The residue from the latter operation was small enough to be ignored.

Determination of Lead

The evaporated filtrate (Fig. 1, (A)) from the silica separation was reduced with sulphur dioxide at an acidity of $2N$, and the excess reductant removed by boiling. Lead and other sulphides (if any) were precipitated with hydrogen sulphide, starting in hot solution, and ending in a cooled solution, with acidity reduced by dilution to $1N$, in the presence of filter paper pulp.

There may be some doubt regarding the completeness of recovery of lead sulphide at so high an acidity (Smales, 1948), but lower acidities might cause some loss of uranium, thorium, or iron (Marble, 1937). The latter author also stated that milligram quantities of lead may be recovered as the sulphide in $1N$ acid. Our experience has agreed with his view.

The sulphides were left overnight in a stoppered flask, filtered and washed in the usual manner. Precipitate and filter paper were then digested with nitric acid to dissolve the sulphides and to decompose the paper. The last traces of organic matter were destroyed with fuming nitric acid, and the residue fumed twice with sulphuric acid. The sulphates

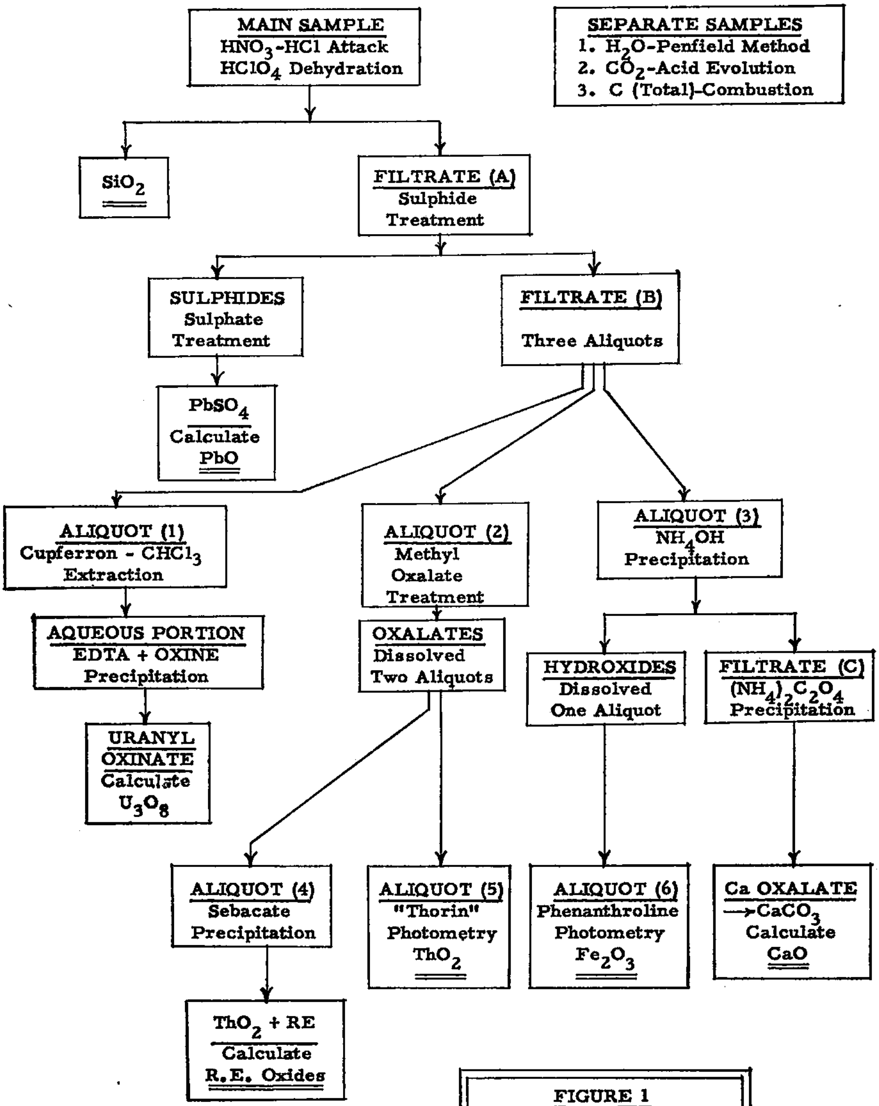

FIGURE 1

CHEMICAL ANALYSIS OF URANOTHORITE

were taken up with water, and sufficient 95 per cent ethanol added to bring the alcoholic concentration to 65 per cent.

After overnight digestion, the lead sulphate was filtered on a fine-porosity sintered-glass filtering crucible, washed with 95 per cent ethanol, dried and weighed. Hot ammonium acetate was then passed through the crucible to redissolve the lead, the crucible was washed with hot water and ethanol, dried and weighed again. The loss in weight was taken as lead sulphate, and lead calculated on an assumed mean atomic weight of 207.

Determination of Uranium

The filtrate (Fig. 1(B)) from the sulphide separation was boiled free of excess hydrogen sulphide and re-oxidized with nitric acid. An aliquot (Fig. 1, (1)) was taken to fumes with perchloric acid and interfering elements were separated from the diluted solution by extraction of their cupferrates with chloroform (Sill & Peterson, 1952). Excess organic matter in the aqueous portion was destroyed by evaporating almost to dryness with nitric and perchloric acids.

The residue was diluted, and ethylenediaminetetracetic acid, disodium salt, was added to mask any remaining interferences (Sen Sarma & Mallik, 1955). The solution was neutralized and buffered to *p*H 5.3, and uranium was precipitated with 8-hydroxyquinoline. After several hours' digestion, the precipitate was filtered on a medium-porosity sintered-glass filtering crucible, washed with dilute hydroxyquinoline solution, dried and weighed.

Determination of Thorium and Rare Earths

A measured volume of standard lanthanum solution, containing 20 mg. of lanthanum oxide, was added to another aliquot (Fig. 1, (2)) of the sulphide filtrate, and the whole evaporated almost to dryness. The residue was diluted, adjusted to *p*H 2 with sodium hydroxide, and thorium and rare earths were precipitated with methyl oxalate and oxalic acid (Kall & Gordon, 1953).

After digestion in a refrigerator at 5 to 10°C for 36 hours, the oxalates were filtered, washed with cold dilute oxalic acid, and redissolved by evaporating precipitate and filter paper with nitric and perchloric acids. The precipitation, digestion, filtration and re-solution were then repeated.

Thorium plus rare earths were precipitated from an aliquot (Fig. 1, (4)) of the resulting solution by the ammonium sebacate method (Carron *et al.*, 1955), ignited, and weighed, with a correction for the added lanthanum.

Thorium alone was determined on another aliquot (Fig. 1, (5)) of the solution obtained from the redissolved oxalates, using the "thorin" reaction (Byrd & Banks, 1953) and a simplified differential spectrophotometry technique (Beroza, 1953). The small amounts of rare earths in these samples caused no interference in the photometric thorium determination.

Rare earths were calculated by difference from the results of the preceding determinations. The thorium-rare earth oxide mixture was also analyzed qualitatively by *x*-ray fluorescence to determine which rare earth elements, if any, were present.

Determination of Iron

Ammonium hydroxide was added to another aliquot (Fig. 1, (3)) of the sulphide filtrate to *p*H 10, plus 5 ml. excess. This high *p*H was used to ensure precipitation of thorium and rare earths (Carron *et al.*, 1955) and thus to avoid their possible interference in the subsequent calcium determination. After a half-hour digestion, the precipitate was filtered, washed with dilute ammoniacal ammonium nitrate solution, and redissolved by evaporating precipitate and filter paper with nitric and perchloric acids. The precipitation, digestion, filtration and re-solution were then repeated. An aliquot (Fig. 1 (6)) of the resulting solution was taken almost to dryness to remove excess perchloric acid, taken up with water, and analyzed spectrophotometrically for iron, using orthophenanthroline (Fortune & Mellon, 1938).

Determination of Calcium

The combined filtrates (Fig. 1, (C)) from the ammonia precipitations were acidified with nitric acid and evaporated to destroy the bulk of the ammonium salts. Calcium oxalate was precipitated from the resulting small volume (Kolthoff & Sandell, 1953), digested for several hours, filtered and washed with dilute ammoniacal ammonium oxalate solution. The precipitate was ignited at a low temperature, treated with a little ammonium carbonate, heated at 300°C, and finally weighed as calcium carbonate.

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