[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MISSOURI, AND THE NEW MEXICO NORMAL UNIVERSITY]

The Determination of Uranium, Thorium, and Lead in Thucholite[1]

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Thucholite was first described and named by Ellsworth[2] in 1928. This is a radioactive carbon mineral which was found in the Parry Sound district, Ontario. Associated with the thucholite is cyrtolite. In his bulletin, Ellsworth[3] describes thucholite on page 46, and gives a more detailed description of the mineral and its occurrence on pages 178–187. Spence[4] tells of the occurrence of the thucholite at Henvey, Parry Sound District, including in his article, photographs of the quarry and of individual specimens of nodular and also pseudomorphic thucholite.

Specimens of nodular thucholite totaling about 47 g. which had originally been supplied by Spence, were sent to the writer by Lane. There are still so many unsolved problems concerning thucholite, that it was thought possible that an age determination by the lead–uranium method would throw some light on a few of these questions, especially those geological questions as to how and when thucholite was formed; also if thucholite is suitable as an age indicator by the lead–uranium method. This also afforded an opportunity to compare some of the analytical methods involved in this sort of a determination. After the analysis of this nodular thucholite was well under way, H. S. Spence sent a few of the almost perfect cubic crystals, which are regarded as pseudomorphs after uraninite. These were analyzed later to determine the relative concentration of thorium and uranium for comparison with the nodular variety.

Analytical Methods

Two samples of the nodular thucholite (ground in an iron mortar and passed through an 80-mesh sieve) were taken for analysis, one of 20 g. and the other 19 g., using most of the available material. The usual care was taken to avoid contamination.

The samples were decomposed and organic matter oxidized with nitric and sulfuric acid. Silica was removed in the usual manner with hydrofluoric acid.

Lead.—Most of the lead was separated as the sulfate, and recoveries made from filtrates (to which a small volume of copper sulfate solution had been added) as the sulfide. All were converted to sulfates, and finally dissolved in nitric acid and taken to the sulfate with sulfuric acid in a weighed crucible. After weighing, these sulfates were purified and corrections applied. A blank on the reagents, which was taken along with the sample was also subtracted.

The filtrate from the lead determination was divided carefully into separate samples for the uranium and thorium determinations. After precipitation with ammonium hydroxide and solution in hydrochloric acid, the rare earths and thorium were separated from the uranium by careful precipitation as oxalates with oxalic acid.

Uranium.—The filtrate from the insoluble oxalate was treated with ammonium carbonate and ammonium hydroxide till alkaline and then hydrogen sulfide passed into it. After filtering, the precipitate was dissolved in hydrochloric acid and the precipitation repeated. The precipitate was discarded. The united filtrates made acid with hydrochloric acid were concentrated to a small volume, and then nitric acid added to decompose the ammonium salts and the oxalates. It was then taken to dryness and dissolved in nitric acid. At this point in the analysis, the samples were again divided. This made the samples from which the uranium was finally determined equivalent to 1 g. of the original thucholite sample. Six of the samples, after the usual preliminary separations, were precipitated with carbonate-free ammonium hydroxide. After ignition the residue was weighed as U_3O_8.[5] The other four were analyzed by the phosphate method[6] and weighed as the pyrophosphate, $(UO_2)_2P_2O_7$. The final residues were in each case tested for impurities.

Thorium.—The oxalate precipitate was dissolved in nitric acid and evaporated to dryness on the water-bath. It was then taken up with concentrated nitric acid and again evaporated to dryness on the water-bath. This was done a third time.

Two of these samples were taken for analysis by the peroxide method as described by Fenner,[7] which consists essentially in precipitating the thorium with hydrogen peroxide from a neutral solution of ammonium nitrate, and then igniting, in a crucible, this precipitate to the oxide. The other two samples were taken by the iodate method,[8] in which the thorium is precipitated with potassium iodate in a strong nitric acid solution, and then the precipitate dissolved in hydrochloric acid, from which the thorium is precipitated with ammonium hydroxide. This precipitate was dissolved in hydrochloric acid and then the

(1) This work is a portion of a project assisted financially in part by a grant from the National Research Council.

(2) Ellsworth, *Am. Min.*, **13**, 8, 419–41 (1928).

(3) Ellsworth, "Rare-Element Minerals of Canada," Geological Survey, Department of Mines, Canada.

(4) Spence, *Am. Min.*, **14**, 11, 499–520 (1930).

(5) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 368.

(6) Muench, *Am. J. Sci.*, **25**, 487 (1933). This reference gives the details of the method.

(7) Fenner, *ibid.*, **16**, 369 (1928).

(8) Method of Meyer and Speter as given by Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, 1929, p. 420.

thorium precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed. In this way a check was obtained by the use of two different methods.

Results of Analyses

The two samples of 20.0000 and 19.0000 g. yielded an average of 0.186% lead, with a maximum deviation of 0.002 from the average. The uranium determinations were made with 1-g. samples; the six samples in which the residue was weighed as U_3O_8 resulted in an average of 4.63% uranium, with a maximum deviation from this average of 0.03 and an average deviation from this average of 0.02. The four samples in which the phosphate method was used also resulted in an average of 4.63%, with an average deviation of 0.015 from this average. The four 5-g. samples used in the thorium determinations yielded an average of 0.903% thorium with an average deviation of 0.0045% from the average. In the analysis of the first two samples for thorium, the peroxide method was used, while in the last two, the iodate method was followed. The silica was 4.53%, and the ash, 21.52%. Lead-uranium ratio

$$\frac{\text{Ra G}}{\text{U} + 0.36\ \text{Th}} = \frac{0.186}{4.63 + 0.36 \times 0.903} = 0.0376$$

Analysis of Two Crystals of Thucholite[9]

Crystal no.	Weight, g.	Uranium, %	Thorium, %
1	1.6657	1.22	4.51
2	1.3530	1.26	3.91

The samples were too small for an accurate quantitative determination of the lead, which was present in small quantities.

Estimation of the Approximate Age of the Mineral.—In the absence of an atomic weight determination of the lead, and assuming that there is no ordinary lead present, besides no replacement having taken place, the approximate age calculated from the lead-uranium ratio is

$$\frac{0.038 \times 1.15 \text{ million years}}{1.57 \times 10^{-4}} = 278 \text{ million years.}$$

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Conclusion

The lead-uranium ratio of the thucholite is 0.038, whereas that of the cyrtolite[10] from the same mine is 0.019. The percentage of uranium in the nodular variety is almost four times as much as in the crystals. On the other hand, the percentage of thorium is four to five times as great in the crystals as in the nodular thucholite, indicating a possibility of a concentration of thorium in the crystals and either a leaching of the uranium or else a replacement of the uranium by the carbon mineral. If there is selective replacement of some of the elements by the carbon mineral, as these results seem to indicate, then thucholite is not suitable and lead-uranium ratios on it are of little value for the basis of an age determination by this method.

Two different methods of analysis for the uranium determination gave identical results. Similarly, in the thorium determination, from the two different methods, practically the same results were obtained, indicating that either method, if carefully carried out, is reliable for work of this character.

Dr. A. C. Lane, after reading this article, writes: "The variation in the lead ratio between the crystal pseudomorphs and the massive thucholite, in particular the enormous difference in the ratio of uranium to thorium, is consistent with the idea that reducing solvents like oils extract the uranium more readily than the thorium, and apparently also the lead, and the variation in lead-uranium ratios between the thucholite, the cyrtolite, and the uraninite, indicates that the deposit was *or is* undergoing alteration, so that the age ratios are of little value. It would be interesting to see by direct determination of radium, to what extent the radioactive series have reached equilibrium. The source of the hydrocarbon, whether tried out of the Grenville limestone, or the result of overthrust faulting on paleogenic limestones, are geologic questions.

It will be noticed that the recent studies by C. M. Alter and F. Hecht (Report of N. R. C. Committee on Geologic Time, 1937) also tend to show an alteration of the outside of crystals by removal of uranium and lead, if black and reduced."

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(9) The entire crystals were dissolved and analyzed. H. S. Spence describes them as follows: "Thucholite . . . perfect crystals after uraninite. Besner Mine, Henvey Tp. Parry Sound, Ontario. These are probably as good as any to be had. Though I have larger, but no more perfect." Spence [*Am. Min.*, **15**, 11, 507 (1930)] writes, "In contrast to the nodular and massive thucholite, which becomes friable and breaks up rather readily on weathering, the crystal thucholite is fairly compact and resistant to the weather." The crystals were fairly resistant to the action of concentrated sulfuric and nitric acids. The nodular thucholite was much easier to decompose.

(10) Muench, THIS JOURNAL, **58**, 2433 (1936).