that acrolein splits off first and then the molecule breaks down to give heptaldehyde. The latter reaction requires a higher temperature.

KINGSTON, R. I. RECEIVED JULY 21, 1936

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

The Lead–Uranium Ratio of Henvey Cyrtolite[1]

BY O. B. MUENCH

In September, 1931, Dr. H. V. Ellsworth of the Department of Mines, Canada, sent a lump of cyrtolite obtained from the Besner Mine, Henvey Township, Ontario, to the University of Missouri. At that time work on the Hybla Cyrtolite[2] was planned and partly under way, so it was found impossible to do more than a little preliminary work on the Henvey Cyrtolite. Work on this cyrtolite was carried to definite results during the summer of 1935. A lead–uranium ratio on this cyrtolite is interesting for comparison with the one on a Besner Uraninite[3] which has been available for some time.

The occurrence of this cyrtolite and its mineral associates are described by Spence[4] and also Ellsworth[3] (p. 173).

The Sample.—The sample was mostly in one large piece with feldspar at one end. It was very homogeneous, of black pitchy luster and seemed to be altered very little, if any. Only the black homogeneous part was taken, and pulverized in an iron mortar until all of it passed through an 80-mesh sieve. This sieve had no solder from which contamination might be derived. The pulverized sample of cyrtolite weighed 242 g.

Methods of Analysis

In general, the procedure followed in the determination of the uranium, after the sample was in solution was as follows. The zirconium and hafnium were removed as phosphates in acid solution, and then after the removal of the iron, etc., as sulfides in ammonium carbonate solution, the uranium was precipitated as the phosphate in a solution slightly acid with acetic acid. The phosphate method was used because phosphate had been introduced in the removal of the zirconium and hafnium and it was therefore the most direct method to follow. The thorium, after the sample was in solution, and the zirconium and hafnium had been removed by precipitation as phosphates in sulfuric acid solution, was precipitated as the oxalate in oxalic acid solution. Two different methods were followed from this point on. In the peroxide method, the oxalate was converted to the nitrate and the thorium precipitated with hydrogen peroxide from a neutral solution of ammonium nitrate. The precipitate on ignition changes to the oxide. In the iodate method, the oxalate was first converted to the nitrate, and then precipitated with potassium iodate in strong nitric acid solution. The iodate precipitate was dissolved in hydrochloric acid and the thorium precipitated with ammonium hydroxide. Finally this precipitate was dissolved in hydrochloric acid and then the thorium precipitated with oxalic acid. The oxalate was ignited to the oxide and weighed. The lead was determined by the usual procedure of separation as a sulfide, conversion to a sulfate, extraction with ammonium acetate and final precipitation as a chromate.

Uranium.—One-gram samples were fused with sodium peroxide (which oxidized all the carbon) in a nickel crucible. The fused samples were then dissolved in hydrochloric acid, baked in a porcelain dish, taken up with dilute hydrochloric acid and filtered. The residue, after volatilization with hydrofluoric and sulfuric acids, was added to the filtrate. The solution was made alkaline with pure ammonium hydroxide. After three precipitations with pure ammonium hydroxide, the precipitate was dissolved in 30 ml. of concd. sulfuric acid. From this point on, the procedure as given in the paper, "The Age of a Canadian Cyrtolite,"[2] near the bottom of p. 489 was followed.

Thorium.—Five-gram samples were taken for analysis. The method as given in the above

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[2] Muench, *Am. J. Sci.*, **25**, 487 (1933).

[3] Ellsworth, "Rare-element Minerals of Canada," Geological Survey, Department of Mines, Canada, Series, No. 11, 1932, p. 268.

[4] Spence, *Am. Min.*, **15**, 11, 513 (1930).

paper[2] was followed, except that after the treatment with hydrofluoric acid the samples were treated with nitric and sulfuric acids and heated to fuming in order to remove carbon. After the samples were taken to the point described at the bottom of p. 491, two samples were analyzed by the iodate method.[5] The third sample was analyzed by Fenner's[6] modification of the peroxide method. His method was followed for this sample from p. 376, when the residue is taken up with 100 ml. of 20% ammonium nitrate solution.

RESULTS OF ANALYSES

Uranium

Sample, g.	$(UO_2)_2P_2O_7$, g.	Uranium, %
1.0068	0.0268	1.77
1.0090	.0283	1.87
1.0025	.0278	1.85
1.0002	.0273	1.82
2.0003	.0545	1.83
	Average	1.83

Thorium

Sample, g.	ThO_2, g.	Thorium, %
5.0100	0.0007	0.01
5.0010	.0008	.01
5.0012	.0007	.01
	Average	.01

Lead

Sample, g.	$PbCrO_4$, g.	Lead, %
30.0000	0.0165	0.035
10.0000	.0059	.037
10.0000	.0058	.037
10.0000	.0057	.036
	Average	.036

SULFUR DETERMINATIONS (SUMMARY)[7]

Total sulfur, %S	Soluble sulfates, as %S	Insoluble sulfides, pyrite, etc., %S	By difference soluble sulfides and insol. sulfates as %S
0.079	0.007	0.006	0.066
Loss at 110°, three hours		.46	
Loss on ignition		9.79	

Lead-uranium ratio,

$$\frac{\text{Ra G}}{\text{U} + 0.36\text{Th}}, \frac{0.036}{1.83 + 0.36 \times 0.01} = 0.019$$

Lead.—The method used for the lead determination was essentially that described in the paper "The Age of a Canadian Cyrtolite."[2]

Recoveries of lead were made on the filtrates and are included in the weights of the lead chromate precipitates. Carefully tested, lead-free reagents were used.

Approximate Age of the Mineral.—We have no atomic weight determination of the lead from this cyrtolite. Assuming the absence of ordinary lead, the approximate age calculated from the above lead-uranium ratio is

$$\frac{0.019 \times 1.15 \text{ million years}}{1.57 \times 10^{-4}} = 139 \text{ million years.}$$

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Conclusion

As pointed out by Lane,[7] the lead ratio is abnormally low and only about a sixth of that of the uraninite from the same mine. He gives a possible explanation of this.

Practically the entire sample was used for the determinations described in this paper, leaving an insufficient amount for an atomic weight determination of the lead. The approximate age of this mineral in the absence of an atomic weight determination of the lead, is calculated from the analysis as one hundred and thirty-nine million years.

The amount of thorium is so small that no critical test of the two methods is indicated by the results.

The percentage of sulfur is higher in this cyrtolite than in the other cyrtolites which were analyzed at the same time for sulfur.

LAS VEGAS, N. M. RECEIVED OCTOBER 14, 1936

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

(6) Fenner, *Am. J. Sci.*, **16**, 369 (1928).

(7) Muench, *Am. Min.*, **21**, 374 (1936).