mental error. The resulting values are shown in Fig. 3, the straight line there drawn through the points being the best one as determined by the method of least squares. Its equation is

$$-\mathrm{d}h/\mathrm{d}t = 4.3 \times 10^{-4}\,[+] \qquad (12)$$

The concordance of these points with a straight line indicates that the reaction of decomposition is unimolecular with respect to the dihydroxotetrammine ion.

Summary

It has been shown:

1. That concordant values of the dissociation constants of diaquotetrammine cobaltic ion as an acid can be obtained by measuring with the glass electrode the concentration of hydrogen ion in solutions of this ammine ion to which various amounts of sodium hydroxide have been added.
2. That the velocity of decomposition of this ion in these solutions is proportional to the first power of the concentration of the dihydroxotetrammine ion in equilibrium with it, as computed from these values of the dissociation constants.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BOSTON UNIVERSITY]

The Lead–Uranium–Thorium Ratio of a Single Crystal of Wilberforce Uraninite

BY CHESTER M. ALTER AND LAURA A. YUILL

It has been shown recently[1] that the composition of a single crystal of uraninite from near Wilberforce, Cardiff Township, Ontario, may not be uniform throughout the crystal. Ellsworth[2] has found the same phenomenon in the case of Villeneuve uraninite. It is interesting to note that in both cases the percentage of thorium is highest in the outer portion of the crystal, decreases toward the interior and then increases again in the core. The variation in thorium content was not great in the case of the Villeneuve crystal but was very noticeable in the Wilberforce crystal. The lead and thorium contents showed certain irregularities which were also difficult to explain, especially by any process of leaching.

Alter and Kipp removed succeeding layers of the crystal by dissolving in nitric acid. In spite of the fact that this dissolution was done very rapidly, it was thought possible that there may have been preferential leaching throughout the crystal while any one layer was being dissolved. In that case the results would be meaningless, as definite layers of the crystal would not have been removed for analysis. In order to preclude such a possibility it was decided to repeat the work by analyzing various layers which had been mechanically removed from a single crystal rather than by acid dissolution.

For this purpose a rather well-developed crystal, a part of a large collection of material from the Wilberforce locality,[3] weighing approximately 42 g., was obtained from Professor Alfred C. Lane. According to Dr. H. V. Ellsworth[4] this material was collected from Pit 4[5] where the uraninite occurs in a gangue of fluorite and calcite. He further reports that the uraninite from this pit is considerably altered. This specimen, however, apparently carried very little of the usual surface alteration products and exhibited very distinct crystal faces and angles. A spot of apparently foreign material appeared on one face, and this proved to penetrate well into the core of the crystal.

The crystal was divided into three parts—outer, middle, and core—by carefully removing successive parts by means of a steel file. Each face was filed down an equal amount, great effort being taken to maintain the original form of the crystal during the process of filing off the outer portions. The outside, middle, and core portions weighed, respectively, 12.7 g., 15.2 g., and 13.5 g.

The particles of steel introduced in the samples were removed by very thorough magnetic separation.

The analytical procedures for the determination of lead, thorium, and uranium were in general those described in detail by Alter and Kipp.[1] Approximately one-gram samples were dissolved

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[1] Alter and Kipp, *Am. J. Sci.*, **32**, 120 (1936).

[2] Ellsworth, *Am. Mineral.*, **15**, 455 (1930).

[3] Report of Committee on Measurement of Geologic Time by Atomic Disintegration, National Research Council, Division of Geology and Geography, May 3, 1930.

[4] Private communication.

[5] Ellsworth, Canadian Geological Survey, Econ. Geol. Series, No. 11, pp. 214, 221 (1932).

in nitric acid, evaporated to dryness, diluted, the insoluble material filtered off, ignited, and weighed. The lead was precipitated from acid solution as sulfide, converted to sulfate, and weighed. Uranium and thorium were twice precipitated as hydroxide. After the combined hydroxides were dissolved in nitric acid, the thorium was precipitated as oxalate, dissolved in nitric acid, and precipitated as thorium sebacate with sebacic acid. The thorium sebacate was dissolved and reprecipitated, washed free from sebacic acid, ignited, and weighed as ThO_2. Iron and aluminum were removed from the uranium solution by precipitation with ammonium carbonate. The uranium was precipitated as ammonium uranate, ignited, and weighed as U_3O_8.

Unusual precaution was taken to carry out precipitations under best conditions to ensure purity. Filtrates were all evaporated and tested for desired constituents.

TABLE OF RESULTS

Section of crystal	Analysis	Insoluble, %	Lead,[6] %	Uranium, %	Thorium, %	$\frac{Pb}{U+0.36Th}$
Outside	1	2.01	9.16	52.98	5.24	
	2	1.99	9.14	53.11	5.22	
	3	2.00		52.88	5.21	
	Av.	2.00	9.15	52.99	5.22	0.1668
Av. Alter and Kipp			9.74	37.85	8.36	.2383
Middle	1	0.93	10.17	54.41	15.26	
	2	.95	9.96	54.46	15.24	
	3	.94	10.06	54.53	15.25	
	Av.	.94	10.06	54.47	15.25	.1678
Av. Alter and Kipp			11.93	58.48	14.09	.1877
Core	1	1.24	10.98	55.51	10.40	
	2	1.28	11.05	55.48	10.45	
	3	1.27	11.11		10.52	
	Av.	1.26	11.05	55.50	10.46	.1864
Av. Alter and Kipp			11.87	60.70	8.05	.1866
Weighted av. for whole crystal			10.10	54.36	10.61	.1736
Av. Alter and Kipp			11.13	47.73	9.55	.2175

Discussion

The ratio Pb/(U + 0.36Th) of the outer layer indicates that the crystal had not been subjected to surface alteration since it is commonly found that any leaching process tends to cause a rise in this ratio. The higher ratio in the core of the crystal is unusual.

The variation of the thorium content in various sections of the crystal is of great interest. It will be seen that this variation is of the same magnitude and direction as that noticed by Alter and Kipp.[1] Since this phenomenon exists in all three cases where methods have been used that would detect it, it would be of great interest to examine, in a like manner, crystals of uraninite from other localities.

The ratios obtained by Alter and Kipp and those reported here are slightly higher than those reported for Wilberforce material by Todd[7] and Ellsworth.[8,2] The latter[9] has pointed out that this is no doubt due to the fact that the Lane material from Pit No. 4 and analyzed in this Laboratory is of inferior quality compared with that analyzed earlier by Todd and by Ellsworth and which was obtained from Pit No. 1.[5] However, it has been observed that the two uraninite-bearing bodies of Pits 1 and 4 are not visibly connected although they are in line.

The results emphasize the necessity for careful selection of material in order to obtain reliable data for age calculations. Erroneous results may be obtained if even a single crystal in its entirety is ground and analyzed. Based on the age formula:

$$\text{Age} = \frac{\log(U + 0.36Th + 1.155Pb) - \log(U + 0.36Th)}{6.6 \times 10^{-5}} \text{ million years}$$

the discrepancy in age using the data for the whole crystal and those for the core amounts to approximately eighty million years, while the discrepancy between the ages calculated for the whole crystal and outside portion is about forty million years. These errors, although large, lose some of their impressiveness when they are compared with the age of this mineral, which is calculated by the above formula to be between 1100 and 1200 million years.

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Summary

1. Determinations of the lead–uranium–thorium ratio of sections of a single crystal of uraninite removed mechanically confirm earlier results in which the sections were removed by acid solution.

2. The composition of a single crystal of uraninite may vary exceedingly, especially in regard to thorium content.

3. The results may throw some light on the conditions in the pegmatite during crystallization.

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[6] 206.195 was used for the atomic weight of lead. See Baxter and Bliss, THIS JOURNAL, 52, 4851 (1930).

[7] See Bull. 80, p. 328, The National Research Council, 1931.

[8] Ellsworth, *Am. J. Sci.*, (5) 9, 127 (1925).

[9] Private communication.