THE VARIATION OF THE LEAD-URANIUM-THORIUM RATIO OF A SINGLE CRYSTAL OF WILBERFORCE, ONTARIO, URANINITE.

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(Contribution from the Chemical Laboratory of Boston University.)

ABSTRACT.

Successive layers of a single crystal of uraninite from Wilberforce, Ontario, were removed by solution in nitric acid and analyzed for lead uranium, and thorium. Methods of chemical analysis are given. The results indicate that uranium and thorium are leached more readily than lead. The necessity of data on fresh, unaltered specimens for age calculations is discussed. A variation of the thorium/uranium ratio in different zones of the crystal indicates a probable change in concentration of these elements in the medium in which the crystal grew during the period of growth. A method is suggested for the calculation of value of the "k factor" of the age formula. The age of this mineral is calculated.

One of the important criticisms of the lead-uranium ratio method of calculating the age of minerals is the suggestion that this ratio may not be constant throughout any given specimen of mineral. Obviously, this ratio will not be a constant for all minerals of a given geologic age if there has been during the life of the mineral any alteration that removed one of these constituents faster than the others. Likewise, any alteration, such as replacement, which increased the content of any of these constituents without altering the composition with respect to the others would render the experimentally determined ratio valueless as a means of calculating age. The purpose of this work was to ascertain, if possible, the effect of leaching on the lead-uranium-thorium ratio by analyzing successive layers of a single crystal of uraninite. For various reasons a specimen of this mineral from near Wilberforce, Cardiff Township, Ontario, was chosen for this study.

Wells[1] has analyzed a specimen of Wilberforce uraninite and found 53.52% uranium, 10.37% thorium, and 9.26% lead. Ellsworth[2] found 55.26% uranium, 11.92% thorium, and 10.25% lead in a considerably altered uraninite plus its decomposition products from the same locality. For hard crystals (presumably less altered) the same investigator[3] found

[1] Baxter and Bliss: Journ. Am. Chem. Soc. *52*, p. 4851, 1930.
[2] Ellsworth: This Journal, 5, vol. 9, p. 127, 1925.
[3] Ellsworth: Am. Mineral, 15, p. 455, 1930.

61.44% uranium, 9.32% thorium, and 10.19% lead. Todd[4] found 60.57% uranium, 10.02% thorium, and 9.65% lead from a part of a selected crystal of the mineral from Wilberforce. Ellsworth[3] analyzed a specimen of Villeneuve uraninite which showed marked zones of alteration to obtain data on the effect of alteration on the lead ratio of such a mineral. For comparison with our results his averages are given in Table I.

TABLE I.

Zone	Uranium	Thorium	Lead	Pb
	%	%	%	U + .36 Th
Outside layer.....	50.24	6.73	13.85	0.263
Middle layer.....	60.33	5.48	9.96	.160
Core	65.34	5.63	10.61	.157

He has concluded that weathered specimens of uraninite tend to give higher ratios than fresh ones of the same age. He states,[4] "This may not always be the case, but it appears to be theoretically reasonable inasmuch as lead compounds formed by weathering are probably on the whole less soluble than similar uranium compounds. This, however, is a point which requires much more investigation."

For this study a rather well-developed crystal measuring about 20 × 10 ×10 mm. was obtained from Prof. Alfred C. Lane, and was a part of a large collection of material from the Wilberforce area.[5] It was apparent that this crystal had been altered to some extent as the color was reddish brown, but it had not lost its distinctly crystalline form. Prof. J. T. Norton by means of X-ray study has determined the lattice constant of some of these Wilberforce uraninite cubo-octahedrons and found that in spite of the great age of the crystals and the large amount of lead generated within them have not lost their original structure.

PREPARATION OF SAMPLES.

The single crystal of uraninite as received was first thoroughly cleansed by vigorous scrubbing and rinsing with water. After drying at 105° C. it was carefully weighed. It was then treated in a dissolving flask with warm dilute nitric acid until apparently about one-third had dissolved. Soon after the process of dissolution began, it became evident that the

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

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

crystal was not homogeneous. Some parts of it were attacked much more readily than others. The original brown surface became pitted and close observation showed that in reality the crystal consisted of a black core surrounded by the brown outer layer of alteration products of the uraninite. This first treatment with acid so loosened the outside layer that it apparently was all removed, leaving nothing but pure black mineral below.

The residual two-thirds of the crystal was carefully removed from the first solution and thoroughly washed with many portions of water, the washings being combined with the solution of the outside layer. After drying, the black residue, which retained the same general shape of the original crystal, was weighed and then treated with acid until it was diminished in weight to approximately one-third of the weight of the original crystal. The residual core was removed, thoroughly washed, dried, and weighed. The last third was in turn dissolved in acid.

Each of the three solutions was evaporated to dryness and dissolved in enough 1 : 1 nitric acid to make the final diluted solution about four per cent in acid concentration. A very slight residue of silica was removed at this point by filtration. The acid solution was transferred to a calibrated 250 ml. flask and diluted to volume. Twenty-five ml. portions of these solutions were removed by means of a calibrated pipette to small flasks where they were stored until they could be analyzed. In this manner ten homogeneous samples of each portion of the crystal were obtained for analysis.

METHOD OF ANALYSIS.

General Principle.

In view of the fact that only lead, thorium, and uranium were to be determined, the method of analysis was varied considerably from the usual procedure. Because this particular specimen was a remarkably pure uraninite, certain precautions often necessary were found to be without value. The lead was first precipitated as the sulfide and then as sulfate, in which form it was weighed. Thorium and uranium were twice precipitated as hydroxide. After dissolving the combined hydroxides in nitric acid, the thorium was precipitated as oxalate, ignited, dissolved, and reprecipitated with sebacic acid. Thorium sebacate was ignited to

ThO_2 and then was weighed. The uranium was precipitated as ammonium uranate, ignited, and weighed as U_3O_8.

Analytical Procedure.

The twenty-five ml. sample was evaporated to dryness, baked, and dissolved in very dilute nitric acid to remove silica. The filtrate was again evaporated to dryness, dissolved, and filtered to remove last traces of silica. In a few cases this process was repeated again to insure the complete removal of silica. The filtered solution was evaporated to dryness and dissolved in 400 ml. of approximately four per cent nitric acid. Acid concentration much larger than this will prevent the complete precipitation of lead as sulfide and less than this will not prevent the precipitation of uranium as sulfide.

Lead.

The lead was precipitated as the sulfide by passing in a stream of washed H_2S for about an hour at room temperature and 15 minutes at the boiling point, and then allowed to cool slowly to room temperature in a stream of H_2S. Under these conditions the lead sulfide is precipitated in such a condition that it can be easily filtered and washed thoroughly with water saturated with H_2S. The filtrate contained the thorium and uranium. The lead sulfide was transferred as completely as possible from the filter paper to a Pyrex evaporating dish to which was added the nitric acid solution of any residual lead sulfide which might have been left in the precipitation flask. The filter paper was ignited, the residue treated with nitric acid, and added to the evaporating dish. The solution of lead was then digested for several hours with concentrated nitric acid, baked almost to dryness, dissolved in water, and the precipitated sulfur filtered off. Due to the presence of occluded lead nitrate and a small amount of lead sulfate this precipitate was strongly ignited. The residue was dissolved in nitric acid and the solution added to the main portion of lead nitrate solution. This solution was evaporated to dryness and then dissolved in 50 ml. of water containing 2 ml. of nitric acid to keep other salts in solution. An excess of sulfuric acid was then added and the solution evaporated until fumes of SO_3 were evolved. Forty ml. of water were added and allowed to stand over night.

The precipitated lead sulfate was filtered, washed with dilute H_2SO_4, and then dissolved in hot 2N ammonium acetate solution. The acetate was removed by evaporating several times with nitric acid. The lead was reprecipitated as the sulfate by evaporating with sulfuric acid. The lead sulfate and solution were then transferred to a weighed platinum crucible. The water was slowly evaporated on a steam bath and the sulfuric acid fumed off on an electric hot plate. The crucible containing the lead sulfate was then placed inside another crucible which was heated by means of a bunsen burner. The temperature was such that the bottom of the crucible containing the lead sulfate was a very dull red. Care was taken to prevent the burner gases from enveloping the crucible. The lead sulfate was then weighed.

Separation of Thorium and Uranium.

The filtrate from the hydrogen sulfide precipitation was diluted to 600 ml. and the excess hydrogen sulfide driven off by boiling. After addition of 15 ml. of 1 : 1 nitric acid, it was again boiled to remove traces of carbon dioxide. An excess of freshly distilled ammonium hydroxide was added and the precipitated uranium and thorium hydroxide allowed to settle. The solution was kept near the boiling point during filtration to prevent absorption of carbon dioxide which would have rendered the uranium soluble as ammonium uranyl carbonate. The washed precipitate was dissolved in concentrated nitric acid, diluted to 600 ml. volume, reprecipitated with freshly distilled ammonium hydroxide, filtered, and this precipitate was washed with two per cent ammonium hydroxide. Traces of uranium were recovered from the filtrate by evaporating to dryness several times with aqua regia to drive off ammonium salts, dissolving the residue in nitric acid and precipitating as above. The uranium and thorium hydroxide were dissolved in nitric acid, evaporated to dryness, and dissolved in four per cent nitric acid. This solution was poured into one-fourth its volume of ten per cent oxalic acid. The white crystalline precipitate of thorium oxalate should stand three or four days before filtering.

Thorium.

The filter containing the thorium oxalate and, if present, rare earth oxalates, was transferred to a crucible and charred at low temperature. The residue of oxides was fumed to

dryness several times with concentrated sulfuric acid until the final residue was pure white. This was then dissolved in concentrated nitric acid and diluted to a volume of 100 ml. The solution was nearly neutralized with ammonium hydroxide. The thorium was precipitated and thereby separated from any traces of rare earths by adding to the hot solution a hot solution of nearly saturated sebacic acid. Excess sebacic acid which separated with the thorium sebacate was removed by washing with hot water. The washed precipitate was dissolved in nitric acid, the solution nearly neutralized, and the thorium reprecipitated with sebacic acid. This process was repeated if necessary until the precipitate was pure white. The thorium sebacate was then ignited to constant weight at the temperature of a Meker burner and weighed as ThO_2.

Uranium.

The filtrate from the oxalate precipitation was evaporated to dryness several times with excess nitric acid to remove the oxalate. When this removal was complete, as evidenced by the absence of red fumes, the solution was diluted to 500 ml. and boiled to remove carbon dioxide. The uranium was then precipitated as ammonium uranate by adding a slight excess of freshly distilled ammonium hydroxide. Traces of uranium were removed from the filtrate as before. The washed precipitate was dissolved in nitric acid, diluted, and reprecipitated. The paper containing the precipitate was transferred to a platinum crucible, charred, and the precipitate ignited to constant weight in the presence of excess air. The uranium was weighed as U_3O_8.

POSSIBLE SOURCE OF ERROR.

In the method of analysis outlined above, no provision was made for the separation of iron and aluminum from uranium. Several tests such as with Na_2CO_3 and with cupferon were made for the presence of these elements in the various sections of this mineral. In the two inner sections they were absent, and only a slight trace was found in the outside section. Since the traces present were precipitated with the uranium, the values found for the percentage of uranium in the outside layer can be assumed to be slightly high. We believe the error introduced to be negligible, however.

The sebacic acid method[6] for thorium, according to Dr. J. P. Marble,[7] may give results that are a trifle high while the peroxynitrate method, more generally used, may give slightly too low results.

TABLE OF RESULTS.[8]

Section of Crystal	Analysis	Lead %	Uranium %	Thorium %	$\frac{Pb}{U + .36\ Th}$
Outside	A	9.283	38.049	8.387	
	B	10.195	37.743	8.333	
	C		37.753		
	Average	9.739	37.848	8.360	0.2383
Middle	A	11.891	58.525	14.014	
	B	11.957	58.422	14.151	
	C	11.934	58.479	14.115	
	Average	11.927	58.475	14.093	0.1877
Core	A	11.875	60.779	8.105	
	B	11.856	60.620	7.997	
	Average	11.865	60.699	8.051	0.1866
Weighted Average for whole crystal		11.127	47.731	9.545	0.2175

DISCUSSION OF RESULTS.

From the standpoint of the original purpose of this study, the most obvious result is the apparent effect of leaching on the ratio and therefore on the calculated age of the uraninite crystal. The outside section has a much higher ratio, probably due to the fact that uranium and thorium have been removed faster than lead, although the possibility that some extraneous lead was deposited in the outer section is also tenable. The analysis substantiates the belief from observation that leaching was confined largely if not completely to the outside portion of the crystal which was removed in the first section. The lead content of the two inner portions was nearly constant. If the whole crystal had been pulverized and homogeneous samples analyzed, the ratio would have been 0.2175, much higher than the ratio of the unaltered core. This

[6] James: J. A. C. S., 34, 281, 1912.
[7] Private Communication.
[8] The average results have appeared in a preliminary note in Science, *82*, No. 2133, 464, 1935.

emphasizes the importance of using only unaltered specimens of minerals for age calculations.

The great difference in the thorium content of the two inner sections is very interesting and may be difficult to explain. It seems impossible to explain the facts on the basis of leaching. It seems more probable that the variation in composition of these two inner sections with respect to thorium and uranium is a result of a variation in concentrations of these two constituents during the process of formation of the crystal. This change in concentration may have occurred in at least one of two ways. Assuming the possibility that the crystal grew in a stagnant medium, the substance that was present in greatest concentration would crystallize out first. In this case we might expect the uranium to be in greater concentration at the beginning, hence, the inside of the crystal would have a higher percentage of uranium. As the process of crystallization continued, thorium which was probably present in smaller concentrations at the beginning, would become relatively more concentrated in the medium and would therefore be present in the outer or later formed portions of the crystal in greater proportions. The other possibility is that the medium from which the crystals grew was subject to flow and the dike may have been fed during crystallization from a source rich in thorium, in which case the increased concentration of thorium would be explained. Until more is known about the conditions prevailing at the time of crystallization, it will be difficult to be sure of the cause of this change.

It is interesting to note that this crystal lost thorium and uranium at nearly the same rate, as the Th/U ratio of the outside section is 0.22 and for the middle section 0.24. Both elements, however, have been leached out much faster than has lead.

If we grant that the time required to form the crystal was insignificant in comparison with its age and assume that there has been little or no alteration of the two inner sections, we can use the data from these analyses to calculate the "k factor," the ratio of the lead producing capacity of thorium to that of uranium, of the age formula:

$$\text{Approximate age} = \frac{\text{Pb}}{\text{U} + \text{k Th}} \cdot 7600 \text{ million years.}$$

Substituting the values for Pb, U, and Th for the two inner

sections and equating the ratios, since we assume equal ages for the two sections, we get $k = 0.42$. Since we are not sure of the validity of the assumption that there has been no alteration, this value for the "k factor" cannot be given great weight in comparison with the results of other methods of determining the value of this important factor. It seems worth mentioning, however, that the value from this data is even greater than 0.36, the value suggested by Kovarik,[9] rather than as low as 0.27 as suggested by Kirsch.[10]

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[9] Bulletin 80, National Research Council.
[10] Kirsch: Geologie and Radioactivität, 1928.