mean value of A leads to $K = 2.20 \times 10^{-5}$, while Harned and Pfanstiel found $K = 2.342 \times 10^{-5}$. It is thus necessary to calculate K from the known value of c. The constants a, b involve x_0, x_∞ and therefore cannot be used.

Four sets of three readings each were interpolated with $\Delta t = 400$ minutes. From these sets, together with the value $c = -39.86$ calculated from the initial concentrations and equilibrium constant, the values $\alpha = 1.701, 1.700, 1.698, 1.691$ were calculated by successive approximations. The trend here, amounting to a total of 0.6%, may be partially due to inaccuracies introduced by the graphical interpolation. From the mean value of α one obtains $K = 2.365 \times 10^{-5}$, which is 1% higher than the value of Harned and Pfanstiel. This method of calculation eliminates the necessity of calculating the initial and final values of the titer as done by Harned and Pfanstiel. It should be emphasized that the value of α would be changed by less than 0.1% by a change of 5% in c.

Summary

An application of the methods of projective geometry to a series of measurements of a property x (of a system reacting in accord with the kinetic equation $kt = \ln c\,(a - x)/(b - x)$) which varies linearly with the progress of the reaction, taken at uniform time intervals, Δt, gives the result

$$A \equiv \frac{x_3 - x_2}{x_2 - x_1} \times \frac{x_4 - x_1}{x_4 - x_3} = 1 + 2 \cosh (k\,\Delta t)$$

By means of this result the necessity of obtaining initial and final values of x is eliminated.

The method is illustrated using the data of Harned and Pfanstiel on the hydrolysis of ethyl acetate.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Atomic Weights of Some Radiogenic Leads

BY G. P. BAXTER, J. H. FAULL, JR.,[1] AND F. D. TUEMMLER

In connection with the programs of the Committee on Geophysical Research of Harvard University and the Committee on Determination of Geologic Time of the National Research Council the atomic weights of some new specimens of radiogenic leads have been determined.

Samarskite from Glastonbury, Connecticut, U. S. A.—The original ground sample, weighing 1130 g., had been cleaned by gravity and magnetic methods by Mr. Harry Berman of the Harvard Mineralogical Laboratory. A preliminary analysis of a part of this material by R. C. Wells[2] shows 6.91% uranium, 3.05% thorium, 0.311% lead.

Treatment with redistilled hydrofluoric acid in platinum followed by repeated evaporation with nitric acid to remove the hydrofluoric acid and extraction of the insoluble residue with nitric acid, all in platinum, was carried out by Dr. C. M. Alter. The nitric acid solution on standing for several months deposited much columbic acid (40 g.). The dried insoluble residue weighed 970 g. This residue was found spectroscopically to contain most of the lead.

Lead was separated from the nitric acid solution by double precipitation of basic acetates and treating the filtrates with hydrogen sulfide. The original insoluble residue and that which separated from the nitric acid solution were digested for long periods with redistilled hydrochloric acid and the lead precipitated from the extract after neutralization with ammonium acetate. About 0.1 g. of lead was obtained from the extract, 1.6 g. from the insoluble residues, together representing about half the lead content of the original mineral.

Purification included the following processes: conversion of sulfide to sulfate through the chloride, solution of the sulfate in ammonium acetate and reprecipitation with hydrogen sulfide, solution of the sulfide in hydrochloric acid and conversion of the chloride to nitrate by repeated evaporation with nitric acid, four recrystallizations of the nitrate from nitric acid in quartz, conversion of nitrate to chloride with hydrochloric acid in quartz, four recrystallizations of chloride in quartz, and distillation of the chloride in dry hydrogen chloride in a quartz tube. All the product was used in one analysis. Lead was recovered from the solution of lead nitrate resulting from the first analysis and from the mother liquors remaining from the purification by precipitation as sulfide, and after conversion to the nitrate through the chloride it was re-purified as above.

Beaverlodge Lake Pitchblende.—This specimen was collected and contributed by Dr. Fred Joliffe from a quartz vein near Beaverlodge Lake, Northwest Territories, Canada, about one hundred miles south of Great Bear Lake. The mineral consists chiefly of an intimate mixture of pitchblende and specularite. Weighted averages from analyses of five lots of similar material, representing 3000

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[1] Research Associate in Geology in Harvard University, 1935. The present work is Paper No. 33 published under the auspices of the Committee on Geophysical Research and of the Division of Geological Sciences at Harvard University.

[2] R. C. Wells, Reports of the Committee on Determination of Geologic Time, of the National Research Council, April, 1935, and Sept., 1936.

lb. (1360 kg.), made in the Canadian Mines Branch, Ottawa, Canada, show 28.9% uranium and 1.57% lead with no thorium. Analysis by Baxter and Averill (see following paper) of material cleaned as below showed 51.2% uranium, 2.49% lead and no thorium.

After being crushed in a diamond mortar the pitchblende (514 g.) was finely pulverized in a specially cleaned grinder. Much of the iron ore was removed by suspension in water. The dried residue (433 g.) was then fractionated electromagnetically. This process was not particularly successful, apparently because of the intimate nature of the original mixture. A considerable quantity of material which could be picked up with an ordinary magnet, as well as a non-magnetic fraction, largely quartz, were thus eliminated. Galena could not be discovered in the nonmagnetic fraction but a microscopic examination of a polished section by Dr. R. S. Moehlmann suggests a trace of this substance.

Of 415 g. remaining, 25 g. was set aside for analysis. The remaining 390 g. was treated with hot 8 *N* nitric acid and after separation from a slightly soluble residue of iron ore, the solution was evaporated with an excess of sulfuric acid and taken up with water. The residue (112 g.) was dissolved in hydrochloric acid and after separation from a nearly white residue (7 g.) the solution was evaporated with an excess of sulfuric acid and taken up with water. Very little lead sulfate was obtained from the hydrochloric acid solution of the iron ore.

The combined precipitates of lead sulfate were dissolved in ammonium acetate, and, after filtration of the solution, lead sulfide was precipitated. This was dissolved in hydrochloric acid, and the chloride was converted to nitrate by evaporation with nitric acid. At this point we had 14.6 g. of lead nitrate. This was further purified as described above in the case of the samarskite lead.

Katanga Pitchblende.—Some years ago Baxter and Alter[3] found the atomic weight of the lead contained in the yellow, hydrochloric acid soluble portion of a specimen of Katanga pitchblende to be 205.97 while that of lead from the black insoluble portion of the same specimen was found to be 206.00. A little later Hönigschmid, Sachtleben and Baudrexler[4] extracted a specimen of Katanga pitchblende with dilute hydrochloric acid and found the atomic weight of the lead in the extract to be 206.02. Recently Hecht and Kroupa [*Z. anorg. allgem. Chem.*, **226**, 248 (1936)] found the atomic weight of the lead contained in the black, less soluble portion of this specimen to be 206.04. Through the great kindness and generosity of Professor H. Buttgengach of the University of Liège we came into possession of a fine specimen of Katanga pitchblende weighing 1150 g. Aside from a considerable mass of yellow secondary minerals at one point, this specimen differed markedly from the one examined by Baxter and Alter in having a much larger proportion of veins of yellow secondary minerals. This was apparent even to the eye in the slightly greenish color, whereas the former specimen was black.

About 615 g. (free from masses of yellow) was broken up on a steel plate and ground in a steel mortar by hand. Nearly half, 298 g., was then extracted with 5% hydrochloric acid until lead chloride ceased to crystallize from the solution and the extract was nearly colorless. The black residue was then thoroughly washed and dried. The weight of this residue, 100 g., was 33% of the original whereas Baxter and Alter found 77% by a similar process with the earlier specimen.

The lead chloride which separated from the extract was collected. The remainder of the lead was precipitated as sulfate and converted to the chloride through the sulfide. In all 18.0 g. of lead chloride was obtained.

The black insoluble portion was dissolved in nitric acid and the greater part of the lead precipitated as chloride. The remainder was separated as sulfate and converted to chloride. The total weight of lead chloride was 8.73 g.

Both samples of lead chloride were converted to nitrate and purified as already described.

A rough determination of uranium was made in aliquot portions of both solutions from which the lead had been removed. The percentages of lead and uranium are given in the following table.

	Pb, %	U, %	Pb/U
Black	6.50	76.7	0.0847
Yellow	6.76	67.5	.1001
Whole	6.67	70.6	.0945

Baxter and Alter (*loc. cit.*) found the following percentages with the first specimen of Katanga pitchblende.

Black	6.7	74.9	0.089
Yellow	8.4	58.5	.144
Whole	7.1	71.2	.100

In an experiment to find the composition of the mineral more accurately, the proportion of black (pitchblende) decreased from 34.9% after one treatment with hydrochloric acid to 31.4 and to 30.8 after two additional treatments. Apparently the pitchblende dissolves slowly in 5% hydrochloric acid. Analysis of the hydrochloric acid extract and the residual material gave the following results:

	Pb, %	U, %	Pb/U
Black	6.48	77.2	0.0839
Yellow	6.74	68.5	.0983
Whole	6.66	71.2	.0935

These values are confirmed by the approximate analysis of the main bulk of material. The lead–uranium ratio in the case of the black material is in general agreement with values obtained by others.[5]

With all the radiogenic samples it was necessary to recover and repurify in order to secure the necessary material.

Common Lead.—Cerussite from Wallace, Idaho, U. S. A., was dissolved in nitric acid, and after filtration of the solution the lead nitrate was four times recrystallized in Pyrex vessels. The nitrate was then converted to chloride and the chloride four times recrystallized in quartz and twice redistilled in hydrogen chloride. Baxter and Grover[6] have already examined lead from this mineral and found it to possess a normal atomic weight (207.21).

The early stages in the purification of the various samples were carried on in Pyrex vessels, but in the crystallization

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(3) Baxter and Alter, THIS JOURNAL, **55**, 2785 (1933).

(4) Hönigschmid, Sachtleben and Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933).

(5) Bull. Nat. Research Council, "Physics of the Earth, IV, The Age of the Earth," 1931, pp. 367–369.

(6) Baxter and Grover, THIS JOURNAL, **37**, 1027 (1915).

of the nitrate and chloride only quartz or platinum vessels were used. Residual silica and organic matter were eliminated easily in the final distillation of the chloride in hydrogen chloride in a quartz tube. No reagents were used which were not free from lead.

Spectroscopic examination of the final products in a carbon arc failed to show any evidence of impurity. Difficulty was experienced in securing graphite electrodes of sufficient purity, especially as regards silver, but this difficulty was finally overcome by the conventional method of heating the electrodes to 1000° in a current of chlorine in a quartz tube for long periods.

In every case the purified lead chloride was prepared for analysis by fusion in a current of dry hydrogen chloride containing more or less nitrogen. No variation in the composition of the salt with the proportion of hydrogen chloride could be detected. The salt was contained in a quartz boat placed in a quartz tube during the fusion. After the fusion it was transferred by means of a Richards bottling apparatus to the weighing bottle in which the empty boat had originally been weighed. The boat remained constant in weight throughout the whole series of experiments.

After the salt had been weighed it was dissolved in warm water to which a small amount of nitric acid had been added to prevent hydrolysis. The solution was then compared with silver in the conventional way, with the use of a nephelometer and 0.01 normal silver and chloride solutions, by the equal-opalescence method. In the precipitation, the solutions were 0.05 normal or less. The silver nitrate solution was always poured into the lead chloride solution.

THE ATOMIC WEIGHT OF LEAD

Analyst	$PbCl_2$, g.	Ag, g.	Ag added, g.	Corrected wt. of Ag, g.	Ratio $PbCl_2:2Ag$	At. wt. of Pb
			Common lead			
F	4.39335	3.40822	0.00000	3.40822	1.28905	207.211
F	3.49797	2.71380	− .00024	2.71356	1.28907	207.216
F	4.21579	3.27043	− .00010	3.27033	1.28910	207.222
T	4.27224	3.31422	+ .00005	3.31427	1.28904	207.210
T	5.99791	4.65309	− .00011	4.65298	1.28905	207.211
T	4.74688	3.68260	− .00010	3.68250	1.28904	207.209
T	3.99080	3.09571	+ .00010	3.09581	1.28910	207.222
				Average	1.28906	207.214
			Samarskite			
F	1.28803	1.00248	−0.00010	1.00238	1.28497	206.331
F	0.75523	0.58750	+ .00019	0.58769	1.28508	206.355
				Average	1.28503	206.343
			Beaverlodge Lake pitchblende			
F	2.61248	2.03519	−0.00030	2.03489	1.28384	206.088
F	2.75235	2.14453	− .00055	2.14398	1.28373	206.070
F	3.17452	2.47283	.00000	2.47283	1.28376	206.070
F	6.38415	4.97299	− .00052	4.97247	1.28392	206.099
F	4.01745	3.12924	− .00003	3.12921	1.28384	206.089
T	2.72167	2.12000	− .00010	2.11990	1.28387	206.093
T	2.17947	1.69745	+ .00020	1.69765	1.28382	206.082
				Average	1.28383	206.084
			Katanga pitchblende, hydrochloric acid extract			
F	3.43131	2.67331	−0.00025	2.67306	1.28366	206.049
F	3.52881	2.74926	− .00025	2.74901	1.28367	206.050
F	2.54121	1.97975	− .00015	1.97960	1.28370	206.057
T	4.28996	3.34186	+ .00020	3.34206	1.28363	206.041
T	4.84228	3.77222	− .00005	3.77217	1.28369	206.054
T	4.50429	3.50891	− .00002	3.50889	1.28368	206.053
				Average	1.283670	206.051
			Katanga pitchblende, unaltered			
F	1.70238	1.32609	+0.00015	1.32624	1.28361	206.038
F	1.60461	1.25088	− .00085	1.25003	1.28366	206.048
T	4.61797	3.59739	+ .00016	3.59755	1.28364	206.045
T	3.73794	2.91212	− .00006	2.91206	1.28361	206.037
				Average	1.28363	206.042

The weights of lead chloride were corrected to vacuum by adding 0.000058 g. per gram and those of silver by subtracting 0.000031 g. per gram.

The average value for common lead is in good accord with recent evidence.

If the samarskite is free from common lead, the atomic weight to be expected from the proportions of uranium and thorium reported (see page 702) may be calculated on the assumptions (1) that uranium lead ($Pb^{206} + Pb^{207}$) has the atomic weight 206.00[7] and thorium lead (Pb^{208}) the value 207.96, and (2) that the relative rates of production of lead by uranium and thorium are 1.00: 0.36. The value thus found is 206.22, and indicates that about 12% of the lead in the samarskite is common lead and that in calculating the age of the samarskite the percentage of lead should be reduced by one-eighth. This assumes, however, that the relative proportions of uranium and thorium in the mineral have not altered with time.

The atomic weight of Beaverlodge Lake lead appears to be slightly higher than that of Great Bear Lake lead (206.06)[8] and since there is no appreciable amount of thorium in the pitchblende, about 7% of the lead is apparently common lead and the age 93% as high as calculated from the total percentage.

The Katanga pitchblende is noticeably different from that examined by Baxter and Alter.[3] In the first place the percentage of black unaltered material is one-half as large. In the second place not only does the lead have a higher atomic weight but the difference between the leads from the black and yellow material, if real, is in the opposite direction from that previously observed, 206.04 and 206.05 against 206.00 and 205.97. Furthermore, if thorium is absent in appreciable amount, as has generally been reported for Katanga lead, about 4% of the lead appears to be common lead and a corresponding correction is necessary in computing the age of the mineral from the percentages of lead and uranium.

Other determinations of the atomic weight of Katanga lead,[9] from both pitchblende and curite,

(7) Baxter and Alter, THIS JOURNAL, **57**, 470 (1935).

(8) Marble, *ibid.*, **56**, 854 (1934); Baxter and Alter, *ibid.*, **57**, 467 (1935).

(9) Hönigschmid and Birckenbach, *Ber.*, **56**, 1837 (1923), 206.048; Hönigschmid, Sachtleben and Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933), curite 206.031, yellow 206.023; Baxter and Alter,[3] curite 206.027.

have yielded values close to 206.03. The specimen described in this paper is particularly interesting in affording additional evidence that the atomic weight of Katanga lead is not constant and therefore by inference may contain common lead in varying proportions. This idea is substantiated by the recent work of Rose,[10] who finds the isotope Pb^{208} in a specimen of Katanga lead.

Summary

1. The atomic weights of certain radiogenic leads have been determined.

Source	Atomic weight
Cerussite, Wallace, Idaho, U. S. A. (common)	207.21
Samarskite, Glastonbury, Conn., U. S. A.	206.34
Pitchblende, Beaverlodge Lake, N. W. T., Canada	206.08
Pitchblende, Katanga, Africa	
Black, insoluble portion	206.04
Yellow, hydrochloric acid-soluble portion	206.05

2. It is pointed out that these values, together with the percentages of important components, point to the presence of several per cent. of common lead in all three radioactive minerals.

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[10] Rose and Stranahan, *Phys. Rev.*, **50**, 792 (1936).

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Lead–Uranium Ratio of Beaverlodge Pitchblende

BY G. P. BAXTER AND M. E. AVERILL

A sample of the ground and mixed specimen of pitchblende from Beaverlodge Lake, N. W. T., Canada, which had been utilized in the determination of the atomic weight of lead described in the preceding paper, was analyzed for lead, uranium and thorium.

Weighed portions were first treated with 8 *N* nitric acid which dissolved the pitchblende but left most of the associated hematite insoluble. After separation, the hematite was dissolved in 7 *N* hydrochloric acid. Both solutions were evaporated to dryness, and siliceous residues were treated with hydrofluoric and sulfuric acids. Lead was separated from both solutions by evaporation with sulfuric acid, and the filtrate of the lead sulfate scavenged with hydrogen sulfide at suitable acidity. Lead so recovered was converted to sulfate and added to the main portions. All the lead sulfate was purified by solution in ammonium acetate and evaporation with sulfuric acid and the filtrate worked up for traces of lead.

Both the nitric and hydrochloric acid solutions were freed from iron by double precipitation of basic ferric acetate. Ammonium uranate was then precipitated from solution in an excess of ammonium carbonate, and collected. The filtrate was evaporated to dryness and after expulsion of ammonium salts a small amount of uranium was recovered as above.

The uranyl sulfate solution resulting from the extraction of lead from about 390 g. of mineral (see preceding paper) yielded several grams of rare earth oxalates, but we were unable to convince ourselves that thorium was present in more than traces. This is in accord with the results of analyses of similar material made by the Canadian Mines Branch (see preceding paper, p. 703).

TABLE I

Sample, g.	$PbSO_4$, g.	Pb, %	U_3O_8, g.	U, %	Pb/U
2.3005	0.0845	2.505	1.3963	51.47	0.0488
1.9146	.0699	2.490	1.1587	51.32	.0485
2.2185	.0807	2.481	1.3265	50.70	.0490
Average		2.492		51.16	.0486

Baxter, Faull and Tuemmler (see preceding paper) have found the atomic weight of the lead contained in this sample of Beaverlodge pitchblende to be 206.08, indicating, in the almost complete absence of thorium, that about 7% of this lead is common lead. With the per cent. of uranium 51.16, and that of lead 2.318 (corrected for common lead) the Pb/U ratio is 0.0453. Analyses by the Canadian Mines Branch give 0.054 (see page 703 of preceding paper). Barring alteration and other unknown effects the approximate age of the mineral is 344 million years, while the logarithmic formula gives 336 million.

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