

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

## THE ATOMIC WEIGHT OF URANIUM LEAD FROM SWEDISH KOLM

BY GREGORY PAUL BAXTER AND ALLEN DOUGLASS BLISS

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In connection with the work of the Committee of the National Research Council on the Measurement of Geologic Time by Atomic Disintegration, the determination of the uranium-lead ratio in the ash of Swedish kolm<sup>1</sup> has recently been completed. Thorium could not be detected. Since the accuracy of the age estimation is vitally dependent on the freedom of the material from lead of non-radioactive origin, the atomic weight of this lead has been compared with that of ordinary lead.

The ash of the kolm constitutes from 20 to 40% of the original, and contains a few hundredths of a per cent. of lead. In the extraction process outlined below the lead recovered amounted to 0.03% of the ash and 0.01% of the original kolm.

After various exploratory experiments the procedure finally adopted for treating the 50 odd kilograms of kolm was as follows. The material was burned in portions in electrically heated muffles of fused quartz. Practically all of the combustible portion was removed in this way. The almost insoluble ash, which yielded little lead to aqueous reagents except hydrofluoric acid, was then heated to redness in a current of dry hydrogen chloride. Almost no lead chloride distilled during this treatment but the solution obtained by digesting the residue with hot water was found to contain the greater part of the lead, for the insoluble residue, when tested spectroscopically in an arc of pure graphite, was found to be nearly lead free. The lead was separated from the solution by double precipitation as the sulfide in ammonium acetate solution, and then was precipitated once as chromate. The total yield of lead chromate from the fifty kilograms of kolm was 7.2 g., equivalent to 4.6 g. of metal.

The outline of the further purification of this material was as follows: (1) conversion of the chromate to chloride by evaporation with hydrochloric acid; (2) conversion of chloride to nitrate by evaporation with nitric acid; (3) three crystallizations of the nitrate, once from concentrated nitric acid, twice from water; (4) conversion of the nitrate to chloride by repeated evaporation with an excess of hydrochloric acid; (5) recrystallization of the chloride, once in glass and twice in platinum;

<sup>1</sup> A shale-like material reported to be an upper Cambrian sedimentary with trilobites. For further details and references as to the lead-uranium ratio, age, etc., see the reports of the Committee on the Measurement of Geological Time by Atomic Disintegration to the Division of Geology and Geography of the National Research Council.

(6) distillation of the chloride in a current of dry hydrogen chloride in a quartz tube. The product was used in Analysis K2.

A second sample was obtained from the combined mother liquors of the nitrate and chloride crystallizations by evaporation with hydrochloric acid, and was crystallized twice in glass and three times in platinum. After distillation in hydrogen chloride the product was used in Analysis K1.

As soon as the first two analyses had been completed, the resulting lead nitrate solution was evaporated, freed from silver with a small amount of hydrochloric acid, and subjected to a new purification consisting of three crystallizations of the nitrate from nitric acid and four of the chloride from water, once in quartz and three times in platinum (Analysis K3). From the chloride mother liquors of K3 a fourth, less pure, sample was prepared by one crystallization of the chloride in glass and one in quartz (Analysis K4).

All of the material was again combined and purified, this time by five crystallizations of the nitrate from nitric acid and five of the chloride from water, once in quartz and four times in platinum (Analysis K5).

Analysis K6 was carried out with the same material after six crystallizations of the nitrate, and six of the chloride, one of the latter being conducted in quartz and five in platinum.

Common lead chloride<sup>2</sup> for comparison was prepared by three crystallizations as lead nitrate, and three as lead chloride. The latter was then distilled once in a current of hydrogen chloride as described above.

To prepare the lead chloride for weighing it was fused, while contained in a weighed quartz boat in a quartz bottling apparatus, in a current of dry hydrogen chloride, and allowed to solidify in an atmosphere of pure dry nitrogen. After displacement of the nitrogen by dry air, the boat was transferred to the weighing bottle and reweighed. Solution in hot water was followed by precipitation with a weighed, very nearly equivalent amount of the purest silver,<sup>3</sup> and the end-point of the precipitation was determined nephelometrically in the usual way. Final observations of the end-point were taken only after a period of from three to five weeks.

Purification of reagents followed conventional lines. Especial pains were taken during the extraction of the lead from the kolm that all reagents should be lead-free.

Weighings were made by substitution, a counterpoise being employed with the weighing bottle containing the boat. Vacuum corrections of +0.000058 and -0.000031 gram were applied to each gram of lead chloride and silver, respectively.

<sup>2</sup> From Coeur d'Aléne lead-silver ores.

<sup>3</sup> The silver used in all analyses except K3 and K4 was purified by Professor S. Ishimaru [THIS JOURNAL, 51, 1729 (1929)]. In Analyses K3 and K4 material was used prepared in the same way for this work with the assistance of Mr. J. P. Marble.

TABLE I  
 THE ATOMIC WEIGHT OF LEAD

	Wt. of PbCl <sub>2</sub> in vacuum, g.	Ag = 107.880	Ag added or subtracted, g.	Corrected wt. of Ag, g.	Cl = 35.457	At. wt. of lead
		Wt. of Ag in vacuum, g.			Ratio PbCl <sub>2</sub> :2Ag	
C1	2.74332	2.12809	0.00000	2.12809	1.28910	207.222
C2	3.60741	2.79852	.00000	2.79852	1.28904	207.209
C3	3.07537	2.38552	+ .00013	2.38565	1.28911	207.224
C4	2.81471	2.18360	- .00009	2.18351	1.28908	207.218
				Average	1.28909	207.218
K1	1.61294	1.25431	+ .00247	1.25678	1.28339	205.990
K2	1.60407	1.24958	+ .00025	1.24983	1.28343	205.999
K3	2.56499	1.99848	- .00006	1.99842	1.28351	206.016
K4	1.83748	1.43153	+ .00014	1.43167	1.28345	206.003
K5	3.32075	2.58750	- .00021	2.58729	1.28349	206.011
K6	3.07451	2.39535	- .00005	2.39530	1.28356	206.027
				Average	1.28347	206.008
				Average omitting K1 and K4	1.28350	206.013

The determinations with common lead are consistent and in accord with the modern value for the atomic weight of this substance. The analytical procedure seems therefore to be satisfactory.

The atomic weight of the kolm lead seems to be close to 206.01 whether or not the two analyses with possibly less pure material, K1 and K4, are omitted. This value is surprisingly low, for the lowest value previously obtained, by Hönigschmid and Horowitz, is 206.046, for lead from Morogoro pitchblende. Since Aston has found the lead isotopes to be integral with the mercury isotopes, and since these, making allowances for the presence of O<sup>18</sup>, possess integral values on the basis of ordinary oxygen, the kolm lead seems to be composed almost exclusively of the isotope Pb<sup>206</sup>. Compensation between isotopes of mass above and below 206 is unlikely, for there is no certain evidence of the existence of lead isotopes below 206.

The low value for the kolm lead excludes the possibility of serious contamination with common lead, which consists largely of the isotopes Pb<sup>207</sup> and Pb<sup>208</sup>, and is in accord with the fact that thorium has not been detected in the kolm ash. If the small excess in the atomic weight of the kolm lead over 206 is due to the isotope Pb<sup>207</sup>, the proportion of this component is not far from 1%. Aston has found this isotope to be more than one-tenth as abundant as Pb<sup>206</sup> in uranium lead from bröggerite. If Pb<sup>207</sup> is the end product of the actinium series, on the basis of Aston's result an atomic weight not less than 206.1 is to be expected for uranium lead unless the bröggerite lead was badly contaminated with ordinary lead.

If actinium is not a direct product of the disintegration of U<sup>238</sup>, but of an isotope, it may be that the organic process which produced the kolm

exerted a selective action upon uranium isotopes, which resulted in the concentration of the isotope of mass 238. Examination of the uranium contained in the kolm might throw some light upon this question. This we propose to do.

CAMBRIDGE, MASSACHUSETTS

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## THE ATOMIC WEIGHT OF URANINITE LEAD FROM WILBERFORCE, ONTARIO, CANADA

BY GREGORY PAUL BAXTER AND ALLEN DOUGLASS BLISS

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As a check on the age determination of a specimen of uraninite occurring in Cardiff township near Wilberforce, Ontario, Canada, by means of the uranium-thorium-lead ratio the atomic weight of the lead has been determined.<sup>1</sup>

A selected crystal of 700 g. was broken up with a clean hammer and anvil and the fragments crushed in a carefully cleaned jaw crusher. The product was then coarsely ground in a Quaker grinding mill. This mill had been previously cleaned by passing through it a considerable quantity of marble. The marble powder was found to be free from detectable quantity of lead.

About 300 g. of the powdered uraninite was boiled with concentrated nitric acid, and the residue, which later was found to consist largely of fluorspar, was separated and washed by decantation. From the solution the lead was precipitated by adding an excess of sulfuric acid and the precipitate was washed by decantation. The lead sulfate was metathesized to the carbonate by repeated treatment with hot sodium carbonate solution, and after the lead carbonate had been washed by decantation it was dissolved in nitric acid and freed from a small amount of insoluble material.

The original insoluble residue was further boiled first with nitric acid, and again after the addition of sulfuric acid, and the whole was evaporated to the fuming point of sulfuric acid. After being washed with water the residue was extracted with hot ammonium acetate solution, and the lead was precipitated as chromate. This in turn was washed and converted to sulfate by treatment with nitric and sulfuric acids. Conversion to nitrate was accomplished as in the case of the main portion and the two portions were then combined.

<sup>1</sup> For a description of geologic occurrence and analyses, by Ellsworth, Todd, Spence and Carnochan, see Exhibit A, appended to the mimeographed report of the Committee on the Measurement of Geological Time by Atomic Disintegration to the division of Geology and Geography of the National Research Council, May 3, 1900. Also *Trans. Can. Inst. Min. and Met.*, 2 (1930); *Amer. Mineralogist*, (Oct., 1930).