

since screening offered opportunity for contamination.

Calculated with International Atomic Weights the percentage of copper in copper sulfate is 25.458. Richards² found 25.449% in material of average particle diameter 0.1 mm. but he also demonstrated that by extremely fine grinding (0.01 mm.) the percentage of water in the salt could be reduced by 0.01%, so that the percentage of copper in this very fine material must have been

25.451, a value not very different from that found with our finer material.

Summary

In the analysis of copper sulfate prepared from common copper and from copper extracted from the blood of the horseshoe crab (*limulus polyphemus*) no difference could be detected between the two specimens.

CAMBRIDGE, MASS.

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

The Atomic Weights of Several Radiogenic Leads

BY GREGORY P. BAXTER AND CHESTER M. ALTER¹

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 several radiogenic leads have been determined.

Uraninite from Besner Mine, Parry Sound, Ontario, Canada

About 3.5 g. of lead sulfate, obtained in analyses of this mineral, was received from Dr. H. V. Ellsworth.² Purification included the following processes:³ conversion of sulfate to carbonate with sodium carbonate, solution of the carbonate in nitric acid, crystallization of the nitrate from nitric acid, twice in Pyrex, three times in quartz, conversion of nitrate to chloride with hydrochloric acid in quartz, crystallization of the chloride once in quartz, three times in platinum, distillation of the chloride in dry hydrogen chloride in a quartz tube. All the product was used in the first analysis of this material. Lead was recovered from the solution of lead nitrate resulting from this analysis and from the mother liquors remaining from the purification by precipitation as sulfide and was converted to nitrate through the chloride. The nitrate was then crystallized twice from nitric acid and once from water and converted to chloride which was four times crystallized and distilled in hydrogen chloride.

Pitchblende from Great Bear Lake, North West Territories, Canada

The atomic weight of lead from Great Bear Lake pitchblende has already been determined by Marble⁴ to be 206.054. Dr. Marble kindly loaned to us the same material with which his experiments were carried out. Our

processes of purification consisted of one precipitation as sulfide, five crystallizations as nitrate from nitric acid, six crystallizations as chloride from water and two distillations in dry hydrogen chloride.

Cyrtolite from Hybla, Ontario

About 9500 g. of finely ground cyrtolite was received from Professor Herman Schlundt. In exploratory experiments it was found that after the mineral had been heated in a current of dry hydrogen chloride most of the lead could be extracted with dilute hydrochloric acid. The heating was carried out in a porcelain tube with portions of about 200 g. After extraction of the product with dilute hydrochloric acid the resulting solution was evaporated with an excess of sulfuric acid to fuming. Treatment of the residue with water was followed by washing and then the insoluble sulfates were several times extracted with hot ammonium acetate. From the acetate solution lead was precipitated as chromate. Then the chromate was reduced with hydrochloric acid and the lead precipitated as sulfide. Conversion of the sulfide to nitrate through the chloride was followed by three crystallizations of the nitrate from nitric acid and four crystallizations of the chloride. Finally the chloride was once distilled in dry hydrogen chloride. All the product was used in the first analysis. For the second analysis the lead was recovered as sulfide from the analytical solution and from the mother liquors of the purification and purified by three nitrate and three chloride crystallizations.

We are greatly indebted to Mr. T. Russell Coyle, who assisted us in the extraction of the lead from the mineral.

Cyrtolite from Bedford, New York, U. S. A., II

Lead extracted from a sample of Bedford cyrtolite has previously been found by us to have a strikingly low atomic weight, 205.93.⁵ The amount of material available was, however, very small, so that we seized the opportunity to secure a larger quantity of mineral stated to come from the same source. The mineral as received was of two sorts,

(5) Baxter and Alter, *ibid.*, 55, 1445, 2790 (1933); also this paper, page 469.

(1) Research Associate in Geology in Harvard University, 1933-34. The present work is Paper No. 15 published under the auspices of the Committee on Geophysical Research and of the Division of Geological Sciences at Harvard University.

(2) Ellsworth, *Am. Mineralogist*, Dec., 1931, p. 577.

(3) For further details see Baxter and Bliss, *THIS JOURNAL*, 52, 4848 (1930); Baxter and Alter, *ibid.*, 55, 1445, 2785 (1933).

(4) Marble, *ibid.*, 56, 854 (1934).

nearly black "unaltered," and brownish "altered." The unaltered material was selected and ground to 40 mesh in a clean mill reserved wholly for our work. The ground material was agitated with water and the finer suspended material removed by decantation. After being dried a large portion of the gangue was separated by means of bromoform. Of the original 4800 g., 324 g. was removed with water and 471 g. with bromoform. About 300 g. was reserved for other purposes, leaving 3700 g. for the extraction of the lead.

The cleaned cyrtolite was treated, in portions of about 100 g., with redistilled hydrofluoric acid in a platinum dish until the insoluble residue was white. In order to remove hydrofluoric acid the solution was evaporated to dryness several times with a large excess of nitric acid. After extraction of the residue with nitric acid, sulfuric acid in excess was added and evaporation was carried to the fuming point. The residue insoluble in dilute sulfuric acid was extracted with hot ammonium acetate and the lead precipitated as sulfide. Again the sulfate was formed by solution of the sulfide in hydrochloric acid and evaporation with sulfuric acid, and the sulfate was dissolved in ammonium acetate. The sulfide was then precipitated, dissolved in hydrochloric acid, converted to nitrate and crystallized as nitrate, four times from nitric acid and twice from water. After conversion to chloride, this salt was five times crystallized and twice distilled in dry hydrogen chloride. This material was used in the first analysis. The remainder of the lead was recovered as sulfide and similarly purified for the second analysis. Unused distilled chloride from the first two samples was combined for the third analysis. All material was recovered and combined to prepare the sample used in the last two analyses.

In all 9.8 g. of lead was extracted from the cyrtolite, or 0.26%. In a recent analysis of a sample of our prepared mineral Muench⁶ has found 0.37% of lead.

Cyrtolite from Bedford, New York, I

Since lead from the second lot of cyrtolite from Bedford, N. Y., appears to be quite different from that contained in the first lot, an additional analysis was made with the lead from the first sample. This lead was recovered as sulfide and purified by three crystallizations as nitrate and four as chloride followed by distillation in dry hydrogen chloride.

Galena from North Carolina, U. S. A.

This mineral was kindly supplied by Mr. O. Ivan Lee. It was described as follows: "galenite and actinolite. Mine No. 1, Headwaters of Crabtree Creek, Yancey Co., No. Carolina. It is believed that the lead in this galenite is radio-lead since galenite is very rare in this region and the specimen was found in proximity to uraninite and its alterations."

After solution of the galena in nitric acid the lead was precipitated as sulfate. The sulfate was next converted to carbonate, which in turn was dissolved in hydrochloric acid. Precipitation as sulfide was followed by five crystallizations as nitrate and four as chloride, and finally by two distillations in hydrogen chloride.

Curite from Katanga Region, Africa

In order to make certain that no personal equation is involved in the analytical operations, by agreement with

Professor Otto Hönigschmid of Munich, Germany, an identical sample of radiogenic lead was subjected to examination simultaneously in his laboratory and by us. The results were then exchanged by mailing them at the same time in the two countries.

In order to provide a sample of atomic weight unknown at the outset Professor Hönigschmid sent to us a specimen of curite from the Katanga region of Africa. This mineral contained a large percentage of kasolite.

The original specimen consisted of two lumps of 155 and 175 g., respectively. The smaller was broken up with a clean steel hammer and dissolved in nitric acid. A 5-g. specimen of the larger was reserved and the remainder was pulverized in a clean diamond mortar and then ground in an agate mortar. A 25-g. portion of this powdered material was reserved and the remainder was dissolved in nitric acid. In all 17 g. of insoluble residue remained. The nitric acid solution was evaporated with an excess of sulfuric acid and the precipitate insoluble in dilute sulfuric acid, chiefly lead sulfate, was dried and weighed (39.9 g.). Purification followed the procedures already outlined for the other samples and included solution of the sulfate in ammonium acetate, precipitation of the sulfide, solution of the sulfide in hydrochloric acid, conversion to nitrate, crystallization of the nitrate, three times from nitric acid and twice from water, conversion to chloride and crystallization of the chloride five times, distillation of the chloride in dry hydrogen chloride. The product, weighing 26 g., was divided into equal portions, of which one was sent to Professor Hönigschmid. The other was once again distilled in hydrogen chloride before analysis.

An approximate analysis of a portion of the powder yielded 65.3% of uranium and 9.7% of lead. Thorium could not be detected.

The early stages in the purification of the various samples were carried on in Pyrex vessels, but in the crystallization of the nitrate and chloride only quartz or platinum vessels were used. Residual silica and organic matter were easily eliminated 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 in a current of chlorine to 1000° 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 com-

(6) Muench, *THIS JOURNAL*, 56, 1536 (1934).

THE ATOMIC WEIGHT OF LEAD

PbCl₂:2Ag. Ag = 107.880. Cl = 35.457

Analy- sis	Mineral	Fusion atmosphere	PbCl ₂ in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Corr. wt. Ag in vacuum, g.	Ratio PbCl ₂ :2Ag	At. wt. lead
1	Besner uraninite	N ₂ + HCl	2.82198	2.19810	+0.00020	2.19830	1.28371	206.059
2	Besner uraninite	N ₂ + 10% HCl	1.17902	0.91839	+ .00010	0.91849	1.28365	206.046
						Average	1.28368	206.052
3	Great Bear Lake	N ₂ + HCl	2.17006	1.69084	- .00033	1.69051	1.28367	206.051
4	pitchblende	N ₂ + HCl	3.44166	2.68127	- .00030	2.68097	1.28374	206.065
						Average	1.28370	206.058
5	Hybla cyrtolite	HCl	0.77361	0.60272	- .00039	0.60233	1.28436	206.20
6	Hybla cyrtolite	N ₂ + 50% HCl	.47163	.36722	.00000	.36722	1.28433	206.19
						Average	1.28434	206.20
7	Bedford cyrtolite II	N ₂ + 10% HCl	2.99554	2.33471	- .00130	2.33341	1.28376	206.070
8		N ₂ + 10% HCl	3.20665	2.49808	- .00020	2.49788	1.28375	206.067
9		HCl	1.06532	0.82984	.00000	0.82984	1.28377	206.071
10		N ₂ + 50% HCl	3.28903	2.56196	+ .00010	2.56206	1.28374	206.067
11		N ₂ + 10% HCl	3.31553	2.58245	+ .00010	2.58255	1.28382	206.083
						Average	1.28377	206.072
12	Bedford cyrtolite I	N ₂ + 50% HCl	0.48244	0.37611	- .00015	0.37596	1.28322	205.954
13	No. Carolina	N ₂ + 10% HCl	3.45151	2.67758	.00000	2.67758	1.28904	207.209
14	galena	N ₂ + 10% HCl	4.29642	3.33295	+ .00010	3.33305	1.28904	207.208
						Average	1.28904	207.209
15	Katanga curite	N ₂ + 50% HCl	2.99570	2.33388	.00000	2.33388	1.28357	206.029
16		N ₂ + 50% HCl	2.01485	1.56973	.00000	1.56973	1.28357	206.028
17		HCl	3.01913	2.35226	- .00014	2.35212	1.28358	206.031
18		N ₂ + 10% HCl	2.93470	2.28629	+ .00010	2.28639	1.28355	206.025
19		N ₂ + 50% HCl	2.00228	1.55987	+ .00010	1.55997	1.28354	206.022
						Average	1.28356	206.027

pared 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. Usually the silver nitrate solution was poured into the lead chloride solution, but occasionally the reverse method was used.

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.

Discussion of Results

It is a satisfaction to draw attention to the fact that in the cases of the samples of lead obtained from Great Bear Lake pitchblende and from Katanga curite our results and those found by other experimenters agree within less than 0.01 unit of atomic weight. Our result for Great Bear Lake material is 206.058 while Marble found 206.054 with identical material. We found for the lead of Katanga curite the value 206.027, while Hönigschmid⁷ with a portion of the same material finds 206.030. Since the experimental error falls on the molecular weight of lead chloride (277) it can be seen that the agreement of the two sets of results is closer than 0.002%. Even if this agreement is partly fortuitous there can hardly be doubt that this method of determining the

atomic weight of lead can be depended upon to give results consistent within 0.01 atomic weight unit, provided of course that adequate quantities of material are available.

The very low atomic weight of the lead from Bedford cyrtolite (I) still remains puzzling. The four original experiments gave the average value 205.924,⁸ a fifth analysis the value 205.938,⁹ while the sixth analysis recorded in this paper yielded a slightly higher, but still low, value, 205.954. The average of all six values is 205.931 with a spread of 0.061 atomic weight unit. Because of the small amount of material available the uncertainty in any one analysis may well be 0.02-3 atomic weight unit, but it seems unlikely that the average value is so much in error. As we have already pointed out, this low value cannot be explained on the basis of present knowledge of the packing fraction and isotopic composition of uranium lead. It was therefore disappointing that lead from the new sample of Bedford cyrtolite (II) turned out to be quite different from that contained in the first.

Examination of polished sections of Bedford I

(8) Baxter and Alter, THIS JOURNAL, 55, 1445 (1933).

(9) Baxter and Alter, *ibid.*, 55, 2790 (1933).

(7) Private communication.

and Bedford II by Mr. Robert Moehlman disclosed that both contained a small quantity of galena crystals. In other respects too the two specimens seem to be similar although one specimen was somewhat darker than the other. Furthermore Muench¹⁰ has analyzed both specimens and finds a similar lead-uranium ratio for the two specimens.

	Pb	U	Pb/U
Bedford I	0.374	7.29	0.0513
Bedford II	.351	6.73	.0522

Muench was unable to detect thorium in Bedford I material, but assumed thorium to be absent in Bedford II and did not test for this element. We carefully tested the solution of Bedford II from which the lead had been precipitated and were unable to detect thorium. To produce the difference in observed atomic weight of lead in Bedford I and Bedford II nearly 7% of thorium lead would be necessary, and if thorium produces lead 0.36 times as fast as uranium this corresponds to 1.4% of thorium in the original cyrtolite, a proportion which could hardly have escaped detection. The difference in the atomic weight of the lead in the two specimens corresponds to 11% of common lead, which would require 0.04% of common lead in Bedford II cyrtolite. It is interesting that Mr. Moehlman estimates the area of galena even in the polished section of Bedford I cyrtolite to be 0.05%. To assume the galena to be of non-radiogenic origin in one and not the other specimen is hardly justifiable.

The lead from North Carolina galena has the same atomic weight as common lead, and while it may be an accidental mixture of uranium and thorium lead there is no particular reason to suppose that it is not common lead.

These results throw little new light on the average atomic weight of uranium lead. Results for this mixture of RaG and AcD obtained from thorium-free or nearly thorium-free minerals are as follows.

Mineral	Approximate age, million years	Atomic weight of uranium lead
Bedford cyrtolite I	400	205.93
Bedford cyrtolite II	400	206.07
Kolm	400	206.01 ¹¹

(10) Muench, *Am. J. Sci.*, **21**, 350 (1931); *THIS JOURNAL*, **56**, 1536 (1934).

(11) Baxter and Bliss, *ibid.*, **52**, 4848 (1930). Since the ash of the kolm contains only 0.075% of lead the small proportion of lead universally distributed in rocks may very well have raised the atomic weight of the uranium lead in kolm by 0.01 to 0.03 unit.

Katanga pitchblende residues	600	206.05 ¹²
Katanga pitchblende	600	206.00 ¹³
Katanga pitchblende extract	600	205.97 ¹²
Katanga pitchblende extract	600	206.02 ¹⁴
Katanga curite	600?	206.03 ¹⁴
Morogoro uraninite	600	206.05 ¹⁵
Morogoro uraninite	600	206.03 ¹⁴
Great Bear Lake pitchblende	1400	205.99 ¹⁶ (corr.)

Of these values that from Bedford cyrtolite (I) is the least certain because of the small quantity of available material. Among the others there seems to be no definite trend in the relation of the atomic weight of uranium lead to the period during which the radiogenic lead has been forming. Aston¹⁶ reports the ratio of Pb²⁰⁶ to Pb²⁰⁷ in leads from Katanga pitchblende and Morogoro uraninite of atomic weight 206.03 to be 93.3 to 6.7 and 93.1 to 6.9, respectively, with little or no Pb²⁰⁸ and no lower isotopes, but to account for lead of lower atomic weight either a smaller proportion of Pb²⁰⁷ or the presence of an isotope of mass less than 206 would be required. A natural explanation to propose for the variations is that some (or all) are contaminated with common lead, which actually seems to be the case with the Great Bear Lake material. Apparently this is not the case with Katanga and Morogoro leads. If the rate of radiogenic production of Pb²⁰⁷ is greater than that of Pb²⁰⁶, as v. Grosse¹⁷ claims, it is hard to understand how the uranium lead from Great Bear Lake could have so low an atomic weight.

If the variations shown by the foregoing data are really due to common lead, the lower values should give a more reliable value for uranium lead. Even with the value 206.00, on the basis of Aston's isotopic analysis of Katanga and Morogoro leads the isotopic weights of Pb²⁰⁶ and Pb²⁰⁷ would be 205.93 and 206.93, respectively, values 0.03 unit lower than those found by Aston.

(12) Residues from radium extraction. Hönigschmid and Birkenbach, *Ber.*, **56**, 1837 (1923).

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

(14) Hönigschmid, Sachtleben and Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933). Also this paper.

(15) Hönigschmid and St. Horovitz, *Monatsh.*, **36**, 355 (1914).

(16) Marble [*THIS JOURNAL*, **56**, 856 (1934)] points out that since Great Bear Lake pitchblende is free from thorium, and since Aston [*Proc. Roy. Soc. (London)*, **A140**, 535 (1933)] finds 2.3% of Pb²⁰⁸ in this lead, there is presumably 4.7% of common lead in Great Bear Lake lead. If allowance is made for this the atomic weight of the uranium lead in Great Bear Lake material becomes 205.99.

(17) A. v. Grosse. *Phys. Rev.*, **42**, 565 (1932).

It should be possible to find the atomic weight of uranium lead from that of a mixture of uranium and thorium lead if the relative proportions of uranium and thorium in the original mineral are known and if these proportions have not changed through alteration of the mineral, through leaching for instance. It is also necessary to know the relative rates of production of lead by uranium and thorium. A probable value for this at present is Th rate/U rate = 0.36. Values computed for certain minerals are given in the following table. The isotopic weight of Pb^{208} is taken as 207.96.

	U, %	Th, %	Average atomic weight	Atomic weight uranium lead	Approximate age, million years
Cyrtolite, Hybla, Ont., Can.	0.529 ¹⁸	0.080 ¹⁸	206.20	206.10	600
Uraninite, Besner, Ont., Can.	67.6 ¹⁹	1.57 ¹⁹	206.05	206.04	800
Bröggerite, Moss, Norway	67.2	4.4	206.06 ²⁰	206.02	800
Uraninite, Wilberforce, Can.	53.5	10.4	206.20 ²¹	206.08	1100
Uraninite, Black Hills, South Dakota, U. S. A.	66.9	2.0	206.07 ²²	206.05	1500

It is interesting that the minimum value found in this way is not much higher than that found from thorium-free minerals.

Obviously more data of all sorts are highly desirable.

(18) Muench, *Am. J. Sci.*, Series V, **25**, 487 (1933).

(19) Ellsworth, *Am. Mineral.*, **16**, 577 (1931); weighted average.

(20) Hönigschmid and St. Horovitz, *Sitzungsber. Kais. Akad. Wien*, **123**, 1 (1914).

(21) Baxter and Bliss, *THIS JOURNAL*, **52**, 4851 (1930).

(22) Richards and Hall, *ibid.*, **48**, 704 (1926).

Summary

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

Source	Atomic weight
Uraninite, Besner Mine, Parry Sound, Ontario, Canada	206.25
Pitchblende, Great Bear Lake, N. W. T., Canada	206.06
Cyrtolite, Hybla, Ontario, Canada	206.20
Cyrtolite I, Bedford, New York, U. S. A.	205.93
Cyrtolite II, Bedford, New York, U. S. A.	206.07
Galena, Yancey County, North Carolina, U. S. A.	207.21
Curite, Katanga region, Africa	206.03

The value for Great Bear Lake material agrees with that found by Marble. That for Katanga curite lead agrees with that found simultaneously by Hönigschmid.

2. It is pointed out that the atomic weight of uranium lead shows little evidence of varying systematically with the age of the mineral source.

3. It is pointed out that the atomic weight of uranium lead appears to be at least as low as 206.00.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF WISCONSIN]

The Diamagnetic Susceptibilities of Palladium Salts

BY R. B. JANES

Ni^{II} , Pd^{II} and Pt^{II} have the same type of electronic configuration in the outermost shell, *i. e.*, eight electrons in a d shell. According to the Hund rule for determining the lowest energy state of a free gaseous ion, all three of these ions are in a 3F_4 state when free; that is, they should have a resultant spin quantum number of two and a resultant orbital quantum number of three. If the metallic ion in the salts of these metals behaves as a free gaseous ion, the salts of all three elements should be paramagnetic. For nickel salts, in general, the orbital contribution of the Ni^{II} ion to the paramagnetic susceptibility of the salts is largely destroyed by the electric fields of

the surrounding ions in the salt molecule, leaving a paramagnetism due only to the spin of the Ni^{II} ion.¹ In the case of platinum for the salts that have been measured the susceptibilities are diamagnetic.² The chemistry of palladium as a rule resembles that of platinum, but in a few ways resembles that of nickel. To see whether the magnetic susceptibility of these compounds correlates with their chemical behavior, measurements of the susceptibilities of Pd^{II} salts have

(1) For a general discussion of this see Van Vleck, "Theory of Electric and Magnetic Susceptibilities," also Schlapp and Penney, *Phys. Rev.*, **42**, 666 (1932).

(2) The measurements of the magnetic susceptibilities of Pt salts are collected in a paper by D. M. Bose, *Z. Physik*, **65**, 677 (1930).