[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL. WORK DONE IN THE CHEMICAL LABORATORY OF THE UNITED STATES GEOLOGICAL SURVEY, WASHINGTON, D. C.]

Lead–Uranium Ratio of Siliceous Pitchblende from Great Bear Lake, N. W. T., Canada, and its Possible Age

BY JOHN PUTNAM MARBLE[1]

A coöperative study has been in progress for some time on the geologic, physical and chemical problems presented by the recently discovered pitchblende deposits at LaBine Point, Echo Bay, Great Bear Lake, N. W. T., Canada. The economic and regional geology and mineral associations have been discussed by several workers, in greatest detail by H. S. Spence,[2] D. F. Kidd[3] and H. S. Robinson,[4] whose papers give full references, including several partial analyses. The chemical and physical investigations are being carried out at the instance of and under the supervision of Professor Alfred C. Lane, Chairman of the Committee on the Determination of Geologic Time. As far as possible, all the work has been done on the identical sample of material, to avoid the uncertainties arising from the neglect of this precaution.

The sample consists of fresh, high-grade pitchblende-silica ore, free from alteration products, from No. 1 Pit, No. 1 Vein, Eldorado Claim, LaBine Point, Great Bear Lake. It was kindly furnished by Mr. H. S. Spence of the Canadian Department of Mines. Petrographic studies on part of the sample have been made by W. Lindgren and W. H. Newhouse[5] among others; C. S. Piggot[6] has studied the isotopic constitution of the lead and uranium; F. W. Aston,[7] the mass spectrum of the lead; A. von Grosse[8] studied the Pa/UI ratio of the mineral and prepared the lead tetramethyl for Aston; the writer[9] determined the atomic weight of the lead, and other work is now in progress. Material for these studies was furnished by the writer from one specific sample, and hence all results should be comparable, as far as possible.

The material is not altogether desirable for a highly accurate age determination, but it is the best that has thus far come out of the region, and in view of the other work it was thought that a determination of the lead–uranium ratio would be of some interest. The deductions made therefrom may well be modified later. This investigation was carried on in the Chemical Laboratory of the United States Geological Survey, by the kind permission of the Director, Mr. W. C. Mendenhall, to whom heartiest thanks are due for the use of the facilities generously placed at the writer's disposal. The advice and assistance of Mr. R. C. Wells, Chief Chemist, are also gratefully acknowledged.

As a large sample was available, considerable time was spent in a study of analytical methods and more determinations than usual were made. The scheme used was adapted from those described by W. F. Hillebrand,[10] R. C. Wells,[11] C. N. Fenner[12] and others, so will be outlined only briefly here.

Tests showed that up to 0.4% lead and traces of uranium remained in the insoluble residue after solution of the mineral in warm 1:1 nitric acid; and fusion of a roasted sample with sodium carbonate with subsequent solution in acid left slightly more uranium insoluble than direct solution in acid. Accordingly the entire sample of ore was in all cases brought into solution as shown below, and the percentages of lead and uranium calculated on this basis. As the same method was used in the determination of the atomic weight of the lead, the percentage of lead can be calculated on this basis with confidence. The retention of lead and uranium is probably due in part to the minute interpenetration of pitchblende and quartz, which the microscope shows, so that a little of the former was completely enclosed by the latter, even after grinding. Also, the small percentage of "common" lead, as revealed by the atomic weight, may be present as sulfide, which would be converted partly to sulfate by the warm nitric acid, and hence be found in the insoluble residue.

After solution of the greater part of the sample by either of the above methods, silica was removed by hydro-

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(1) Research Associate, Committee on the Determination of Geologic Time, Division of Geology and Geography, National Research Council.

(2) H. S. Spence, Section III of "Investigations in Mineral Resources and the Mining Industry," Department of Mines, Mines Branch, 1931, p. 55, Ottawa (1932); *ibid.*, Sands, Clays, and Minerals, **2**, No. 3, pp. 1–16 (1935).

(3) D. F. Kidd, in *Can. Geol. Surv., Ec. Geol. Bull. Ser. Bull.* No. **11**, p. 139 (1932).

(4) H. S. Robinson, *Can. Min. Met. Bull.*, No. **258**, 609 (1933).

(5) See Report of Committee on Geologic Time, p. 44, Washington (1932).

(6) C. S. Piggot, *Phys. Rev.*, **43**, 51 (1933).

(7) F. W. Aston, *Proc. Roy. Soc.* (London), **A140**, 535 (1933).

(8) A. von Grosse, *J. Phys. Chem.*, **38**, 487 (1934).

(9) J. P. Marble, THIS JOURNAL, **56**, 854 (1934).

(10) W. F. Hillebrand, U. S. G. S. *Bull.* **78**, 46 (1891).

(11) R. C. Wells and R. E. Stevens, *J. Wash. Acad. Sci.*, **21**, 409 (1931).

(12) C. N. Fenner, *Am. J. Sci.*, [5] **16**, 369 (1928).

TABLE I

LEAD RATIO

Pb = 206.05 U = 238.14

Analysis	Sample, g.	PbSO₄, g.	∞ %Pb	ThO₂, g.	∞ %Th	U₃O₈, g.	∞ %U	$\frac{\text{Pb}}{\text{U} + 0.36\,\text{Th}}$
II	1.9723	....	....	0.0002	[0.009]	1.2188	52.405	....
III	2.1935	....	....	....	...	1.3504	52.209	....
V	1.0528	0.1621	10.502	< .0001	< .005	0.6472	52.133	0.2014
VI	2.2061	.3384	10.462	< .0001	< .005	....	....	....
VII	1.0800	.1664	10.509	< .0001	< .005	.6648	52.203	.2013
VIII	2.0800	.3196	10.480	< .0001	< .005	....	....	....
XII	2.2317	.3445	10.529	.0002	[.008]	1.3793	52.414	.2009
XIII	2.0438	.3164	10.559	....	...	1.2655	52.534	.2011
XIV	2.0012	....	....	.0001	.004	....	....	....
Average			10.507		.004		52.316	.2012

$$\frac{10.507}{52.316 + 0.36 \times 0.004} = 0.2008 \text{ (P. E. } \pm 0.0094)$$

fluoric acid, and the small residue dissolved in nitric acid, with a second sodium carbonate fusion, if needed. Hydrogen sulfide was passed into the solution, containing about 5% nitric acid, the washed sulfides dissolved in warm dilute nitric acid, and dilute sulfuric acid added. The sulfates were evaporated to fuming, diluted, lead sulfate filtered off, and washed with dilute sulfuric acid. The filtrate was evaporated to fumes and again diluted to recover a few milligrams of lead sulfate. The sulfate was purified by repeated solution in hot 2 *N* ammonium acetate, filtration, and removal of ammonium acetate by evaporation with nitric and sulfuric acids in turn. The final white lead sulfate was transferred without filtration to a tared platinum crucible, fumed gently to dryness with the addition of a few ml. of fuming nitric acid to remove organic matter, and finally heated to constant weight in an electric furnace at not over 600°. A few milligrams of lead was in all cases recovered from the filters by fusion of the ash therefrom with sodium carbonate, solution of the melt in nitric acid, and precipitation as sulfate.

Uranium, rare earths, iron, etc., were removed by repeated precipitation of the freshly boiled sulfide filtrate with carbonate-free ammonia; rare earths and any thorium by oxalic acid in nearly neutral solution free from ammonium salts; iron, aluminum, etc., by repeated precipitation with ammonia and excess ammonium carbonate in a warm, not boiling, solution, after removal of excess oxalic acid with nitric acid.[13] To the carbonate-free filtrate from this treatment, in a dilute sulfuric acid solution, was added a few milliliters of 6% "cupferron" solution to scavenge any remaining heavy metals. Usually none were found. Cupferron was removed by repeated evaporation with nitric acid, and gentle ignition of the residue, and uranium removed by double precipitation with carbonate-free ammonia. The ammonium uranate was roasted in the air at a dull red heat for at least two hours, and then briefly ignited over the Méker burner till the weight of the U_3O_8 was constant.

The rare earth fraction, amounting only to about one per cent. of the sample, was examined in most cases for thorium. Usually only an unweighable trace, less than 0.1 mg., was found. The maximum percentage of pure thorium oxide obtained corresponded to 0.004% thorium. In two analyses 0.009% thorium was found, but in both cases the oxide was deep buff in color, from traces of rare earths. This virtual absence of thorium is checked by A. Merkel,[14] who estimated the thorium content as less than 0.01% by x-ray spectroscopy in another sample from the same pit. The peroxynitrate method of Fenner, the iodate method of Meyer and Speter, and the sebacic acid of Smith and James all gave the same results. A large sample, 50 g., was also tested for thorium, but with negative results.

In several analyses tests were made to determine the effectiveness of the different separations, and the purity and stability of the final products, with results showing that the procedure seemed adequate. All reagents were tested to ensure the absence of lead, uranium and thorium, and the sulfuric acid was redistilled in glass before use to ensure adequate purity.

The results of all completed analyses, not vitiated by known errors, are shown in Table I. The atomic weight of the lead in the identical material, as determined by the writer, is used in the computations.

The calculation of an age for this mineral is a problem of some difficulty. Pitchblende in vein deposits is generally supposed to be more readily subject to alteration than pegmatitic uraninite, and is frequently highly contaminated with galena.[15] If the galena is due to infiltration of "common" lead, the simple "lead-ratio" is worthless as an age indicator. The presence of "common" lead can be shown by atomic weight determinations, especially if thorium is absent, when values much above 206 for the atomic weight of the lead may be taken to indicate contamination. The recent determinations of Baxter and Bliss[16] on lead from the kolm of Westergötland, Sweden; and of

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(13) M. F. Connor, Report of Committee on Geologic Time, p. 27 (1933).

(14) A. Merkel, *Centr. Min., Geol.*, Abt. A, 313 (1934).

(15) A. Holmes, Bull. 80, Nat. Res. Council, Washington (1931), pp. 428–431.

(16) G. P. Baxter and A. D. Bliss, THIS JOURNAL, **52**, 4848 (1930).

Baxter and Alter[17] on leads from different minerals, indicate that we may safely use 206.00 as a round value for the atomic weight of an uncontaminated "uranium"-lead. The value 206.05 found by the writer for the material here analyzed would show about 4% of "common" lead in the lead in this pitchblende. Aston's figures, as corrected, indicate about 4.7%. Using 4% as a first approximation, by which to correct the lead percentage, we obtain the "corrected" results of Table II.

TABLE II

AGE CALCULATIONS

	Ratio	%Pb	Age by formula: $\frac{\log(U+0.36Th+1.155Pb(-\log(U+0.36Th)}{6.6 \times 10^{-5}}$ Million years
Original	0.201	10.507	1373
"Corrected"	.193	10.087	1323

The analyses of Great Bear Lake pitchblende made by the Canadian Department of Mines and included in Spence's report,[2] from various sampling pits show uranium varying from 25.73 to 52.66%, lead from 5.55 to 13.40%, uncorrected lead ratio from 0.11 to 0.27, mean ratio 0.21. No determinations of atomic weight or isotopic composition were made, so the results cannot be compared directly with the present ones but the slight difference between this mean "uncorrected ratio" and that of the writer may perhaps indicate a general uniformity of the ore-body as a whole. Dr. F. Hecht has recently completed studies of atomic weight and lead ratio on an independent sample. The results have not yet been published, but preliminary figures kindly submitted through Professor Lane point to a "corrected ratio" very close to that given here. An earlier micro-analysis by Hecht[18] was not accompanied by atomic weight determinations, and the larger lead-ratio points to a concentration of galena in the microsample used.

If we knew the exact isotopic composition of uranium, and could connect a given isotope of lead directly with its parent, the calculations would be of a higher order of accuracy. Since this cannot, as yet, be done, we must content ourselves with this first approximation. The extreme variation in the "lead-ratios" is less than the other uncertainties, so that a figure for possible error of the age, based on these would, it is felt, be misleading.

Von Grosse[19] states that, due to the more rapid decay of "actino-uranium," the isotope from which the actinium series is descended, than of uranium proper, there is less lead now being formed therefrom than in early geologic time. Since, as a first approximation, Ac gives rise to Pb^{207}, the older the mineral, the higher should be the atomic weight of its lead. From his curve, assuming an age of about 1300 million years, we find about 13 atoms of AcD for 100 atoms of RaG. Using Aston's figures for the "atomic weights" of the lead isotopes,[20] and transferring to the chemical scale as von Grosse has done, we may calculate

$$\frac{205.96 \times 100 + 206.96 \times 13}{113} = 206.08$$

a value in fair agreement with that found by the writer, but the addition of about 4% of common lead, known to be present, makes this agreement poorer. If leaching has occurred—which might account for the discrepancy—presumably uranium has been removed, as removal of AcD in preference to RaG would represent the separation of isotopes by selective solution, a process not elsewhere observed. However, the work of Baxter and Alter indicates no immediate connection between age and atomic weight of uranium lead, and the petrographic studies do not disclose any signs of extensive removal. Alter and Kipp[21] among others have recently suggested that uranium may be removed faster than thorium, but the present material is essentially thorium-free. Further work needs to be done on selected material from this locality before the problem of the extent of alteration can be settled; and the present puzzles as to the isotopic composition of leads and their parents cleared up before attack on theoretical grounds becomes strictly valid.

On the geologic side we also have a conflict of opinion, though studies so far made are by no means complete. Robinson associates the pitchblende with a sill or dyke of diabase-norite, which he refers provisionally to the Keweenawan; Kidd associates it with an earlier granite, which Robinson doubtfully, and Furnival[22] apparently refer to the Keewatin. On the basis of the Pb/U ratio as corrected for the presence of "common" lead, the latter correlation seems preferable.

Further field work obviously needs to be done to obtain a geologic check on these results. More-

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(17) G. P. Baxter and C. M. Alter, THIS JOURNAL, **55**, 1445, 2785 (1933); **57**, 467 (1935).

(18) Report of Comm. on Geol. Time for 1933, p. 24.

(19) A. von Grosse, *Phys. Rev.*, **42**, 565 (1932).

(20) F. W. Aston, *Nature*, **129**, 649 (1932).

(21) C. M. Alter and E. M. Kipp, *Science*, **82**, 464 (1935).

(22) G. M. Furnival, *Can. Min. J.*, **55**, No. 1, 5 (1934).

over, it is hoped that pitchblende freer from impurities, a sample of which has recently been received from Spence, will yield results subject to a smaller correction for "common" lead. In the meantime the above tentative age offers a basis for geologic correlation.

Summary

1. A sample of pitchblende from LaBine Point, Echo Bay, Great Bear Lake, N. W. T., Canada, yields a "corrected" lead-ratio of 0.193, corresponding to an age of 1323 million years.

2. As the atomic weight and isotopic composition of the lead, and the Pa/UI ratio of this same sample have been determined, ages, etc., calculated by different methods should agree. This agreement has not been obtained in all instances, and possible reasons have been outlined.

3. The age found indicates that a possible Keewatin granite may be the source of the pitchblende.

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[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT COMPANY]

Sodium Benzylsulfonate: A Case of Dimorphism

BY FRANCIS D. DODGE

Some years ago the writer had occasion to prepare sodium benzylsulfonate by the usual reaction of benzyl chloride with sodium sulfite in alkaline solution. At the completion of the reaction, the mixture was filtered hot, and on slow cooling deposited the salt in transparent rectangular plates, which invited examination under the microscope. In parallel polarized light, the crystals showed parallel extinction; in convergent light, the symmetrical interference figure of a positive orthorhombic crystal.

For purification, the crystals were redissolved in sufficient warm water and again allowed to crystallize slowly. On examination, a week or so later, a change in the appearance of the crystals was noted. The thin plates were longer, and showed a tendency to radiate from a center. The terminations were less distinctly rectangular, with occasional faces inclined to the elongation. Under the microscope the crystals presented a picture quite different from the first crop. Very thin plates showed an extinction angle of about 28°, and, in convergent light, the emergence of one axis near the center of the field. Thicker plates showed unusual optical properties, as will be described below.

It was evident that the two crops of crystals were not identical, and the first obvious hypothesis was that two different hydrates existed.

Analysis of the recrystallized product gave figures agreeing with those of Fromm.[1]

Anal. Calcd. for $C_7H_7SO_3Na \cdot H_2O$: loss at 110°, 8.49; Na_2SO_4, 36.6 (on dry salt). Found: loss 8.77; Na_2SO_4, 36.08.

The preparation of pure orthorhombic crystals for analysis presented at first some difficulty. Without going into details of numerous experiments, it was found that the orthorhombic form was comparatively stable in the original mother liquor, which contained sodium chloride, sulfite, sulfate and hydroxide, but in a pure solution the crystals were rapidly converted into the asymmetric form.

For example, if an orthorhombic plate, about 6 by 13 mm., is placed upright in a small tube, and covered by a solution of the pure salt, saturated at the room temperature, and the tube kept at this temperature, observation with a lens will show that the plate is gradually converted into a mass of small prisms.

This transformation occurs in the recrystallization of the crude orthorhombic salt. From strong solutions, orthorhombic crystals are deposited on cooling, which on standing pass into the stable form. From weak solutions, by slow evaporation. the stable form may be obtained directly. Conversely, the stable form may be changed into the orthorhombic form by recrystallization from the original mother liquor, or from water containing 5 to 10% of sodium chloride, and about 0.5% hydroxide.

For some reason the original mother liquor is especially favorable to the stability of the ortho-

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(1) Fromm, *Ber.*, **39**, 3308 (1906).