

TABLE II
VAPOR PRESSURE DATA

Substance	B. p., °C.	Log P	ΔH , cal.	Trouton's constant
SiFCIBr ₂	59.5	7.5669 - (1558/ T)	7,095	21.38
SiFCl ₂ Br	35.4	7.0982 - (1301/ T)	5,954	19.30

The melting points were determined by the method described by Skau,⁵ the specimens being sealed in wafer-thin ampoules provided with thermocouple wells in which a copper-constantan thermocouple was inserted. Heating and cooling curves were then taken potentiometrically in the Skau apparatus. The melting points so determined are $-112.3 \pm 0.2^\circ$ and $-99.3 \pm 0.2^\circ$ for SiFCl₂Br and SiFCIBr₂, respectively.

Summary

1. Two fluorochlorobromides of silicon have been prepared for the first time, silicon fluorochlorodibromide, SiFCIBr₂, and silicon fluorodichlorobromide, SiFCl₂Br. These substances are the first halides of silicon to be reported in which silicon is linked to three different halogen atoms.

2. The new compounds were prepared by three methods: the fluorination of silicon chlorobromides, the chlorination of silicon fluorotribromide, and the reaction of antimony trichloride

(5) Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).

with silicon fluorotribromide. The formulas of the compounds were established by analysis and molecular weight determinations.

3. SiFCIBr₂ is a colorless, mobile liquid of b. p. 59.5° , m. p. -99.3° . Its vapor pressure is represented by the equation, $\log P = 7.5669 - (1558/T)$. SiFCl₂Br, also a colorless, mobile liquid, boils at 35.4° , and melts at -112.3° . Its vapor pressure is given by the equation, $\log P = 7.0982 - (1301/T)$.

4. Both liquids hydrolyze completely in moist air. In ice-cold water the hydrolysis products are silicic, hydrochloric, hydrobromic and hydrofluoric acids, with practically no fluosilicic acid.

5. Incidental to the main objective of the work, several new methods of preparing the three chlorobromides of silicon were developed, including the reaction of antimony trichloride or phosphorus trichloride with silicon tetrabromide; the refluxing of silicon tetrabromide for forty-eight hours in a sealed container in an atmosphere of chlorine; and the reaction of hexachlorodisilane with bromine.

CAMBRIDGE, MASS.

RECEIVED FEBRUARY 10, 1937

[CONTRIBUTION FROM THE COMMITTEE ON DETERMINATION OF GEOLOGIC TIME, DIVISION OF GEOLOGY AND GEOGRAPHY, NATIONAL RESEARCH COUNCIL]

Atomic Weight of Lead from Galena, Great Bear Lake, N. W. T., Canada

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The fundamental assumption on which we base the "lead-ratio" method for measuring geologic time is that a given mineral has neither lost nor gained lead, uranium, or thorium since its first crystallization. As the writer recently pointed out,² further evidence on this point, either general or specific, is greatly desired in determining the age of the pitchblende at Great Bear Lake, Canada.

One of the mineral systems at this locality is a replacement band of sulfides in the country rock, which is cut by the pitchblende veins. Mr. Hugh S. Spence of the Mines Branch, Canada Department of Mines kindly furnished a generous sample of this material, with the following description:³

"Fine-grained galena from chalcopyrite-galena

(1) Research Associate, Committee on Determination of Geologic Time.

(2) J. P. Marble, *THIS JOURNAL*, **58**, 434 (1936).

(3) Personal communication; see also H. S. Spence, Sec. III, Investigations in Min. Res. and Mining Indus., Ottawa, 1931, p. 61.

band in the country rock, cut by the No. 2 Vein at LaBine Point, Great Bear Lake, N. W. T., in the No. 2 pit on the easterly (siliceous) portion of the vein. The pieces were taken from the band approximately at the contact with the vein, and the galena carries some fine native silver, presumably introduced from the vein."

The question at once arises: "Is the lead in this ore 'common' lead, 'uranium' lead, or a mixture of the two?" If the first, it offers a source for the "common" lead found in the pitchblende;⁴ if the second or third, it indicates that more or less lead may have been leached from the pitchblende, which would make it valueless as an "age-index" mineral.

Preliminary work showed that if the sample contained uranium or thorium, the amounts were too

(4) (a) J. P. Marble, *THIS JOURNAL*, **56**, 854 (1934); (b) F. W. Aston, *Proc. Roy. Soc. (London)*, **A140**, 535 (1933); (c) F. Hecht and E. Kroupa, *Z. anorg. allgem. Chem.*, **226**, 248 (1936).

TABLE I

PbCl ₂ /2Ag AND ATOMIC WEIGHT OF LEAD FROM GREAT BEAR LAKE GALENA						
Anal. no.	Vac. wt. PbCl ₂ , g.	Vac. wt. Ag, g.	Ag added in soln., g.	Corr. wt. Ag, g.	PbCl ₂ /2Ag	Atomic weight
I	0.54549	0.42293	+0.00025	0.42318	1.28903	207.206
II	2.77993	2.15663	= .00000	2.15663	1.28902	207.204
IV	1.17288	0.90980	+ .00010	0.90990	1.28902	207.205
Average					1.28902	207.205

Total PbCl₂ = 4.49830. Total Ag = 3.48971. PbCl₂/2Ag = 1.289018.

Atomic Weight Pb = 207.205.

small to detect by careful qualitative tests on a fair-sized sample, and a radiograph produced no trace of darkening on a photographic plate in forty-eight hours. A quantitative determination by the sulfate method showed 15.53% lead, and since over 100 g. was available, the lead was extracted, purified, and its atomic weight determined to see if an answer to the above question could be obtained.

The greater part of the sample was broken up on a clean hardened steel anvil, coarsely ground with a hardened steel muller, and finely powdered in a clean agate mortar. The powder in separate portions was decomposed with aqua regia, and the lead precipitated as sulfate, which was then extracted with hot ammonium acetate solution. A very small residue was decomposed by hydrofluoric acid, and a trace of lead recovered in the same way. The lead was then precipitated as sulfide, which was dissolved in hydrochloric acid, and again precipitated as sulfate. After several repetitions of this cycle, the lead was precipitated as sulfide from acid solution, again dissolved in hydrochloric acid, converted to nitrate, repeatedly crystallized as nitrate with centrifugal draining, converted to chloride, repeatedly crystallized as chloride, distilled in pure dry hydrogen chloride, and finally fused in pure dry hydrogen chloride, cooled in pure dry nitrogen and bottled in pure dry air in a Richards bottling apparatus. The water, acids and ammonia used were redistilled according to the customary Harvard technique, and hydrogen sulfide was obtained from cylinders of the purest commercial gas. Except for the sulfide precipitations, all operations were carried out in quartz or platinum.

The weighed sample was dissolved in warm water containing 1 or 2 drops of dilute nitric acid, and the chloride precipitated with purest silver in the dark room. The final concentration of lead and silver was about 0.03 *N*. The end-point was adjusted by equal opalescence nephelometry in the usual way. Weighings were made in duplicate by substitution on a sensitive balance at virtually constant temperature, using weights standardized by the Richards method. Vacuum corrections of +0.000058 g. per gram for lead chloride and -0.000031 g. per gram for silver were applied. The silver used had been found adequately pure in other atomic weight investigations.

The weight of lead chloride in Analysis III, made on the same portion as Analysis II, was incorrectly recorded due to an accident, and this analysis is omitted from the calculations. As a large part of the first lot worked up

was lost by accident, Analyses II and IV were made on further portions of the sample. The method of purification was essentially the same for each.

The results of this work are in agreement with the most recent values for the atomic weight of "common" lead, by the chloride-silver ratio,⁶ and indicate that the lead from this sulfide replacement band contains virtually no "uranium" lead. The possibility that we have a balancing of "uranium" and "thorium" leads to give the observed value is most improbable, as there is neither uranium nor thorium present in the ore, and the pitchblende at Great Bear Lake is essentially thorium-free. From this we may perhaps draw the following conclusions.

1. At Great Bear Lake there are at least two separate sources of mineralizing solutions, which have had little effect on each other, either during or after the first periods of deposition.

2. The pitchblende has not lost appreciable quantities of lead by leaching, as "uranium" lead has not travelled into the galena.

3. The small amount of "common" lead in the pitchblende may perhaps have come from the nearby galena, which might thus be older than the pitchblende.

General Conclusions

This work may be considered from another point of view as adding one more to the list of determinations of the atomic weight of "common" lead, in which the geologic provenance and horizon of the material is known, as shown in Table II.⁶ This table lists only those determinations made on material of known provenance, using the ratio PbCl₂/2Ag, so as to provide a standard of comparison. In all cases the methods used for the purification of the lead chloride and the determination of the ratio have been described in sufficient detail to allow an evaluation of the precision

(5) Report of International Committee on Atomic Weights, *THIS JOURNAL*, 59, 219 (1937).

(6) Some of the earlier determinations are also listed in A. Holmes, *Bull. 80, Nat. Res. Council*, p. 218, Washington, D. C., 1931.

TABLE II
ATOMIC WEIGHT OF "COMMON" LEAD

Mineral		Locality	Geologic age	Atomic weight
Cerussite	(1915) ^a	British Broken Hill Mine, N. S. W.	Pre-cambrian	207.21
Galena	(1915) ^a	Joplin, Mo., U. S. A.	Post-carboniferous	207.22
Cerussite	(1915) ^a	Wallace, Idaho, U. S. A.	Tertiary	207.21
Cerussite	(1915) ^a	Cömmern, Eifel Mts., Germany	Carboniferous	207.20
Galena	(1915) ^a	Grube Holzappel, Lahn, Germany	Carboniferous	207.21
Wulfenite and Vanadinite	(1915) ^a	Tucson Mts., Arizona, U. S. A.	Tertiary	207.22
Galena	(1915) ^a	Metalline Falls, Washington, U. S. A.	Tertiary?	207.21
Complex sulfides	(1931) ^b	Coeur d'Alene district, Idaho, U. S. A.	Tertiary	207.22
Complex sulfides	(1933) ^c	Coeur d'Alene district, Idaho, U. S. A.	Tertiary	207.21
Galena	(1935) ^d	Yancey County, N. C., U. S. A.	Pre-cambrian	207.21
Galena	(1936) ^{4e}	Tetüche, U. S. S. R.	Permian	207.22
Galena	(1937)	Great Bear Lake, N. W. T., Canada	Early? Pre-cambrian	207.21

^a Baxter and Grover, *THIS JOURNAL*, 37, 1027 (1915). ^b Baxter and Bliss, *ibid.*, 52, 4848 (1930). ^c Baxter and Alter, *ibid.*, 55, 2785 (1933). ^d *Ibid.*, 57, 467 (1935).

of the work. The total variation, 2 parts in 20,000, is close to the limit of error of careful nephelometric titration, especially when small samples of lead chloride have been taken. No evidence is present of any variation of the atomic weight of "common" lead as a function of geologic age. It seems worth while making this point, as Vernadsky⁷ has recently brought up the question as to the constancy of atomic weight of various elements once more.

One further point may perhaps be made, but with extreme caution. The constancy of the atomic weight of "common" lead indicates that it probably cannot have been formed by processes of radioactive decomposition in the crust of the earth, with the generated lead removed and concentrated away from its parents by processes of solution and subsequent precipitation or crystallization. Since uranium and thorium have different half-lives, lead formed by radioactive decomposition at different times would have a varying isotopic composition and hence a varying atomic weight. If such a process is responsible for the formation of "common" lead, it must have taken place during "pretelluric" time, when the earth had no solid crust containing radioactive elements disintegrating as such in place. There seems to be little unequivocal cosmic evidence for such a process, as distinct from the processes by which other elements came into being. This

(7) V. I. Vernadsky, *C. R. Acad. Sci. U. S. S. R.* [N. S.], 3, 129 (1936).

leads to the conclusion that "common" lead owes its existence as such to the ordinary cosmic processes, whatever they may be, while leaving still unexplained the reason for the chemical identity of this element with the stable end-products of radioactive disintegration.

Acknowledgments.—Especial thanks are due to the Director of the U. S. Geological Survey, and to Professor Gregory P. Baxter of Harvard University, for permitting the use of their laboratories for this investigation. Dr. R. C. Wells of the Survey coöperated in the preliminary investigations, and Dr. J. H. Faull, Jr. and Mr. F. D. Tuemmler at Harvard aided in the purification of reagents and the setting up of apparatus. Professor Alfred C. Lane, Chairman of the Committee on the Measurement of Geologic Time, has provided constant inspiration.

Summary

1. The atomic weight of lead from galena at Great Bear Lake is 207.21.
2. The "common" lead contaminating the "uranium" lead of the pitchblende may have come from this source.
3. Presumably the pitchblende has not lost appreciable quantities of lead by leaching.
4. Further evidence is presented as to the constancy of the atomic weight of "common" lead as a function of its geologic age.

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RECEIVED FEBRUARY 10, 1937