DETERMINATION OF LEAD IN SILICATE ROCKS.

IVAN TH. ROSENQVIST.

ABSTRACT. Determinations of the lead content of some Norwegian silicate rocks have been made. An enrichment of the lead was accomplished by co-precipitation as sulfate with strontium as "carrier," and the lead was determined electrolytically as lead dioxide in the enriched product. The efficiency of the different operations was controlled throughout the work by the use of thorium B as radioactive indicator.

The superiority of strontium as "carrier" as compared with other methods is shown. The proportion of lead in the rocks studied is fairly constant, in spite of different origin and some variations in chemical composition.

THE writer in a recent paper[9] dealt with the geology and petrology of certain parts of the Opdal area in western and central Norway. While this work was in progress it became clear that the determination of the age of some gneisses was desirable. Professor Holtedahl suggested the use of radioactive methods, and in particular the determination of the content of radium and radium G.

Up to the present few attempts have been made to determine the age of silicate rocks in this way. Due to the presence of accessory minerals they contain radioactive substances, but in quantities so minute that exact determination is difficult.

Another difficulty is that in rocks radium G is always associated with "common" lead. Accordingly the mixture of lead isotopes must be separated in quantities large enough to permit mass-spectrographic examination to give the percentages of isotopes in the mixture. Just at present this determination cannot be made in Oslo, and Dr. A. O. Nier of the University of Minnesota has kindly undertaken to do it. His results will be published later. In this paper appear some details of the extraction and determination of lead. The work was done at the Chemical Institute of the University in the laboratories of Professor Ellen Gleditsch.

It is evident that when lead is to be separated for further examination, a gravimetric analytical method is needed. For mass-spectrographic studies 2-3 mg. lead are sufficient. According to Goldschmidt[1] and Hevesy and Hobbie,[2] rocks such as those here studied contain only 10-20 mg. lead per kg., so 100-300 g. rock is needed for an analysis. This will consist of two parts: a preliminary enrichment of lead, and a subsequent determination of the lead in the enriched product.

Earlier Methods of Enrichment and Determination of Lead.

A. *Enrichment.* E. B. Sandell[5] transformed the lead into dithio-carbazonate and extracted this with carbon tetrachloride. Most investigators have used co-precipitation of lead with a "carrier," such as silver, copper, or calcium, as did Hevesy and Hobbie, who precipitated the lead as sulfide after addition of silver nitrate solution.

We believe that rather serious objections may be raised against this method. Lead sulfide is not absolutely insoluble, moreover the sulfides of lead and silver are not isomorphous. In the present work the lead was precipitated as sulfate, with strontium as "carrier." This was used because of the great similarity of $PbSO_4$ and $SrSO_4$ from a crystallo-chemical aspect, first order isomorphism being found, according to V. M. Goldschmidt.[6] Both substances crystallize in the rhombic-holohedric class, with the axial ratios:

$SrSO_4$	a:b:c = 0.779:1:1.280
$PbSO_4$	a:b:c = 0.785:1:1.289

Strontium sulfate, accordingly, should be an ideal "carrier" for lead determinations.

B. *Determination.* For the gravimetric determination of lead in quantities as small as those found in silicate rocks, two methods have been chiefly used. One is to convert the lead, after enrichment, into sulfate or some other insoluble form, and weigh. The other is to convert the lead into dioxide by electrolysis with anodic oxidation. This method has been worked out by Alders and Stähler[3] and by H. Töppelmann.[4] We have followed the directions of the latter. Hevesy and Hobbie also determined lead as dioxide, correcting their final results by the radioactive indicator method, adding radium D to the pulverized rock sample. This followed the lead through the different operations, and the final result was corrected for the percentage of radium D in the lead dioxide. The published figures indicate that the methods used were not all absolutely reliable, the corrections in some analyses being considerable.

I should have liked to use radium D, but unfortunately none was at my disposal, and therefore I used thorium B. This has the disadvantage of a much shorter period, 10.4 hours as opposed to 12 years, so each operation had to be controlled separately. The procedure was: thorium B was deposited in the usual way on a platinum foil. This was treated with dilute

nitric acid, and the solution made up to 100 ml. An aliquot, say 25 ml., was used for a blank test, while 25 ml. served as control substance for the desired chemical operation. Some lead nitrate was added to the blank, and precipitated with the thorium B, the precipitate dissolved in nitric acid, and the solution evaporated on a glass disk. The activity of the main product and of the blank were measured at the same time, thus avoiding all calculations of decrease of radioactivity with time. I wish here to express my gratitude to Dr. Elisabeth Rona who kindly helped me with the preparation of the thorium B.

Purification of Reagents. For this work it is absolutely necessary that all reagents should be lead-free. All were tested and, when need be, purified. HF, hydrofluoric acid medicinale, Merck, was found to contain 2.06×10^{-4}% lead. It was purified by adding 10 ml. of ten per cent strontium chloride solution per kg. acid, the precipitate of strontium fluoride carrying down the lead fluoride. This was done twice, and the lead content of the final filtrate determined by electrolytic oxidation with Cu_2Cl_2 as "carrier." Two hours electrolysis showed less than 0.002 mg. lead per kg.* $SrCl_2$ was purified by repeated additions of Cu_2Cl_2 and subsequent precipitation with H_2S.

$Na_2CO_3+K_2CO_3$ was dissolved in water, and 1 ml. of 10 per cent strontium chloride added dropwise with vigorous stirring. After filtration of strontium carbonate, the solution was evaporated in platinum. H_2SO_4 and HNO_3 were redistilled in an apparatus of Jena glass. Cu_2Cl_2 and $Pb(NO_3)_2$ were "pro analyse" salts from Merck. All water used was redistilled in an apparatus of Jena glass.

The purity of the reagents was also tested by spectrographic examination. Sulfides prepared from the reagents were compared with those prepared from known mixtures of copper and lead salts, and with a sulfide precipitate obtained from a sample of nordmarkite porphyry, after removal of silica. The results of 27 spectrograms showed:

unpurified HF, about .....2.0 x 10-4% Pb
purified HF, too little Pb for spectrographic determination
purified H_2SO_4, about .....2.5 x 10-6% Pb
nordmarkite porphyry, about .....1.1 x 10-3% Pb

* ThB was added as a control, but only 36% of the amount taken was found on the electrode. This is probably accounted for by the need of an extremely high overvoltage to precipitate PbO_2 in so minute a concentration; usually the electrolyte will decompose before precipitation is complete.

I am greatly indebted to Professor V. M. Goldschmidt and Konservator I. Oftedahl for permission to use the spectrograph of the Geological Museum in Oslo, and for valuable help and interest.

Reliability of the analytical determination. Samples of lead nitrate solution of known lead content were electrolyzed at 1.5 amps. for 2 hours at 60°, with results as follows:—

mg. Pb taken	mg. PbO_2 found	mg. Pb in PbO_2	% Pb recovered
0.355	0.426	0.368	103.8
0.887	1.057	0.914	102.8
0.887	1.021	0.889	100.1
0.887	1.017	0.882	99.4
		Average	101.53%

Two further tests were made, to which thorium B was added as control.

0.887 + 25 ml. ThB solution	1.007	0.784	98.0
0.887 + 25 ml. ThB solution	1.016	0.881	99.5

In these two analyses, the PbO_2 was dissolved in hydrochloric acid, evaporated on a glass disk, and the α-ray activity measured by an electrometer. The spent electrolyte was also evaporated and its activity measured. The results were:

% ThB taken, on electrode	in solution	% recovered
96	2.8	98.8
99.3	0.2	99.5

The method seems reliable. The high results in the first two analyses may be due to adsorbed nitrogen oxides. In any case, the considerable losses of lead found by Hevesy and Hobbie do not seem to appear at this point.

Reliability of the enrichment process. As stated above, the co-precipitation of lead with silver, as sulfide, did not appear to be completely quantitative. The solubility of lead sulfide is somewhat high, and the two sulfides Ag_2S and PbS are not isomorphous. Also, according to V. M. Goldschmidt,[6] they have rather different ionic radii: $Pb^{++}=1.32$ Å; $Ag^{+}=1.13$ Å. To check on this point, tests were made by precipitating known amounts of lead, silver, and thorium B as sulfides together under varying conditions. The activity of the solution of the precipitate was compared with that of a "blank" containing lead and thorium B alone, using a Wulff quartz string electrometer.

A sample test showed:

Time	Material	Scale div./min.
16:45	Pb + ThB, blank	4.62
16:50	" "	4.57
16:55	Pb + Ag + ThB	3.83
17:02	Pb + ThB, blank	4.55
17:10	" "	4.55

Natural leak of instrument = 0.02 scale div./min.

This shows that 83.7 per cent of the total thorium B added was found in the mixed lead-silver precipitate. Two further tests, with precipitates prepared under different conditions, showed 92.0 and 95.5 per cent ThB remaining with the precipitated mixed sulfides. This indicates that this method of co-precipitation of lead is not completely quantitative.

Similar tests were applied to co-precipitation of lead and strontium as sulfates. In one test, 10 mg. lead as nitrate was dissolved in 500 ml. water, 25 ml. thorium B solution added, then 5 ml. concentrated sulfuric acid, then 25 ml. strontium chloride solution, carrying 0.2 g. $SrCl_2$. The precipitate was filtered off, and 0.2 g. $SrCl_2$ solution added to the filtrate. The activity of the two precipitates was compared with that of 100 mg. lead nitrate + 25 ml. thorium B solution, precipitated with sulfuric acid in 50 per cent alcohol. A test showed:

Time	Material	Scale div./min.	%ThB ≏ %Pb
16:00	Blank test	3.84	
16:15	$SrSO_4$, 1st ppt.	3.75	98.
16:30	Blank test	3.77	
16:45	$SrSO_4$, 2nd ppt.	0.06	1.1
17:00	Blank test	3.71	
	Natural leak	0.02	
			Total 99.1%

In a second test, the two precipitates were combined and their activities measured together, the activity of the filtrate being also tested. In this case 99.8 per cent of the total thorium B, and consequently of the lead, was found in the precipitates. This indicates the greater reliability of the sulfate co-precipitation. A few tests indicated that the preparation of lead dioxide from granite would not involve losses of lead.

In theory, the next step should be the analysis of an artificial mixture of known composition, containing those elements to be expected in a rock of the type to be analyzed. It would be extremely difficult adequately to purify all the necessary chemicals, and some of the interfering elements, e.g. antimony and

bismuth, which might be present in reagents, are known to occur in rocks in much smaller amounts than does lead.* They would not be expected to follow the lead in the preliminary enrichment.[8]

Method of Analysis. The pulverized rock sample was treated with hydrofluoric and sulfuric acids in a platinum dish until all silica was volatilized, then heated to fumes of sulfur trioxide. The residue, largely sulfates, was leached with water in amounts from 3/4 to 3 l., according to size of sample. To the filtered, strongly acid solution was added enough strontium chloride to give a concentration of 1 g. $SrCl_2$/l. The precipitated sulfates were filtered off and added to the undissolved sulfate residue. The combined sulfates were fused twice with from 10 to 50 g. potassium and sodium carbonate. The cake was leached with water, and the residue treated with dilute nitric acid. To this solution was added 0.1 g. copper nitrate, and it was then electrolyzed at about 60° for 2 hours, with a current of 1.5 amps. The usual type of gauze electrode served as cathode, and a platinum rod as anode, the latter weighing about 2 g. A Kuhlmann micro-balance was used for weighing the electrode and deposit.

After weighing, the anode with the lead dioxide was treated with warm, dilute hydrochloric acid, the lead chloride solution evaporated to dryness, and the residue dissolved in the smallest possible volume of hot one per cent hydrochloric acid. This was transferred to a centrifuge vessel, the bottom of which was drawn out to a tube 2 cm. in length, and 1 mm. diameter. Five times the calculated amount of potassium iodide was added, and after cooling, the precipitated lead iodide was centrifuged down into the capillary. The clear solution was decanted, the precipitate washed twice with ice-cold water, the centrifuge tube dried for 2 hours at 150°, and the capillary containing the lead iodide sealed off. This material has been sent to Doctor Nier.

The following rocks were analyzed for lead. In most cases radioactive control was used throughout the analysis.

* Sagartschev,[7] using ThB and ThC as indicators, has shown that up to 60% of bismuth is precipitated with lead as sulfate. This holds only for low acid concentrations. At 0.25N acidity, precipitated lead sulfate is free of ThC, and hence of bismuth.

No.	Weight sample, g.	%Pb found
Ia.	300	2.17×10^{-3}
Ib.	200	2.06×10^{-3}
		Average = 2.12×10^{-3}
II	50	1.06×10^{-3}
III	200	1.65×10^{-3}
IV	200	1.17×10^{-3}

Source of samples:

I. Granite from Oddersjå, near Kristiansand S., Norway. Doubtless of Archaean age. Rather dark, reddish, coarse-grained. Further described in a note by the writer.[9]

II. Gneiss-granite from Hol, in the Lønset anticline, Opdal area, Norway. Light grey in color. For petrological description see ref.[9]

III. Augengneiss from Hol, in the Lønset anticline. See ref.[9]

IV. Nordmarkite porphyry from a dyke at Blindern, by Oslo, Norway.

The object of this work was to determine whether the rocks from the Opdal area (II and III) were pre-Cambrian or Caledonian. If the former, it seems reasonable to expect the same age as for the Oddersjå granite. On the other hand, the nordmarkite porphyry is younger than the Caledonian, and could serve for comparison. A fuller discussion will be given when the lead isotope ratios have been determined, and the age can be calculated. Meanwhile, it may be pointed out that the lead content of all these rocks is rather constant, c. 10-20 g./ton, though they are of rather different chemical composition, of different origin, and from different localities.

LITERATURE.

1. Goldschmidt, V. M.: 1937, Geochemische Verteilungsgesetze der Elemente, IX. Norsk Vid. Akad. Oslo, Mat.—Nat. Kl., No. 4.
2. Hevesy, G., and Hobbie, O.: 1926, Z. anal. Chem., B. 68, p. 1.
3. Alders and Stähler: 1889, Z. anal. Chem., B. 28, p. 595.
4. Töppelmann, H.: 1929, J. prakt. Chem., B. 121, p. 289.
5. Sandell, E. B.: 1937, Ind. Eng. Chem., Anal. Edn., Vol. 9, p. 464.
6. Goldschmidt, V. M.: 1934, Kristallchemie, Handwörterbuch der Naturwissenschaften, 2te Aufl., V Bd., G. Fischer, Jena.
7. Sagartschev, B.: 1939, Z. anal. Chem., B. 116, p. 21.
8. Rosenqvist, I. Th.: 1939, Norsk Geol. Tids., Bd. 19, p. 110.
9. Rosenqvist, I. Th.: 1941, Norsk Geol. Tids., in press.

Revised by J. P. Marble, Vice-chairman, Committee on Measurement of Geologic Time, Division of Geology and Geography, National Research Council, by permission of Dr. E. Gleditsch and Dr. I. Th. Rosenqvist.

University of Oslo,
Oslo, Norway.