petroleum ether catalyzes the reaction between nitrogen trichloride and nitrosyl chloride referred to in 2.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

RADIUM AND GEOLOGY[1]

BY CHARLES SNOWDEN PIGGOT

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This article is a brief account of the general problem of the relation of radioactivity to geologic phenomena and of some of the experimental results so far obtained by the author in this field of investigation.

As soon as the experiments of Strutt (Lord Rayleigh) and Joly had revealed the apparently universal distribution of radium and its associated disintegration products throughout the lithosphere and perhaps throughout the entire earth, and when the work of Rutherford, Curie and others had demonstrated the extraordinary properties of these substances, it immediately became a subject of speculation as to the significance of so universal and so powerful an agent on the great earth phenomena which were known to have taken place.

The general problem has three main subdivisions:

1. The determination of the radium content of, and its distribution throughout, the lithosphere, and possibly an estimation of the amount and distribution throughout the earth.

2. The heat energy made available for the melting of the sub-crustal structure and its role in mountain building.

3. The radioactive disintegration of uranium into lead and its application to the determination of geologic time.

Since the problem was taken up by this Laboratory, there has not been time for the accumulation of any great quantity of data, but a satisfactory apparatus and technique have been developed and a number of measurements made in each of the above subdivisions.

Determination of Radium in Rocks.—For measuring the radium in ordinary rocks, where the quantity is of the order of 10^{-12} grams per gram of rock, the determination was made by decomposing the rock by fusing with a flux, collecting the radium emanation thereby liberated, and determining it by means of an electroscope.[2]

Calibration was accomplished by making a number of runs on a rock alone, and then another series, identical in every respect except that a

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[1] In memory of Ira Remsen.

[2] A detailed description of the apparatus and technique, including drawings, dimensions, etc., will appear shortly in the *American Journal of Science*.

known amount of radium, in equilibrium with its disintegration products, was added. This added radium was secured by pipetting a standard radium solution[3] containing 32.2×10^{-12} grams of radium element per cubic centimeter into small thin-walled glass bulbs, evaporating slowly to dryness, and then sealing the bulbs. These were kept for more than thirty days to permit the radium to come into equilibrium with its emanation. Bulbs containing 1 and 3 cc. of solution, respectively, were used. A bulb would be embedded in the mix and the fusion carried out in the usual way.

The flux alone showed some radioactivity; 100 g. gave an electroscope reading of 0.0014 division per second[4] and a 200-g. sample of the same material gave a reading of 0.0029 division per second.

A sample of granite from Stone Mountain, Georgia, was used to calibrate the apparatus and procedure. Sixteen measurements on this rock gave an average of 0.01089 division per second; this less 0.0014 for the effect of 100 g. of flux, gave 0.0095 division per second for the rock alone.

On adding bulbs containing 1 cc. and 3 cc. of standard radium the results were, in divisions per second

	1 cc.	3 cc.
		0.0179
		.0179
	0.0137	.0197
	.0137	.0197
	.0131	.0179
Average	0.01350	0.01856
Less effect of flux and rock	.01089	.01089
		3) .00767
1 cc. of standard Ra solution	0.00261	0.00256

The average of the two series is therefore 0.00259.

Since 1 cc. of radium solution is equivalent to 32.2×10^{-12} grams of radium element, 0.00259 div./sec. is equivalent to 32.2×10^{-12}, or

$$1 \text{ div./sec.} = \frac{32.2 \times 10^{-12}}{0.00259} = 12702 \times 10^{-12} \text{ g. of Ra}$$

So that

$$\frac{(E - F) \cdot 12702}{W} = \text{grams} \times 10^{-12} \text{ of Ra per gram of rock}$$

where E = electroscope reading (corrected for natural leak), F = effect of flux alone and W = weight in grams of rock sample used.

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[3] Tested and certified by the U. S. Bureau of Standards.

[4] The gold leaf of the electroscope is observed to pass across the field of a low-powered microscope in the image plane of which is a scale of 100 divisions. The rate across the same ten divisions is determined with a stopwatch.

Experimental

Using the above calibration and formula, the radium content of seven representative granites of the eastern seaboard of the United States, from Georgia to Maine, has been determined.

Table I

Determination of the Radium Content of Seven Representative Granites of the Eastern Seaboard of the United States

Locality	Description	G. of Ra per g. of rock
Stone Mountain, Georgia	Fine-grained, gray, biotite-muscovite granite	4.826×10^{-12}
Mt. Airy, North Carolina	Light-gray, coarse-grained biotite granite	0.655×10^{-12}
Woodstock, Maryland	Gray biotite granite with considerable allanite and epidote	1.448×10^{-12}
Ilchester, Maryland	Gray biotite diorite with accessory epidote	1.935×10^{-12}
Milford, Massachusetts	Very light pink, mottled, biotite granite	0.378×10^{-12}
Rockport, Cape Ann, Massachusetts	Hornblende-biotite granite	0.955×10^{-12}
Hurricane Island, Maine	Pinkish-buff, gray, coarse-grained biotite granite	3.65×10^{-12}

Complete chemical analyses and petrographic examinations were made on each rock studied.

The granite from Stone Mountain, Georgia, was separated into its constituent minerals by Kline's solution (aqueous solution of cadmium borotungstate) and each of these minerals examined separately for radium, with the following results in grams of radium per gram: quartz, 0.019×10^{-12}; potash feldspar, 1.129×10^{-12}; plagioclase, 1.657×10^{-12}; muscovite, 3.832×10^{-12}; biotite, 8.637×10^{-12}; from which it is apparent that in this rock, and presumably in others, the radium is associated more with those minerals having a high specific gravity rather than with those that have a low specific gravity, and that it is particularly associated with the micas.

Radioactive Heat.—Although the concentration of radium in the rocks of the lithosphere is very small, it seems to be universally distributed, and when one considers the masses involved there is a considerable amount of radium to be reckoned with. Since radium, in equilibrium with its disintegration products, produces 100 cal. per curie per hour, and since the heat conductivity of rocks is low and geologic time is long, there is good reason to believe that the accumulation of heat is sufficient to have a very real effect upon the earth's thermal gradient, and it is possible, as Joly believes, that there is quite enough heat from this source to furnish the heat of fusion of the subcrustal basaltic layer.[5]

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[5] See J. M. Joly, "The Movements of the Earth's Crust," *Phil. Mag.*, [6] **45**, 1167 (1923).

Also Holmes[6] has shown that potassium must be considered; that although its radioactivity is slight, its relative amount makes it of considerable importance.

Geologic Time.[7]—Of the various methods which have been used or suggested for obtaining a more or less accurate estimate in terms of years of geologic time, that one which uses the uranium-lead ratio is by far the most promising and the most definite.[8]

Theoretically a chemical analysis of a mineral containing uranium or thorium or both, together with their corresponding lead, should give all the data necessary for a calculation of the age of the mineral and presumably of the rock with which it was associated. However, the estimates made in this way vary greatly, due to a number of factors. The necessary separations are difficult and tedious, and the amounts of the significant elements are so small that legitimate analytical errors produce disproportionately great effects upon the ultimate results. The extrapolation in terms of years over vast geologic ages is so great that these analytical errors may cause a difference of hundreds of thousands of years in the indicated age.

But the chemical analysis alone cannot show whether or not the lead obtained is all of radioactive origin, or whether it came partly from uranium, partly from thorium or partly from some other source. The possibility of enrichment by lead from some non-radioactive source must be considered, and also the partial removal of the lead already radioactively produced. However, these are problems for the geologist at the time of selecting the sample and are not part of the mechanism of age determination being considered here.

What is emphasized here is that the uranium-lead ratio method, as now applied, has two inherent uncertainties associated with it. They are

(1) The uncertainty associated with the disintegration of the thorium series—the time required and the amount and origin of the lead produced. The thorium series of radioactive disintegrations has not yielded to experimental examination as readily as the uranium series has. Consequently there is considerable uncertainty associated with the time required for a given amount of thorium to form its corresponding amount of lead. Also, the quantity of lead produced by a given quantity of thorium is not known with satisfactory accuracy. Therefore the presence of thorium in a mineral to be used for an age determination injects an element of uncertainty into the result, and as some thorium is always present this

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[6] Arthur Holmes, *Phil. Mag.*, [7] **2**, 1218 (1926).

[7] For a general discussion of the problem and methods used, see Arthur Holmes, *Phil. Mag.*, [7] **1**, 1055 (1926).

[8] See "Factors Involved in the Calculation of the Ages of Radioactive Minerals," Arthur Holmes, *Am. J. Sci.*, [5] **13**, 327 (1927).

cannot be avoided. The formula now used contains a corrective factor to take care of the thorium content, but it is admittedly unsatisfactory.

(2) The fact that there is no actual measure of that proportion of the total lead which is known to have been produced from the uranium alone.

If this latter could be determined by actual experimental measurement, the thorium uncertainty could be disregarded and the only other uncertainty which would remain inherent and unmeasured in this method would be the existence of possible isotopes of uranium which might have disintegrated more rapidly in the past than the uranium which we know today.

If the lead in any given mineral being studied could be obtained in sufficient quantity and converted into some compound capable of giving lines in the mass-spectrograph, and if the intensity of these lines could be accurately measured, we would then have a direct experimental method for determining the actual amount of uranium lead present. The position of the line would identify it with the uranium lead isotope and its relative intensity would furnish a measure of its relative amount, and since the actual weights of uranium and lead would be known from the chemical analysis, we should then have all the information necessary for a direct comparison of the amounts of uranium and uranium-derived lead. Other isotopes of lead could be disregarded and no reliance need be placed upon assumed proportions figured from atomic weight determinations of lead associated with uranium and thorium, while any enrichment by ordinary lead would probably be revealed by an abnormally intense "207 line."

With these considerations in mind the author secured the coöperation of Dr. F. W. Aston in a proposed plan to convert samples of lead into some volatile compound such as lead tetramethyl and to endeavor to secure with it the identification and determination of any isotopes by means of his mass-spectrograph. In July, 1927, the author took a sample of lead tetramethyl[9] prepared from ordinary laboratory lead to Dr. Aston, who shortly thereafter carried out several experiments with this material. The results were most satisfactory and were first published by Dr. Aston in a brief note to *Nature* dated July 30, 1927.[10]

The experiments demonstrated very clearly the existence of the three anticipated isotopes, namely, those of masses 206, 207 and 208 in the approximate ratios of 4, 3 and 7, respectively, and also revealed the existence of other isotopes of lead, present in very small proportions, of which 203, 204 and 205 were indicated and 209 was reasonably certain.

The isotopes having been thus definitely separated and identified, the

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[9] Prepared for him by Mr. S. C. Witherspoon of the U. S. Chemical Warfare Service.

[10] Aston, *Nature*, **120**, 224 (1927).

next step was to do the same for "radioactive lead," that is, lead which had been formed mostly or entirely by the radioactive disintegration of uranium and thorium.

For this purpose the author secured some very pure Norwegian bröggerite, a mineral containing considerable proportions of uranium and lead but a very small proportion of thorium. This material was carefully analyzed[11] for uranium, thorium and lead and a sufficient quantity "worked up" to yield about 15 g. of "radioactive lead" chloride.

Five grams of this material has been converted into lead tetramethyl[9] and sent to Dr. Aston, and he proposes to test this in the mass-spectrograph this autumn.

Meanwhile Dr. Aston has been developing an instrument for accurately measuring the relative intensities of the lines on the photographic plates from his mass-spectrograph. This will eliminate the personal equation from this determination and render it capable of exact repetition and comparison.

Since there is very little thorium, relative to uranium, in this bröggerite, it is anticipated that these next experiments will show a very heavy line at 206, a very light one at 208, and possibly none at all at 207. It will be interesting to see whether any of the other isotopes show up stronger from this radioactive lead than they did with the ordinary lead.

From the data obtained from these two series of lead isotope measurements and from the determinations of the uranium, thorium and total lead of the bröggerite, we hope to be able to determine directly the uranium: uranium lead ratio for this sample of bröggerite and thereby secure a reliable estimate of its age, to determine definitely the thorium: thorium lead relationships with time, and possibly to throw some light on the other isotopes of lead and their origin. Experiments are now under way with the object of identifying and determining the isotopes of uranium. If these are successful the amounts involved at both ends of a radioactive series will be experimentally determined.

Summary

1. The significance of radioactivity in geologic problems is outlined.

2. A method for the determination of the radium in ordinary rocks is outlined and the radium content of seven representative granites of the eastern seaboard of the United States is given.

3. The geologic significance of the heat-producing power of radium is mentioned but the discussion of this should await the accumulation of more data.

4. A direct experimental means of determining the uranium and uranium-derived lead involved in an age determination is given.

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[11] By Dr. C. N. Fenner of the Geophysical Laboratory.

5. The circumstances of the first determination of the isotopes of lead are given.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, H. A. METZ LABORATORIES, INC., AND THE U. S. BUREAU OF STANDARDS]

III. THE REVERSIBLE ADDITION OF ETHYL ALCOHOL TO PARA-BROMOBENZONITRILE CATALYZED BY SODIUM, POTASSIUM AND LITHIUM ETHYLATES[1]

BY C. N. MYERS AND S. F. ACREE

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Introduction

In earlier papers of this series it was shown that the quantitative data available in sixty-two examples of different types of chemical changes can apparently be coördinated on the theory of the activity of both the ions and the non-ionized forms of electrolytes. This hypothesis was advanced in 1907 by Acree[2] and by Senter,[3] who did not have the good fortune to put it on a firm experimental basis supplied later by the co-workers[3] of Acree, Lapworth, Arrhenius, Goldschmidt, Bredig, Dawson and more recently Brönsted.

In the study of many of these reactions the solutions were fairly concentrated and varied from $N/1$ to $N/32$. Certain physical properties were therefore different from those in very low concentrations and were partly the cause of those deviations from the mass law which are called changes in activity, abnormal salt effects, etc. In the more concentrated solutions the ionic mobilities, viscosities and other physical factors can neither be considered the same as in the dilute solutions nor used without proper modifications in calculating the percentage of ionization of the ethylate or other electrolyte present.

In view of these facts it seemed desirable to investigate the catalytic activities of sodium, potassium and lithium ethylates in very dilute solu-

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[1] In memory of Ira Remsen.

[2] (a) Acree, *Am. Chem. J.*, **37**, 410 (1907); (b) **38**, 258 (1907); (c) **43**, 505 (1910); (d) **48**, 352, 368, 378 (1912); (e) **49**, 116, 127, 345, 369, 474 (1913); (f) THIS JOURNAL, **37**, 1902, 1909 (1915); (g) **38**, 2145 (1916); (h) **39**, 376 (1917); (i) *J. Phys. Chem.*, **19**, 381, 589 (1915); (j) **20**, 118, 353 (1916).

[3] (a) Senter, *J. Chem. Soc.*, **94**, 472 (1907); (b) Taylor and Arrhenius, *Mem. Nobelinst.*, **2**, Nos. 34, 35, 37; (c) Goldschmidt, *Z. Elektrochem.*, **15**, 6 (1909); (d) *Z. physik. Chem.*, **70**, 627 (1910); (e) Bredig, *Z. Elektrochem.*, **18**, 535, 543 (1912); (f) *Z. physik. Chem.*, **80**, 129, 170, 211 (1913); (g) Stieglitz, THIS JOURNAL, **34**, 1687, 1688, 1689, 1690, 1694 (1912); (h) **35**, 1774 (1913); (i) Dawson, *J. Chem. Soc.*, **103**, 2135 (1913); (j) **107**, 1426 (1915); (k) **130**, 2282 (1926); (l) Brönsted, THIS JOURNAL, **49**, 2554 (1927).