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Intercalibration and Comparison in Two Laboratories of Measurements Incident to the Determination of the Geological Ages of Rocks

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In an effort to extend the scope of geological age measurements based on the accumulation of helium in igneous rocks, researches were initiated which indicated disagreement when compared with previously published results from the same geological horizons. Cooperative investigations, undertaken by the authors, show that the radium determinations used in formulating the previous helium time scale are incorrect by more than a factor of two. The magnitude of the necessary downward revision of ages varies, depending upon the Th/U ratio of the individual rock specimens. Helium age determinations have been made on a number of igneous rocks by two entirely different techniques, the alpha-helium method and the radon-thorium-helium method. The alpha-helium method is independent of radioactive standards, and its results are in agreement with the new measurements by the radon-thorium-helium method. These researches also represent the first comparison of helium age measurements on the same specimens by two or more observers. While the helium ages of many individual geological horizons are lowered by these new results, the total span of geological time remains unreduced. Precision radium standards in the region of 10^{-12} gram have been verified.

I. INTRODUCTION

THE ultimate aim of the historical geologist is the accurate reconstruction of the consecutive geographies of the past. The fundamental criteria used in delimiting geologic periods are: (1) index fossils, (2) unconformities and, (3) cycles of sedimentation. Within recent years a fourth criterion, based upon the accumulation of the decay products of radioactivity, has been added. This method is particularly applicable to igneous rocks and minerals, which invariably contain at least measurable traces of the slowly decaying parent elements uranium, actino-uranium, and thorium. The three earlier criteria cannot be applied directly to igneous rocks, which constitute about 95 percent of the earth's crust.[1] Hence the radioactive method promises to be an extremely valuable aid in solving geochronological problems.

During the last quarter-century a fairly complete time scale, extending over most of the recognized range of geological time, has been built up from radioactivity measurements. The apparent agreement between ages based upon the accumulated radiogenic lead in radioactive minerals[2] and those obtained from the helium method applied to close grained igneous rocks[3–7] was the most convincing evidence for the validity of both methods.[5, 7] In an effort to extend the scope of this work, researches were initiated to develop a direct, physical method (Evans and Goodman[8]), and to test the applicability of the helium method to coarse grained igneous rocks which are predominant in the earth's crust (Keevil).[9] These researches indicated a serious disagreement in ages when compared with published results from the same geological horizons. A cooperative investigation, with two independent methods of measurement, was undertaken to determine the source and magnitude of these differences. As a result there is now complete agreement between the alpha-helium method and the radon-thoron-helium method but all radium determinations published by Urry since July, 1934,[4–6] are low by a factor of over two. Between 30 and 40 per-

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[1] F. H. Grout, *Petrography and Petrology* (McGraw-Hill Book Co., 1932).

[2] National Research Council Bull. 80, "Age of the Earth" (1931).

[3] W. D. Urry, Chem. Rev. **13**, 305–343 (1933).

[4] A. C. Lane and W. D. Urry, Bull. Geol. Soc. Am. **46**, 1101–1120 (1935).

[5] W. D. Urry, Bull. Geol. Soc. Am. **47**, 1217–1233 (1936).

[6] W. D. Urry, J. Chem. Phys. **4**, 34–48 (1936).

[7] A. Holmes, *The Age of the Earth* (Thos. Nelson & Sons Ltd., 1937), p. 178.

[8] R. D. Evans and C. Goodman, Phys. Rev. **51**, 595A (1937).

[9] N. B. Keevil, Trans. Roy. Soc. Can. Sec. 4 (1938).

cent of this difference is explicable by radium standard differences and the remaining source of discrepancy, although not definitely ascertained, is possibly due to the use of very dilute standard solutions.

With a constant thorium to uranium ratio in rocks, the use of the revised radium calibrations would lower evenly all the published results.[4–7] But this ratio varies and causes an uneven decrease in the present helium time scale. An even more important difficulty is the apparent disagreement of the revised helium ages with the accepted lead ages[7] for minerals supposedly from the same geological period. In addition certain experimental evidence[10] supporting the lack of leakage of helium from close-grained rocks is invalidated as a result of this revision of the radium content of the rocks measured. Thus it is seen that while the techniques used for helium age measurements have been improved and their reliability established, the geological significance of the results is still to be evaluated.

The present paper has as its fivefold purpose: (1) to describe discrepancies in past work, (2) to show the accuracy and validity of the new techniques, (3) to indicate the concurrence of various workers, (4) to give a critical consideration of age measurements and (5) to serve as a basis for sounder age determinations by radioactive methods.

II. Radioactivity Measurements

A. Importance

Wide variations, even in order of magnitude, in the determination of the radium and thorium contents of rocks have been obtained by different workers in the past. These differences emphasize the need for the international intercalibration between the various workers which has recently been initiated.[11]

The Rn-Tn-He method of age analysis, as the name implies, depends upon the measurement of the emanation products in assumed equilibrium with the parent elements in a known amount of rock sample. Calibrations are made with standard radium and thorium solutions. The rates at which helium is being produced by the two radioactive series are then determined by use of the appropriate decay constants. A distinct advantage of this method, particularly for very inhomogeneous rocks, is that all measurements are made on the same portion of the sample. The alpha-helium method[12] involves a measurement of the helium content of the rock and a direct electrical count of the total rate of alpha-emission, which equals the rate of production of helium.

Separate radium and thorium determinations are not necessary in ascertaining the age of young rocks by the alpha-helium method.[12] But in all age analyses by this method, the radium content has been determined by the direct-fusion technique as routine procedure. This additional determination affords (1) a rough check on the alpha-count, (2) the correction factor[13] for the decay of parent elements which is applied to old rocks (over 400 million years), (3) a means of more direct comparison of results by other methods, as for example the radon-thoron-helium method, and (4) a measurement of the actual amounts of the three radioactive series present in terrestrial materials, which is of value in geophysics.

At a Th/U ratio of 3.7, the rates at which helium is being generated by the thorium and uranium series are equal. Averages of previous determinations of this ratio range between 2 and 3 for igneous rocks[2] and a value of 7 is reported for 2 suites of rocks,[14, 15] but results on a larger number of specimens indicate that a lower value, between 3 and 4, is more representative.[16, 17] Hence for most terrestrial materials, the thorium and uranium series are of about equal importance as sources of helium and lead, and in the generation of heat within the earth's crust.

B. Methods for radon measurements

Largely because of its medical importance, the quantitative relationship between radium and

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[10] Reference 4, p. 1115.

[11] R. D. Evans and C. Goodman, Phys. Rev. **53**, 916A (1938).

[12] C. Goodman and R. D. Evans, Phys. Rev. **53**, 916A (1938).

[13] This correction is less than 10 percent for most rocks.

[14] R. D. Evans, G. D. Finney, A. F. Kip and R. Mugele, Phys. Rev. **47**, 791 (1935).

[15] R. D. Evans and R. W. Raitt, Phys. Rev. **48**, 171–176 (1935).

[16] N. B. Keevil, Econ. Geol. **33**, 685–696 (1938).

[17] A. O. Nier, J. Am. Chem. Soc. **60**, 1571 (1938).

radon has been well established. The determination of the radon in rocks gives a direct and accurate measure of the radium with which it is in equilibrium. These radium determinations involve two problems, first, removal of radon from the material being tested, and second, the accurate measurement of this radon by means of its alpha-ray ionization.

(*1*) *Release of radon*

When heated without flux, Evans[18] has demonstrated the necessity for complete fusion in order to insure 100 percent release of radon. Some investigators use the carbonate-fusion method, in which the finely ground rock is fluxed with alkali carbonates. In the direct-fusion method the equilibrium amount of radon in the rock is measured directly, while in the carbonate-fusion method the radon has usually been allowed to escape during fusion and subsequently reaccumulated and removed for measurement by boiling an acid solution of the flux. A recent improvement involves collection of the rock radon, together with the CO_2 released during fluxing, in a liquid-nitrogen trap.[19]

The results in Section C indicate that the direct-fusion and carbonate-fusion-solution methods are in good agreement on a variety of different kinds of rocks and hence that both methods are accurate for quantitative release of radon.

While the carbonate-fusion-solution method and the procedures to circumvent previously just criticisms have been described,[3, 6] it might be well to mention briefly these possible sources of error and indicate the procedures used to avoid them. A complete description including recent improvements is appearing elsewhere.[20] The chemical treatment used in preparation for the emanation measurements commences with the fluxing of the rock with Na_2CO_3 plus $Ba(OH)_2$.[6] The soda ash was obtained free of any activity, but it was necessary to recrystallize the $Ba(OH)_2$ in order to free it from radium contamination. Ordinary distilled water contains sufficient radioactivity to introduce error when such small concentrations, as occur in rocks, are to be measured. Consequently, all the water used in the chemical procedure, as well as that used in the standard solutions, must be redistilled. Even with these precautions, it is advisable to make blank runs, in which similar amounts of water and chemicals are taken as in the usual procedure for rocks. In this way a slight correction may be made if necessary and any unknown source of contamination revealed.

Aside from the possible loss of active elements during the chemical manipulations, there are two other effects which may cause low results. The emanations may be adsorbed by precipitated silica; hence cloudiness of the solutions used for emanation measurements should be avoided. Also the emanating power of sulfates has been shown to be low. The addition of an excess of barium, avoids the difficulty of sulfate formation by the radioactive elements, because any sulfate ions present have about an equal affinity for the much more abundant barium.

(*2*) *Detection apparatus*

The double ionization-chamber method has been developed independently by Evans[21, 22] for alpha-rays and by Steinke[23] and Schindler[24] for cosmic rays, who later suggested the similar apparatus for radon measurements used in Paneth's laboratory. The use of this method in conjunction with a Compton electrometer arranged for visual observation has been described by Urry.[6] This apparatus has been used for intercalibration and comparison with Evans's string-electrometer, photographic recording instrument.[22] The advantages of the automatic sensitivity calibration and photographic recording have been clearly emphasized when analyses by the two methods were made on the same samples. No significant changes in apparatus or technique have been found necessary in over 10,000 hours of almost continuous performance of the Evans a.c.-operated instrument.

(*3*) *Calibration*

The principal purpose of calibration is to enable the results to be expressed on an absolute basis. In addition, the standard solutions used

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[18] R. D. Evans, Rev. Sci. Inst. **4**, 223–230 (1933).

[19] N. B. Keevil, Am. J. Sci. **36**, 304–309 (1938).

[20] N. B. Keevil, (in preparation).

[21] R. D. Evans, Phys. Rev. **39**, 1014L (1932).

[22] R. D. Evans, Rev. Sci. Inst. **6**, 99–112 (1935).

[23] E. Steinke, Physik. Zeits. **31**, 1019 (1930).

[24] H. Schindler, Zeits. f. Physik **72**, 625 (1931).

for such calibrations offer the most convenient means of intercomparison between different investigators. Even more important is the check on the proper operation of the apparatus afforded by frequent calibration. Both Evans and Urry have used standard solutions, kindly supplied by Professor S. C. Lind, as primary standards of calibration. Because these standards were of different concentration and received different treatment, for purposes of differentiation, the original solutions as received from Lind will be designated as the L-E (Lind-Evans) and the L-U (Lind-Urry) standards, respectively.

(*a*) *L-E standard.*—In December, 1932 one liter of solution containing 1.573×10^{-11} gram of Ra per cc (as of the date of separation 1919) plus 2 percent $BaCl_2$ and 2 percent HCl sealed in a Pyrex flask was received by Evans from Lind. This solution was prepared in Lind's laboratory by a 100-fold dilution of the original final standard solution prepared in 1919 by Lind and Roberts.[25] In preparing subdilutions of this standard, the extended tip of the flask has been open only long enough to allow two small portions for rinsing and one full portion of the solution to be withdrawn in a delivery pipette. Immediately following this operation the flask has been carefully sealed. No dilution of the original solution has occurred and possibilities of contamination and evaporation have been reduced to a minimum.

TABLE I. *Early radium calibrations by Urry with L-U standard. The apparent increase in calibration constant with decreasing radon in the ionization chamber was interpreted as a real effect. The apparent agreement between the higher values of K_U and that computed from the Duane-Laborde equation* led to the use of 0.00945 v/hr.·10^{-13} curie† prior to the discovery of the discrepancy in this value, Table II.*

DATE	Ra CONTENT (10^{-12} G)	Rn ACCUMULATED (10^{-12} CURIE)	**K_U OBSERVED (V/HR.·10^{-13} CURIE)
4/18/34	0.50	0.48	††0.0102 0.00867
5/ 8/34	0.50	0.48	0.00941 ††0.00951
6/ 6/34	0.50	0.50	0.00945
2/ 4/35	0.50	0.50	0.00944
4/20/34	1.25	1.21	0.00741
3/29/34	6.25	3.26	0.00827
3/29/34	31.3	15.9	0.00665

* Reference 26.
† Reference 6, p. 44.
** Collecting potential, 180 volts.
†† Determined by the null method (reference 6, p. 45).

(*b*) *L-U standard.*—In February, 1934 about 25 cc of the original Lind and Roberts final standard solution,[25] containing 1.573×10^{-9} gram Ra per cc (1919) with $Ba/Ra=7.1\times 10^{+6}$ and about 2 percent HCl sealed in a Pyrex flask were received by Urry from Lind. The entire solution was then diluted by weight to contain 6.25×10^{-10} gram Ra per cc (corrected to 1934) and sealed in a manner similar to the L-E standard.

(*c*) *Earlier calibrations.*—Seven calibrations to obtain the conversion constant for Urry's apparatus K_U, in volts per 10^{-13} gram of radium, were made in 1934–35 by using subdilutions of the L-U diluted standard, and various quantities of radon in the ionization chamber. These values are given in Table I. The average $K_U=0.00945$ was used for all published radium determinations after July, 1935,[4, 5, 6] with a few exceptions as explained below. In Table I the value of K_U diminishes with increasing radon concentration in the chamber. Urry believed this to be caused by a dependence of the ionization current with respect to the saturation current, i/S, on the total number of ions present. Such a case is treated by Meyer and Schweidler[27] and by substitution the two last values in Table I gave a value of $K_U=0.0090\pm 0.0005$ for 0.3×10^{-12} curie of radon compared with $K_U=0.00945$ as found for the very dilute standard solutions.[28] Consequently for a few cases of analysis with high electrometer charging rates, the appropriate value of K_U was read off a curve from the values in Table I.

(*d*) *Recent results.*—Discrepancies began to appear about two years ago between the helium ages obtained on the same hand samples by different investigators. With the geologically inferred ages used as a basis for comparison, the ages obtained by the alpha-helium method were consistent among themselves but considerably

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[25] S. C. Lind and L. D. Roberts, J. Am. Chem. Soc. **42**, 1170 (1920).

[26] Duane and Laborde, Comptes rendus **1**, 1421 (1910).

[27] S. Meyer and E. v. Schweidler, *Radioaktivität* (Teubner, Berlin, 1927), p. 183.

[28] Reference 6, page 44.

lower than the corresponding published ages. At first it was suspected that there might be contamination of the thin rock film as deposited in the alpha-helium method, but numerous blank runs indicated no appreciable error from this source. The possibility of unknown alpha-emitters in terrestrial materials was considered, but subsequent work has reduced this to a low probability.

In the summer of 1937, Keevil, working in Urry's laboratory, while the latter was in Europe, found differences in the age results and obtained different apparatus constants from those used by Urry. In order to ascertain the source and magnitude of these differences, a cooperative program of intercalibration and comparison of results was undertaken. The primary source of discrepancy was found to be in the calibration of the radium apparatus. These results are described in detail in the next section.

(4) *Intercalibration*

Table II presents the calibration constants obtained by the two sets of apparatus on separate portions of the same standard solutions. It indicates no variation in the value of the calibration constant with radon concentration down to concentrations of about 1×10^{-12} curie in the ionization chamber. Below this concentration Urry thinks there may be an increase because of a small extraneous source of radon having no measurable effect at the higher concentrations but of the same order of magnitude as the very low concentrations. Others think these effects are spurious and caused by contamination or to the increased experimental error at low concentrations.

(5) *Selection of standard*

At the time this research was undertaken, no facilities were available for direct comparison of less than a milligram of radium with the National Radium Standard. However, the National Bureau of Standards will shortly have standard solutions covering the range from 10^{-11} to 10^{-5} gram of radium which should fill a serious need in the field of radioactivity.

When the above differences were found in supposedly reliable standards, it was necessary to evaluate the probable accuracy of various standards. The method of standardization of the Physikalisch Technische Reichsanstalt solutions, which were available, was not known, and the manipulation of the ampoule in which the solution is contained, during dilution introduces a possible source of error. Hence, the selection was between the L-E and the L-U standards mentioned above which had both been prepared from the original solution prepared in 1919 by Lind, using 206.7 mg of 100 percent radium chloride (equivalent to 157.3 mg of elemental radium by calculation and confirmed by gamma-ray comparison of the National Bureau of Standards against the National Radium Standard in 1920).

That the L-E Standard is the more reliable of the two Lind standards and within a small probable error is correct on an absolute basis may be inferred from the following:

(1) The solution obtained from Lind has not been diluted or transferred from the original flask.

(2) The solution as received from Lind contained 2 percent $BaCl_2$ and 2 percent HCl to prevent possible precipitation of the Ra as sulfate. No other chemicals have been added.

(3) Because of the extremely low concentration of Ra in the standards, ordinary contamination would tend to increase the Ra content. Precipitation as sulfate would produce the opposite effect; however, in correctly protected solutions one would favor the solution giving the lower value.

(4) One of the best known characteristics of radium is the rate of alpha-particle emission, which affords an independent and accurate means of standardization. The results of alpha-counts on de-emanated portions of these standards are given in Table III. Thus it is seen that the L-E standard is nearest to the recent determination of Gleditsch and Foyn[29, 30] in which the value, 3.50×10^{10} alphas per sec. per gram of Ra, was obtained.

(5) The L-E standard is in complete agreement with the theoretically predicted ionization[32] produced by its Rn, Ra A, and Ra C′ alpha-rays in a cylindrical ionization chamber of accurately known geometrical and electrical characteristics. Urry's selection of the higher values of K_U in

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[29] E. Gleditsch and E. Foyn, Am. J. Sci. **24**, 387 (1932).

[30] E. Foyn, Arch. Math. Natur. **41**, No. 4 (1935).

Table I was largely based on the rough agreement with the calibration constant predicted by the Duane-Laborde equation.[26] This criterion is invalid, as Evans[31] has pointed out the inapplicability of this empirical formula for plain ionization chambers. It is even less reliable when applied to chambers containing nets, such as those used by Urry.

(6) Subsequent to the selection of L-E as the primary standard, we were fortunate in securing, through Dr. L. F. Curtiss, four ampoules of Ra solution prepared as subdilutions of an accurately known amount of $RaCl_2$, determined both gravimetrically and by gamma-ray comparison with the National Radium Standard by the National Bureau of Standards. These ampoules contained 2.00, 2.00, 1.00 and 1.00 micrograms of Ra, respectively, as shown by gamma-ray comparison with one another in which the counting-rate meter circuit gamma-ray apparatus[32, 33] equipped with a continuous photographic recorder was used. Accurate dilutions of one of the 1.00-microgram ampoules were compared with the L-E standard by the emanation

TABLE II. *Calibration constants of radium apparatus with various standards. In the determination of radium by the emanation method, in which an electrometer is used for the ionization measurements, it is necessary to calibrate the instrument with a solution of known* Ra *content in order to reduce the observations to an absolute basis. Such solutions also afford a convenient means of intercomparison between two apparatus as in the present case. Four different standard solutions were used, the L-E and the L-U (diluted), as defined in* **B**(*3*), *and two prepared from Physikalisch Technische Reichsanstalt ampoules (PTR-1 and PTR-2). For the nine reasons presented in* **B**(*5*), *the L-E standard has been selected as the most reliable and has been adopted as our primary reference standard. In the last column of the table, the ratio of the average calibration constants observed for the other standards are referred to that found for the L-E. On this basis the PTR standards appear to be slightly higher than their labeled value and the L-U (diluted) substantially higher by a factor of 1.32 as an average for the two instruments. These values are in good agreement with those found by the alpha-counts, Table III. The high* Ra *content of the L-U (diluted) standard only partially explains the difference between the former Urry calibration constant, 0.00945,* and the present accepted value of 0.00444±0.0005, the ratio in this order being 2.13. Because of this discrepancy, all of Urry's measurements in which the higher constant was used are subject to revision.† The calibration constant,* K_E, *of the Evans' apparatus with the L-E standard is somewhat higher than was formerly used†† on the basis of the same standard, because the installation of drying trays and a new type of head on the ionization chambers has increased the capacity by about 10 percent.*

DATE	OBSERVER	STANDARD	Ra CONTENT IN 10^{-12} G	Rn ACCUMULATED IN 10^{-12} CURIE	COLLECTING VOLTAGE	CALIBRATION CONSTANT	RATIO TO L-E
	URRY'S COMPTON ELECTROMETER APPARATUS					K_U** IN V/HR.·10^{-13} CURIE	
9/ 6/37	Keevil	PTR-1	10.08	7.67	315	0.0048	
9/17/37	Keevil	PTR-1	10.08	6.52	315	0.0045	
9/28/37	Keevil	PTR-2	10.08	6.02	315	0.0048	
10/ 2/37	Keevil	PTR-2	10.08	3.10	315	0.0045	
					Average	0.00465±0.00006	1.05
9/20/37	Keevil	L-E	19.50	8.43	315	0.0043	
9/27/37	Keevil	L-E	19.50	12.50	315	0.0041	
1/27/38	Keevil	L-E	19.50	0.80	315	0.0041	
1/18/38	Urry	L-E	19.50	7.93	315	0.0043	
1/14/38	Urry	L-E	19.50	5.77	315	0.0043	
1/15/38	Urry	L-E	19.50	2.80	315	0.0046	
1/21/38	K & U	L-E	19.50	0.69	180	0.0043	
1/24/38	K & U	L-E	19.50	0.59	180	0.0050	
1/24/38	K & U	L-E	19.50	1.11	180	0.0050	
			Average (corrected to 315 volts collection)			0.00444±0.0005	1.00
10/27/37	K & U	L-U (dil.)	31.3	4.02	315	0.0053	
12/ 1/37	Urry	L-U (dil.)	6.26	0.56	180	0.00694	
11/30/37	Urry	L-U (dil.)	6.26	0.72	180	0.00799	
11/23/37	Urry	L-U (dil.)	6.26	0.88	180	0.00560	
11/26/37	Urry	L-U (dil.)	6.26	1.74	180	0.00666	
12/ 4/37	Urry	L-U (dil.)	6.26	3.19	180	0.00577	
11/19/37	Urry	L-U (dil.)	6.26	5.91	180	0.00547	
12/30/37	Urry	L-U (dil.)	6.26	6.05	180	0.00534	
			Average (corrected to 315 volts collection)			0.0061±0.0003	1.38

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[31] R. D. Evans, Phys. Rev. **48**, 177–186 (1935).

[32] N. S. Gingrich, R. D. Evans and H. E. Edgerton, Rev. Sci. Inst. **7**, 450–456 (1936).

[33] L. I. Schiff and R. D. Evans, Rev. Sci. Inst. **7**, 456–462 (1936).

TABLE II. (*Continued.*)

DATE	OBSERVER	STANDARD	Ra CONTENT IN 10^{-12} G	Rn ACCUMULATED IN 10^{-12} CURIE	COLLECTING VOLTAGE	CALIBRATION CONSTANT	RATIO TO L-E
	EVANS' STRING ELECTROMETER PHOTOGRAPHIC-RECORDING APPARATUS					K_E‡ IN 10^{-12} CURIE·HR./V	
12/18/35	Cooper	L-E	19.52	3.30	300	3.75	
3/ 9/36	Cooper	L-E	19.52	19.52	300	3.96	
3/30/36	Cooper	L-E	19.52	6.70	300	3.95	
5/26/36	Goodman	L-E	19.51	4.80	300	4.03	
6/20/36	Goodman	L-E	19.51	19.50	300	3.97	
9/ 3/36	Goodman	L-E	19.51	13.0	300	3.88	
10/30/36	Goodman	L-E	19.51	18.0	300	4.10	
9/20/37	Goodman	L-E	19.50	7.70	300	4.04	
10/ 1/37	Goodman	L-E	19.50	17.0	300	3.90	
10/10/37	Goodman	L-E	19.50	16.0	300	3.80	
10/13/37	Goodman	L-E	19.50	8.6	300	3.95	
12/ 8/37	Goodman	L-E	19.50	0.94	300	3.65	
3/ 5/38	Goodman	L-E	19.50	19.50	300	3.93	
3/ 7/38	Goodman	L-E	19.50	6.10	300	3.77	
3/12/38	Goodman	L-E	19.50	11.80	300	3.74	
					Average	3.89±0.02	1.00
9/ 7/37	Goodman	PTR-1	10.08	1.18	300	3.69	
9/26/37	Goodman	PTR-2	10.08	3.75	300	3.67	
10/12/37	Goodman	PTR-2	10.08	9.60	300	3.80	
					Average	3.72±0.03	1.04
10/15/37	Goodman	L-U (dil.)-1	12.50	1.46	300	3.20	
10/16/37	Goodman	L-U (dil.)-1	12.50	2.50	300	3.14	
12/18/37	Goodman	L-U (dil.)-2	12.50	2.25	300	2.90	
12/20/37	Goodman	L-U (dil.)-2	12.50	5.20	300	3.20	
					Average	3.07±0.05	1.26

* Reference 28. † References 4–6. †† Reference 34.

‡ All values of K_E are referred to zero sensitivity of the electrometer. Note that K_E is expressed in the reciprocal manner to K_U.

** The ionization current, and therefore, the calibration constant is dependent upon the collecting voltage. For comparison purposes, the average values of K_U have been computed to 315 volts collecting potential.

method, and found to be in agreement within the probable observation uncertainty of ±1.5 percent.

(7) A new portion of Lind's solution having 100 times the Ra concentration of the L-E standard has recently been supplied by Professor Lind. Comparison of this solution with the L-E standard (both undiluted) by the emanation method indicates agreement within ±1 percent.

TABLE III. *Alpha-counts on standard radium solutions. The rates of alpha-particle emission from de-emanated portions of standard radium solutions are given. These values were obtained from a plot of observed counts against time, extrapolated back to the time at the end of the de-emanation, in order to obtain the alpha-emission from the radium alone.* The theoretically expected counts are based on Gleditsch and Foyn's latest measurement of the curie as 3.48×10^{10} alphas per second per gram of radium. Their published value of 3.50×10^{10} has been corrected for the now generally accepted change in the Avogadro number to 6.03×10^{23} atoms per gram atomic weight. A 4-percent correction for the presence of* Po *has been included in the tabulated results. The magnitude of this correction was determined by deposition on nickel of the* Po *from the radium solution with subsequent measurement of the surface alpha-activity.*

STANDARD	Ra CONTENT IN G $\times10^{12}$	ALPHA COUNT OBSERVED	ALPHA COUNT THEORETICAL	RATIO MEASURED TO THEORETICAL
L-E	1.56	95±3	97.5	0.975±0.03
PTR-2	0.806	51±2	48.7	1.05 ±0.04
L-U (dil.)	1.25 (label)	109±3	78.0	**1.40 ±0.04
	†1.70 (meas.)		106.0	1.03 ±0.03

* References 30 and 31.

** This ratio of 1.40 is approximately equal to the average value 1.32 found from emanation measurements, Table II. Thus the alpha-activity confirms the inaccuracy of the labeled value of the radium content of the L-U (dil.) standard after dilution.

† Radium content based upon emanation measurements.

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[34] R. D. Evans, Ph.D. Thesis, California Institute of Technology (1932).

TABLE IV. *Comparison of radium determinations on rocks by two methods. In addition to calibrations of the two radium apparatus with the same standard solutions (Table II), divided portions of granulated rock samples were measured by both the carbonate-fusion and the direct-fusion methods. Since the average ratio of the results is very close to unity (1.02), no consistent difference between the two techniques is indicated.*

Sample	Ra in 10^{-12} g/g of Rock		Ratio: Carbonate-Fusion to Direct-Fusion
	Carbonate-Fusion	Direct-Fusion	
RF[1] [2] [3]	1.95 ±0.06	2.14±0.07 1.96±0.06 2.81±0.10	0.91
RG[3]	1.88 ±0.05	1.80±0.06	1.04
M-6[3]	1.29 ±0.04 1.24 ±0.05	1.24±0.03	1.02
FG[2]	0.78 ±0.03	0.88±0.03	0.89
HOR-2[3]	0.72 ±0.02	0.68±0.03	1.06
No-3[3]	0.51 ±0.03	0.46±0.03	1.11
C-1[3]	0.47 ±0.03	0.57±0.04	0.83
HOK-2[3]	0.40 ±0.025	0.32±0.02	1.25
8b[2]	0.495±0.03	0.47±0.04	1.05
7[2]	0.46 ±0.02	0.46±0.04	1.00
C-10-A[1]	0.265±0.04	0.24±0.04 0.33±0.05	1.10
O[2]	0.23 ±0.015	0.25±0.01 0.16±0.02	1.09
37[3]	0.14 ±0.03	0.16±0.02	0.88
15b[3]	0.135±0.02	0.14±0.02 0.11±0.03	1.08
		Average	1.02

[1] Acid solution of carbonate fluxed rock.
[2] Separate portions of same hand specimen.
[3] Quartered portions of granulated rock used for both methods.

(8) The activity index measurements indicated in Section D afford an independent confirmation of the accuracy of the L-E standard to within the experimental uncertainty of ±9 percent.

(9) Finally, the age agreement, to be described later, between the radon-thoron-helium and the alpha-helium methods represents another independent confirmation of the L-E standard.

C. Comparison of radium determinations on rocks

From apparatus constants based on the L-E standard, a number of radium determinations on rock samples were made by the two techniques, the direct-fusion and the carbonate-fusion methods. These results are tabulated in Table IV. Because of the inherent inhomogeneity of rocks and the probable error of the measurements, some variation between the results by the two methods is to be expected. Thus the agreement is quite good, particularly on samples of higher than average radium content and in those cases where divided portions of the same prepared rock sample were used. The differences which do exist have a random distribution in sign, with an algebraic average of only 2 percent which indicates no systematic disagreement between the two methods when correct constants are used.

TABLE V. *Thorium calibration constants. The calibration of the constant streaming thoron apparatus was made by three* observers using thorium X solutions prepared from minerals of accurately analyzed thorium content.*†

Date	Observer	Apparatus**	Standard g Th $\times 10^6$	Constant α/hr.$\cdot 10^{-6}$ g Th
5/16/33	Urry	I	3.4	2.80
5/17/33	Urry	I	6.9	2.86
5/17/33	Urry	I	13.7	2.72
5/18/33	Urry	I	27.4	2.68
11/21/33	Urry	I	5.2	2.69
11/22/33	Urry	I	10.4	2.88
11/23/33	Urry	I	20.8	2.73
11/24/33	Urry	I	19.8	2.64
11/25/33	Urry	I	29.7	2.75
			Mean	2.75±0.01
5/13/35	Urry	II	10.2	2.91
5/13/35	Urry	II	20.4	2.94
			Mean	2.93±0.02
4/27/37	Urry	III	10.3	2.99
4/27/37	Urry	III	20.6	2.94
			Mean	2.97±0.02
8/ 8/37	Keevil	IV	10.3	3.07
8/ 8/37	Keevil	IV	20.6	3.05
8/27/37	Keevil	IV	20.6	3.00
			Mean	3.04±0.02
9/19/37	Keevil	V	20.9	3.10
9/19/37	Keevil	V	20.9	3.08
			Mean	3.09±0.02

* Some of the calibrations were made with the assistance of Mrs. N. B. Keevil.

† References 36 and 37.

** I, Apparatus as originally constructed in 1933. II. New chamber, constant as computed on basis of previous value: 2.94. III. New chamber, about same volume as II but dead space decreased. IV. Rotameter rebuilt, new dead-spare tubing. V. Cleaned chamber and replaced dead-space tubing.

D. Thorium measurements

(*1*) *Detection apparatus*

As in the case of the uranium series, for the minute concentrations found in rocks, the gaseous product in the thorium series is the most convenient member to measure. Because of the short half-life of thoron ($T=54.5$ sec.), however, it is not feasible to follow the method used for radon ($T=3.82$ days). The streaming method first used by Strutt[35] has been adopted by Urry[6] for direct alpha-counting on the thoron itself, instead of ionization measurements on the thoron active deposit which would require several hours to build up. The source of thoron is a solution containing Th X, derived from the carbonate flux of the rock. The efficiency of the thoron counting, and its dependence on apparatus geometry and gas flow rate has been given elsewhere by Evans,[32] and by Urry.[6]

(*2*) *Calibration*

The apparatus constant used to convert the observed number of alpha-particles per hour into the equivalent amount of thorium is obtained from measurements on standard thorium solutions. These standards are more readily obtained than those of radium, because the concentrations involved allow convenient quantities of accurately analyzed thorium minerals[36, 37] to be fluxed with carbonate and the equilibrium amount of Th X separated out to form a solution of known content. Table V indicates the constants obtained from solutions of various concentrations. All of the constants obtained are in good agreement when the changes in apparatus indicated are taken into consideration.

TABLE VI. *Rate of helium production in igneous rocks. In the alpha-helium method the rate of helium production is observed as the number of alpha-particles (helium nuclei) per hour per milligram of rock, which we define as the "activity index." This quantity is determined indirectly in the radon-thoron-helium method from the measured* Ra *content (in 10^{-12} gram per gram of rock) and* Th *content (in 10^{-6} gram per gram of rock). The multiplicative factors involved are obtained as follows:*

$$\lambda_{\mathrm{Ra}}=4.68\times 10^{-8}\ hr.^{-1};\qquad \lambda_{\mathrm{Th}}=5.69\times 10^{-15}\ hr.^{-1}$$

Activity Ratio (AcU *series to* UI *series*):

$$=\frac{\lambda_{\mathrm{AcU}}N_{\mathrm{AcU}}}{\lambda_{\mathrm{Ra}}N_{\mathrm{Ra}}}=0.046\pm0.002.^{*}$$

$$\begin{aligned}\textit{Activity Index}&=8\lambda_{\mathrm{Ra}}N_{\mathrm{Ra}}+7\lambda_{\mathrm{AcU}}N_{\mathrm{AcU}}+6\lambda_{\mathrm{Th}}N_{\mathrm{Th}}\\&=8.32\lambda_{\mathrm{Ra}}N_{\mathrm{Ra}}+6\lambda_{\mathrm{Th}}N_{\mathrm{Th}}\\&=1.04\mathrm{Ra}+0.0886\mathrm{Th}.\end{aligned}$$

SAMPLE	ACTIVITY INDEX (1.04 Ra +0.0886 Th) (1)	ALPHAS/HR. MG (2)	RATIO (2)/(1)
RF	4.00±0.14	3.94±0.10	0.99
HOR-2	1.14±0.07	1.26±0.08	1.11
8b	0.88±0.06	0.67±0.06	0.76
No-3	0.72±0.05	0.64±0.08	0.89
HOK-2	0.725±0.07	0.62±0.08	0.86
C-10-A	0.46±0.03	0.34±0.06	0.74
O	0.44±0.02	0.42±0.03	0.96
15b	0.28±0.03	0.22×0.03	0.79
		Average	0.89

* Reference 39.

(*3*) *Thorium determinations on rocks*

In Urry's previous thorium determinations, de-emanated air was streamed through the Th X solutions to act as a carrier for the Th emanating from the solutions. Because the activities to be observed are so small, background runs must be made to determine the natural alpha-count coming from the ionization chamber materials. Urry[38] sometimes shut off the chamber from the rest of the system during background observations. In this way it is possible* that higher counts would be obtained for the backgrounds than actually occur during a rock determination.

This possible error was circumvented in all the present work by the simple expedient of streaming de-emanated air through the system and chamber at the same rate for both the background and rock determination. Backgrounds were observed before or after every run.

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[35] R. J. Strutt, Proc. Roy. Soc. London **A76**, 88 (1905).

[36] Reference 6, page 39.

[37] Reference 22, page 111.

[38] Reference 6, pp. 35–36.

[39] A. O. Nier, Phys. Rev. **55**, 150–153 (1939).

* The authors are not in entire agreement as to the effects of different methods of streaming the carrier gas in the flow method of thoron measurement. Dr. Urry explains the effect as follows: In an incompletely tight system laboratory air infiltration produces, with no streaming, a continuously rising background which, however, quickly drops to a constant background on streaming as in the actual rock runs. A tight system shows no difference with or without streaming. To obviate this possible source of error in obtaining background counts higher than actually occur in the rock runs and to circumvent the necessity for periodic control of the background with and without streaming, it is advisable to reproduce always the same streaming conditions for both run and background. With Apparatus II (Table V) only, was the chamber shut off for background runs but the agreement of the constant for Apparatus II indicates a correct background.

Since no separate thorium determinations are made in the alpha-helium method, the thorium measurements cannot be compared directly on the rocks analyzed. However, a very significant comparison can be made on the basis of the "*activity index*," herein defined as *the total number of alpha-particles emitted per hour by the radioactive material contained in one milligram of rock.* This quantity is observed directly in the alpha-helium method but is calculated in the radon-thoron-helium method, from the decay constants of the parent elements. Table VI contains a comparison of the activities observed by the two methods on separate portions of the same rock sample.

Three conclusions can be drawn from the agreement in activities observed by these two, entirely independent methods of measurement:

(1) There are no unknown strong alpha-emitting radioactive elements in ordinary terrestrial materials.[40]

(2) The accepted decay constants of the parent elements thorium and uranium are correct to within the experimental accuracy of our measurements (±5 to 10 percent).

(3) The radon-thoron-helium method modified as indicated above, yields radioactivity measurements in agreement with the alpha-helium method.

III. HELIUM MEASUREMENTS

A. Importance

Only in radioactive *minerals* is the content of active elements sufficient to produce gravimetrically measurable quantities of radiogenic lead during geologic time. In *ordinary* terrestrial materials the minute amounts of the parent radioactive elements produce so little lead that even for the oldest rocks the radiogenic lead content is extremely low, and is usually greatly exceeded by the common lead present. Hence helium affords the only readily observable evidence of the number of radioactive atoms which have decayed since the formation of the rock. Helium, being gaseous and inert chemically, may escape to some extent during geological changes such as metamorphism, weathering, and recrystallization, but theoretical considerations of the size of the helium atom, and the interatomic forces in rocks[41] show that the tendency to escape from perfect crystal structures of common rock minerals during geological time is negligible. The presence of relatively large amounts of helium in certain rocks also attests to its retention over hundreds of millions of years.

What was previously considered the most convincing experimental evidence[10] for helium retention in fine grained basic igneous rocks has been invalidated by the revision of those data as shown in this paper. There is some evidence that helium may escape from highly altered feldspars, but is retained in quartz and certain ferromagnesian minerals.[42, 43] Further studies on this important question of helium retention are now in progress.

The number of atoms of helium can be readily calculated from a measured volume of the gas at a known pressure. When divided by the rate of generation, such a determination affords a direct measure of the length of time required to accumulate the helium found in the sample. Hence, in both the alpha-helium method and the radon-thoron-helium method, the calculated age is directly proportional to the observed volume of helium in the rock. If no leakage of helium has occurred since solidification of the magma, and no important amount was originally present, the ratio thus obtained represents the true age of the igneous rock.

B. Methods of helium measurement

Similar to the radioactivity measurements, the determination of the helium content of rocks can conveniently be divided into two operations, (1) the release of the gas from the rock and (2) the measurement of its volume. It is necessary to separate the minute quantity of the inert helium from the relatively large volume of other gases released during the fusion of the rock. Since helium is not adsorbed to any appreciable extent, all the other gases can be completely removed, with the exception of the last traces of hydrogen, by adsorption on charcoal at liquid-air temperatures. The apparatus, purification procedure, and

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[40] R. D. Evans and R. W. Raitt (see reference 15, p. 174) have previously shown that there are no strong unknown gamma-ray emitters in terrestrial materials.

[41] N. B. Keevil, Proc. Am. Acad. Arts and Sci. (in press)

[42] N. B. Keevil, Am. J. Sci. **36**, 406–416 (1938).

[43] N. B. Keevil, Nature **143**, 32A (1939).

methods of measurement have been described in detail in a series of papers by Paneth and his co-workers[44] and only the factors concerning comparative determinations will be considered here.

(*1*) *Apparatus for release of helium*

The carbonate-fusion vacuum furnace has been applied successfully by Paneth and his co-workers[45, 46] for stony meteorites, tektites, and igneous rocks and was modified by Petersen and Urry. Recently Paneth[47] has employed a vacuum induction furnace on South African rocks and minerals and compared the results on samples from lump to fine powder, and with and without various fluxes.

TABLE VII. *Calibration factors for helium apparatus. In the helium determinations the McLeod gauge used, for measuring the volume of helium at a known pressure, contains a certain fraction of the total helium released from a weighed quantity of rock. We have chosen the reciprocal of this fraction to represent the calibration factor C of the apparatus. C is defined as the ratio of the effective total volume of the apparatus to the volume of the McLeod. C is most easily determined following an ordinary measurement by retaining the rock helium in the McLeod gauge while the remainder of the apparatus is flushed out with oxygen and evacuated. By allowing the helium in the McLeod to be redistributed throughout the system and following the regular adsorption procedure, the ratio of the effective volumes can be determined.*

DATE	OBSERVER	CALIBRATION FACTOR *C*	MEAN *C*
	Rn-Tn-He Apparatus		
3/ 5/34	Urry	2.263	
4/10/34	Urry	2.278	
4/25/34	Urry	2.281	2.274±0.004
7/18/37	New McLeod Gauge Installed		
7/20/37	Urry	*2.268	2.268±0.010
8/21/37	Keevil	1.96	
8/26/37	Keevil	1.93	
9/13/37	Keevil	1.94	
10/ 1/37	Keevil	2.00	
10/ 5/37	Keevil	1.95	1.956±0.008
11/ 8/37	Urry	2.022	
11/ 9/37	Urry	1.997	
11/ 9/37	Urry	2.052	
11/10/37	Urry	†2.064	2.024±0.011
	Direct-Fusion Apparatus		
11/ 1/36	Goodman	‡1.89	
5/17/37	Goodman	1.72	
5/17/37	Goodman	1.78	
9/13/37	Goodman	1.72	
1/13/38	Goodman	1.72	
2/25/38	Goodman	1.69	1.726±0.01

* Hydrogen present, reburned over Pd and adsorbed over-night.
† Hydrogen present, not included in the mean value.
‡ Determined with He and Ne from air; this value is high due to the greater adsorption of Ne relative to He, and is therefore not included in the mean value.

TABLE VIII. *Comparison of helium determinations by two methods. Helium determinations on rocks of various types were made by Keevil and Goodman who used the carbonate-fusion and the direct-fusion methods, respectively. The conversion factors given in Table VII were used. With the exception of sample "O" (Oldwick basalt), in which case separate portions of the same hand specimen were used, quartered portions of granulated rock were used as samples, and the measurements were made concurrently on the two apparatus. Sample* RG *is excluded from the average ratio because of insufficient heating in the direct-fusion measurement. Sample No-3*A *was not measured by the direct-fusion method until 3 days after granulation; the lower result is attributed to loss of helium during this time and was not included in the average ratio.*

SAMPLE	HELIUM CONTENT IN 10^{-5} CC/G OF ROCK		RATIO: CARBONATE-FUSION TO DIRECT-FUSION
	CARBONATE-FUSION	DIRECT-FUSION	
15b	18.0	17.1	1.06
C-10-A	14.7	15.6	0.94
RF	11.6	11.2	1.04
RG	10.5	7.9	—
8b	6.6	7.9	0.84
7	6.8	7.7	0.88
No-3A	5.7	3.9	—
FG	3.5	2.6	1.34
HOK-2	1.7	1.8	0.95
O	0.85	0.80 0.71 0.77 0.68	1.14
		Average	1.02

The difficulties in this method, which generally can be made small compared to the experimental uncertainty, are the necessity of using finely ground samples leading to possible loss of helium in grinding and during evacuation of the furnace, and the use of chemicals which must be examined for possible radioactive contamination, or preferably used in blank runs. One might also mention the low temperatures which are sufficient for carbonate fusion, but which might not liberate all of the helium from insoluble grains in some

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[44] For complete list of references: F. Paneth and W. D. Urry, Zeits. f. physik. Chemie **152**, 110 (1931).

[45] F. Paneth, H. Gehlen and K. Peters, Zeits. f. Anorg. Chemie **175**, 363 (1928).

[46] F. Paneth, H. Gehlen and P. Günther, Zeits. f. Elektrochem. **34**, 645 (1928).

[47] A. Holmes and F. Paneth, Proc. Roy. Soc. London **A154**, 385 (1936).

instances, and the time required in the operations. The important advantage is the measurement of helium on the same portion of rock sample used for the subsequent radioactivity measurements.

As indicated elsewhere[8] the direct-fusion method avoids these difficulties and gives a very rapid method for release of the helium from rock by directly boiling the sample in a graphite crucible at about 2000°C. However, it is necessary to use separate portions of the sample for the helium and alpha-ray measurements. This disadvantage might in some cases necessitate several determinations in order to obtain a reliable average value for the sample. The use of the radon condensation method[19] in conjunction with the helium determination, serves to minimize such errors. Test series already made, and the agreement between the alpha-helium and the radon-thoron-helium ages indicate that the inhomogeneity of most rock samples is not important enough to make this difficulty serious.

(2) *Purification and measurement of helium*

(*a*) *Removal of other gases.*—One of the main problems is the complete removal of the last traces of hydrogen before an accurate volumetric determination of the helium can be made. The direct-fusion method generates somewhat more hydrogen than the carbonate-fusion method, probably because of the reducing atmosphere and the higher temperatures reached. The addition of a small auxiliary charcoal trap and the inclusion of spongy palladium in the last trap adequately take care of this extra hydrogen.

TABLE IX. *Comparison of helium re-determinations with previous results. In seeking the cause of the difference in ages observed by Goodman and Keevil on the same hand specimens analyzed by Urry (Table XI), a limited number of these rocks were re-determined for helium by Urry, and the results are presented in column 3. No consistent ratio can be inferred from the comparison with the earlier measurements, although the fluctuations show the inhomogeneity present in some rocks.*

SAMPLE	HELIUM IN 10^{-5} CC PER GRAM OF ROCK		RATIO 1938 TO 1934–1937
	1934–37	1938	
No-3A	6.40	6.28	0.98
No-3B	6.34 6.34	5.56	0.88
HOK-2	3.31	—	—
HOK-1	2.84	2.3 2.2	0.79
HOR-2	8.86	6.3	0.71
HOR-1	6.91	6.6	0.96
Kew 11	6.82	7.1	1.04
Kew 26	5.36	4.4	0.82
G 1	6.50	6.7	1.03
			Mean: 0.90

(*b*) *Measurement of helium.*—For most determinations about five grams of rock are used, although several times this amount can conveniently be used in the direct-fusion method. Ordinary rocks have helium contents between 10^{-6} and 10^{-4} cc (referred to 0°C and 760 mm Hg) per gram. The volume of the system in which this gas is distributed during purification is about one liter, of which the McLeod gauge represents about one-half. The accurately determined ratio of the volume of the entire system to that of the McLeod constitutes the helium apparatus constant *C*. Determinations of this constant for the two apparatus are included in Table VII.

(*c*) *Comparative determinations.*—In order to test the extent of agreement between the two sets of apparatus for release and measurement of helium, analyses of duplicate samples were

TABLE X. *Comparison of age measurements by two methods. The ages indicated were obtained by substitution of the helium content (Table VIII) and the measured "activity index" (Table VI) in the simplified age equation:*

$$\text{Age in million years} = K\frac{\text{Helium in } 10^{-5}\ \text{cc/g of rock}}{\text{Activity Index (in } \alpha/\text{hr}\cdot\text{mg})} = 30.8\ \text{He}/I,$$

where I ≡ activity index, He ≡ *helium content. For ages greater than 400 million years (C-10-A and 15b) an old-age correction*[13, 48] *for the decay of the parent elements* UI, AcU *and* Th *has been included. With the single exception of specimen 8b, the agreement between the two sets of results is well within the experimental uncertainty of the measurements. There is no reason to suspect either determination of 8b, hence this sample was included in the average ratio. With 8b excluded the average ratio is 1.02.*

SAMPLE	AGE IN MILLION YEARS		RATIO: ALPHA-HELIUM TO Rn-Tn-He
	ALPHA-HELIUM GOODMAN	Rn-Tn-He KEEVIL	
O	54 ± 2	59 ± 3	0.92
HOK-2	89 ± 8	77 ± 7	1.16
RF	88 ± 5	89 ± 3	0.99
RG	110 ± 6	95 ± 4	1.16
HOR-2	100 ± 6	109 ± 6	0.92
No-3A	255 ± 18	242 ± 15	1.05
8b	350 ± 25	226 ± 15	1.55
C-10-A	820 ± 110	890 ± 50	0.92
15b	1850 ± 300	1800 ± 200	1.03
			Mean: 1.08

TABLE XI. *Re-determination of previously published ages. An attempt has been made to reconcile some of Urry's previous age measurements*[4–6] *with the newer values of Goodman and Keevil by recalculating (column 7) the former results (column 3) with the revised radium calibration of Table II. Although this correction does account for a good share of the difference, a serious lack of agreement is still evident by comparing column 7 with columns 4 and 5. Repeat measurements were made by Urry (column 6) in an effort to determine the cause of this remaining difference. Urry believes the lower 1938 values to be due to helium leakage from the hand specimens depending upon the nature of the rock.*

		AGE IN MILLION YEARS				
SAMPLE	GEOLOGICAL HORIZON	URRY 1933–36	GOODMAN 1937	KEEVIL 1937	URRY 1938	URRY (COL. 3 RECOMPUTED)
O	Triassic	—	54± 2	59± 3	—	—
H 1	Triassic	180±11	—	—	—	104± 7
HOK-2	Post-Devonian	215± 8	89± 8	80± 7	—	140± 9
HOK-1	Post-Devonian	215± 8	—	—	110± 8 115± 9	140±10
HOR-2	Post-Devonian	220± 4	100± 6	109± 6	120± 5	140± 7
HOR-1	Post-Devonian	200± 5	—	—	130± 7	125±10
No-1	Keweenawan	485±20	—	—	—	335±15
No-3A	Keweenawan	525±25	255±18	242±15	260±14	365±15
No-3B	Keweenawan	520±25	—	—	290±15	365±18
Kew 11	Keweenawan	490±20	—	—	205±10	270±15
Kew 26	Keweenawan	555±25	—	—	355±13	365±15
G 1	Late Huronian?	515±25	—	—	290±11	320±16
G 1A	Late Huronian?	550±25	—	—	300±12	285±13

undertaken concurrently. The results presented in Table VIII indicate good agreement. The algebraic mean deviation between the two methods is only about 2 percent, which indicates no systematic difference. The variation observed is largely due to the inhomogeneous distribution of helium in the sample, because the probable error of the actual measurement is quite low as shown by the consistency of the measured values of C (Table VII).

Part of the search for the cause of age differences consisted of a re-determination of helium on a number of rocks. In Table IX Keevil and Goodman find consistently lower helium contents than Urry's published values. Urry's re-determinations are also in general lower than the early results for the same hand specimens. Some of the differences observed may be due to inhomogeneity of the specimens, but the possible leakage of helium during the intervening time is suggested. A better comparison is that of the ages, given in the following section, which should be independent of any such inhomogeneity.

IV. AGE MEASUREMENTS

The age of a rock calculated from the individual He, Ra, and Th determinations should agree with that obtained from measurements of the rate of alpha-particle emission from rocks and the helium content. The ages obtained from these independent methods are in very good agreement, as indicated in Table X. The alpha-ray counting method is a direct determination of the rate of production of helium in the rock, and age results by this method are therefore entirely independent of all radioactive standards. Except for the second-order correction on very old rocks;[13, 48] alpha-helium ages do not depend in any way on standard radium or thorium solutions, nor upon the decay constants of thorium, uranium or actino-uranium.

The agreement of the radon-thoron-helium method (with the new calibration constants described above) with the direct alpha-helium method is cogent evidence for the validity of these revised calibration constants. It also strengthens the radioactive concepts upon which the helium age methods are based.

Because of emphasis on quantity of results from the numerous geological periods in order to obtain a broad view of the value of ages based on radioactivity, very little comparative work has

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[48] Reference 7, page 153, N. B. Keevil, Am. Jour. Sci. **237**, 195–214 (1939).

TABLE XII. *Age data on radioactive minerals by the lead method. Of the many radioactive minerals which have been examined by the lead method, four have been selected as most nearly fulfilling the three criteria for lead ages. Thus far no direct comparison of the lead and helium age methods has been made, so that it is impossible to say with certainty that the two techniques yield ages which are in disagreement.*

MINERAL	LOCALITY	GEOLOGICAL AGE	LEAD AGE IN MILLION YRS.	METHODS	REMARKS
Samarskite[50, 51]	Spinelli Quarry, Glastonbury, Conn.	Pre-Triassic	270±75	Pb/U and Pb/Th ratios	No determination of isotopic constitution
Pitchblende[39, 52, 53]	Jachymov, Bohemia	Late-Paleozoic	220±40	Pb^{207}/Pb^{206} Pb/U and Pb/Th ratios, atomic wt. and isotopic analyses	No accurate geological data
Thorite[39, 55, 56]	Brevig, Norway	Permian (?)	230±30	ditto	Geological age somewhat uncertain
Kolm[39, 53, 54]	Güllhögen, Sweden	Upper Cambrian	450±75	ditto	Accurately dated geologically; sample somewhat porous and loss of emanations possible

heretofore been done in this field. In fact, so far as we are aware the present age results constitute the first agreement between two observers working on the same geological specimens. The importance of such intercomparisons in the early stages of development of such a technique should be emphasized.

The above ages found by both methods are lower by approximately a factor of two or more than Urry's time scale. When these relatively low ages were obtained, the question naturally arose as to whether the discrepancy was partially due to the particular geological specimens being investigated. Hence, a limited number of rocks previously analyzed by Urry were redetermined by the two methods. The results are summarized in Table XI and indicate that the previous ages are too high by about the same amount found in the determinations on the other rocks. The data for Urry's early radium determinations (1933-36) have been recomputed with the corrected radium calibration constant, and result in the ages given in the last column of Table XI. These recomputed values are still somewhat higher than the redeterminations of Goodman, Keevil and Urry, and suggest that some unknown source of error exists in Urry's previous age measurements, which, however, might be partially or completely accounted for by a leakage of helium from the hand specimens in the 3–5 years intervening between measurements.

Until a large number of existing problems have been settled and many more rocks analyzed, it does not seem advisable to prepare a revised helium time scale in which the geologic periods are delimited. However, some benefit derives from a presentation of the ages obtained, together with their most likely geological horizons, in order to show the relative values and the wide extent of time represented. It will be noted (Table X) that the range of ages is from 5 to 1800 million years, which is equivalent to the previous helium and lead age scales. In fact, if the oldest age of 1800 million years were based on the previous calibration constants used by Urry, the age would be considerably in excess of any found by the lead method.[49]

Thus the revised helium ages do not indicate any decrease in the generally accepted total span of geologic time, popularly called the "Age of the Earth," but only suggest *a redistribution of this time among the various geologic periods.*

V. LEAD AGES

In Holmes' recent publication[7] the ages calculated from lead ratios and from Urry's radon-thoron-helium measurements have been compared. It is thus concluded that "it is remarkable how consistently the age estimates fall into appropriate positions. That this stringent test of internal consistency is satisfactorily met must be

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[49] Reference 7, page 207.

[50] R. C. Wells, National Research Council Report of the Committee on Geological Time, p. 76 (1935).

[51] Reference 7, p. 165.

[52] Reference 7, p. 159.

[53] Rose and Stranathan, Phys. Rev. **50**, 792 (1936).

[54] Reference 7, pp. 176, 178.

[55] Reference 2, pp. 6, 7, 101 and 210.

[56] Reference 7, pp. 161–163, 172.

regarded as the final proof that the ages calculated from the lead- and helium-ratios are at least of the right order and that no serious error is anywhere involved." At the time this statement was being written, the first observations were being made which revealed the unfounded optimism of Holmes' conclusion. Since the apparent agreement between the two radioactive methods of age measurements has been emphasized as such strong evidence for the accuracy of both methods, it is only natural to inquire into the actual extent of this apparent agreement and the fundamental principles underlying the lead method, now that the previous helium ages have been definitely invalidated.

In many radioactive minerals an easily measurable amount of lead has accumulated since crystallization. By use of the so-called lead ratio,[2] and the appropriate decay constants, the length of time required for the production of this amount of lead by the parent radioactive element can be determined readily. However, any common lead present in the mineral would increase the observed ratio resulting in an inordinately high age.

Recent developments in accurate isotopic abundance[39] and atomic weight determinations enable the exact proportions of the isotopes in the mineral lead to be ascertained. These measurements dictate the required correction in the lead ratio and yield reliable ages, provided other criteria are fulfilled. Because ages were obtained on a large number of minerals prior to the realization of the importance of common lead as a contaminant, the workers in this field are reluctant to discard these results, particularly where agreement with the newer ages exists. The result of this inclusion of earlier measurements is to present an almost solid front of what at first sight appears to be indisputable evidence for the absolute validity of lead ages. Upon further investigation, however, uncertainties begin to appear and individual consideration of each measurement must be made before the results can be properly weighted.

While independent geologic evidence for the horizon of either minerals or rocks cannot be obtained for every sample analyzed, nevertheless, for the formulation of a time scale it seems desirable that specimens should have their positions determined with an accuracy comparable to that of the analysis. This is even more important when there is uncertainty as to the agreement between two methods of measurement. Anomalous rock and mineral analyses should not be discarded, but the reasons for variations from what might be expected should be investigated.

Among the large number of lead ages on radioactive minerals, only four[39, 50–56] have been definitely established which are (1) free from alteration, (2) of well-established geological horizon, and (3) based on isotopic abundance or atomic weight determination of the lead. The important age data on these four minerals are summarized in Table XII. Even in these specimens the span of possible horizons is so great that no sharp disagreement exists between the corresponding helium ages found for rocks (See Table X.) The most important result to be drawn from this critical consideration of the lead time scale is the obvious necessity for further age measurements on well-authenticated minerals and rocks, preferably from neighboring formations with unquestioned relative ages.

VI. Geologic Notes for Rock Specimens

O—Lat. 40°40′N, Lon. 40°45′W. Specimen collected from a basalt flow by A. C. Hawkins in 1936, fifty feet from the surface in a working quarry at Oldwick, N. J. The top of the flow has been removed by erosion, and the bottom is not visible. Similar flows in the area of slightly different periods of eruptivity have been identified as being of Triassic age from fossils in adjacent sedimentary beds (red shales and sandstones).[57] Age: Probably Triassic.

HOK 1 and 2, and HOR 1 and 2. Lat. 55°45′N, Lon. 5°3′W. Monchiquite dike specimens sent by Arthur Holmes in 1936 from Kilchattan and Riasg Buidhe on the Island of Colonsay, Scotland. Geological relations nowhere provide evidence of their age beyond the fact that they cut formations regarded as Torridonian.[58] Age: Post-Devonian.

RG—Lat. 42°40′N, Lon. 70°35′W. Granite collected by N. B. Keevil August 18, 1937 from freshly quarried block from the Upper Pigeon Hill Quarry, Cape Ann, Mass. Intrudes Salem gabbro diorite, which in turn cuts Pre-Cambrian rocks and is possibly of Devonian Age. It is cut by diabase dikes which are generally considered to be related to similar dikes interbedded with Triassic sedimentary beds at Deerfield and Mt. Holyoke, Mass.[59] Age: Probably Pre-Triassic and Post-Cambrian.

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[57] J. V. Lewis and H. B. Kümmel, Bull. 14, Geol. Survey of New Jersey, pp. 62, 95 (1915).

[58] Arthur Holmes, private communication.

[59] B. K. Emerson, U.S.G.S. Bull. **597**, 188 (1917). C. H. Clapp, U.S.G.S. Bull. **704**, 25–26 (1921). T. N. Dale, U.S.G.S. Bull. **738**, 293 (1923). C. H. Warren and

RF—Fine-grained cognate xenolith from the same large hand specimen as RG.

7 and 8b—Lat. 44°56½′N, Lon. 109°29½′W elev. 9800 ft. Trap rocks collected by A. C. Lane in July, 1937 from the center and two feet from the margin, respectively, of a 100-ft. dike at Long Lake, Wyoming. The specimens were taken from a small working quarry for road metal. The dikes of this series are intrusive into the early pre-Cambrian complex (Stillwater series), and appear to be older than the middle-Cambrian rocks of Bear Tooth Butte, but the exact relations are obliterated by overburden for a considerable distance.[60] Age: Possibly Pre-Middle Cambrian, and post early Pre-Cambrian (younger than 15b).

No-3 and No-3A—Lat. 43°15′N, Lon. 79°2′W. Diabase specimen collected by P. Price three feet from the chilled contact of a north-south dike at the 17th level (1975 ft.) of the Horne Mine at Noranda, Quebec. The dikes of this set are unaltered and cut all the other rocks of the region, including the Cobalt series of the late Pre-Cambrian.[61] Age: Post-Cobalt.

C10A—Lat. 48°14′N, Lon. 77°54′W. Hornblende granodiorite collected by W. C. Güssow in 1936 from a specimen freshly blasted from a road cut ten feet from the surface. The granodiorite is intrusive into a sedimentary complex of Keewatin or possibly earlier age, and is thought to be older than the diabase dikes in the area, and the Cobalt series to the southwest.[62] Age: Probably Pre-Cobalt and Post-Keewatin.

L15—Lat. 45°1′N, Lon. 109°25′W. Norite from the metamorphosed Stillwater complex collected in July 1937 by A. C. Lane from Quad Creek, Montana, one mile north of the state line. The Stillwater complex is bordered by a Cambrian conglomerate at an erosional contact,[63] and is cut by granite and basic dikes. Age: Probably early Pre-Cambrian.

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[60] E. C. H. Lammers, private communication.

[61] Specimen from Loc. 14, Map 241, Can. Inst. of Min. and Met.; P. Price, Can. Min. Inst., March (1934); M. E. Wilson, Can. Min. Inst., pp. 389-390, August (1934).

[62] W. C. Güssow, Trans. Roy. Soc. Canada, Sec. IV, **31**, 130, 150 (1937).

[63] J. W. Peoples, Rept. of XVI Int. Geol. Congress, Washington, 1933. Reprint issue, pp. 353–360, October (1936).

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Conditions for Producing Intense Ionic Beams

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Conditions for the optimum production of positive ions and their complete removal from the ionization region to form a beam are developed. The calculations take into account the variation in ionization cross section as a function of electron energy. The mechanism of proton production is considered and the efficiency of arc type sources is discussed.

I. INTRODUCTION

ALONG with the development of the field of nuclear physics it has become increasingly important to have a device capable of supplying large numbers of ions, especially protons, deuterons and alpha-particles. In response to the demand a number of ion sources have been built, most of which are modifications of the arc type in which use is made of the positive ion current to the wall surrounding the arc plasma. It was by no means certain that the greatest number of ions could be produced and delivered as a beam with this type of source. Consequently a systematic study of the whole problem was undertaken to determine the best method for producing an ion beam of a prescribed intensity. The results of the study are set forth below, wherein it will be seen that in principle it is possible to produce beams of extremely high intensity.

Before discussing in detail the various factors involved in the formation of ion beams it will be well to note what characteristics are generally desirable in a good ion source. In the first place the source should deliver an approximately