

# **Determination of the Radium Content of Rocks**

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presence of actinon, and expressed in alphaparticles per sec. The average value of  $Q_{\text{Tn}}$  for the first hour of streaming from  $Z = f \cdot \alpha \cdot Q_{Tn}$ equals the true value at some given time after commencing streaming independent of when this began (1290 sec. for the present chamber and conditions). With the value of  $Q_{\rm Tn}$  so obtained, Eqs. (5) and (6) where t=time elapsed since separation of the Th X from Ra Th, Eq. (8a) where t = 1290 sec. and Eq. (13) are solved for  $X_0$ which is converted by the radioactive equilibrium law into the number of atoms of thorium and hence the weight present in the original specimen. A graphical solution usually suffices. For two chosen values of the Th concentration, values of Z for t=0-1st hour after separation from the Ra Th are obtained by the converse of the above procedure and Z plotted against Th concentration. The relation is linear since  $f \cdot \alpha$  is independent of the concentration. Z for the unknown solution is reduced to t=0-1st hour by the factor  $N_{\text{Th }X_0}/N_{\text{Th }X_t} = e^{\lambda_{\text{Th }X_t}}$  where t is the time elapsed since separation of the Th X to the commencement of streaming, and the concentration read off from the plot. A similar procedure is adopted for the determination of protactinium from  $Q_{Aen}$ .

#### PROBABLE ERROR

The nature of statistical fluctuations in counting experiments has been dealt with in detail by Evans and Neher.<sup>12</sup> The probable error of a

single observation is given by

$$r = \pm 0.67(2x+y)^{\frac{1}{2}} \tag{22}$$

where x is the background count per hour and y=3600Z. When x=18 the observational limit given by Evans and Neher's Eq. (9) is found to be 2.9 alphas per hour. For the mean of ten hourly intervals the probable error varies from 49 percent for a count of 3 to 2 percent for a count of 160 per hour. The count due to Th A is directly controlled by the thoron and hence is not an independent random process. As a first approximation the value of y may be taken to be

$$\frac{3600Z(\lambda_{\rm Tn}N_{\rm Tn} + 0.50\lambda_{\rm Th \ C}N'_{\rm Th \ C})}{(1.62\lambda_{\rm Tn}N_{\rm Tn} + 0.50\lambda_{\rm Th \ C}N'_{\rm Th \ C})}.$$
 (23)

The bracketed portion of the numerator is the theoretical count were there no alphas from Th A. Since the mean background x remains reasonably constant, a family of curves is drawn plotting the probable error expressed as a percentage against y for values of n (number of observational intervals) from 3 to 12 hours. Having determined y from Eq. (23) the probable error is read off the appropriate curve.

The results of a long series of thorium measurements on rocks, with the helium and radium contents necessary to calculate ages are given in Determination of the Radium Content of Rocks.<sup>2</sup>

I wish to express my thanks to the American Philosophical Society for their generous support of this research.

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### Determination of the Radium Content of Rocks\*

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The determination of the age of common rocks by the "helium method" necessitates accurate measurements of the radium content. The method of compensating the background by the use of two opposed ionization chambers is applied to radium determinations and the apparatus has an observational limit of  $5.5 \times 10^{-14} \times n^{-1}$  g radium for n hourly readings. With the thorium content determined as in the preceding article a summary of results for a suite of rocks from a single horizon and the present status of a geological time scale is given.

<sup>12</sup> Evans and Neher, Phys. Rev. 45, 144 (1934).

<sup>\*</sup> This research was supported by a grant from the Penrose Fund of the American Philosophical Society.

<sup>&</sup>lt;sup>1</sup> Contribution No. 356 from the Research Laboratory of Physical Chemistry.

HE measurement of the radium content of certain naturally occurring material like the iron meteorites and even the accurate determination of this quantity in some basic rocks falls beyond the scope of the ordinary single ionization chamber system. The difficulty lies in the fact that the very small ionization due to the radon is superimposed on a much larger background. The work of G. Halledauer<sup>2</sup> constitutes a step forward in these measurements in that variations in the background with time were canceled out with a second ionization chamber. After a certain charging interval the charge from each chamber, one containing the radon, the other only the background gas, was shared in turn with an electrometer the difference being the charge due to the ionization by the radon. Paneth and Koeck<sup>3</sup> have considerably improved the technique of this method but the practical difficulties of maintaining constant capacity in a charge sharing system are well known. In cosmic-ray work the subtracting of the background from the background plus the effect to be measured has for some time been conducted automatically by connecting the electrodes of two identical equal and oppositely charged chambers permanently to an electrometer. Such a system has been described by Steinke<sup>4</sup> and Schindler, 5 was personally suggested by Steinke to Paneth for radon measurements and is now in operation in Königsberg, Germany<sup>6</sup> and at this Institute. At the same time the adoption of this differential system to the measurement of radon has been developed independently at the California Institute of Technology by Evans.7 The advantages of the system are in the elimination of errors due to variations in the background exterior to the chambers, battery variations and contact potentials and particularly in the added accuracy of the differential reading insofar as this can now be spread over a larger scale. The one disadvantage is that the statistical variation

is  $\sqrt{2}$  times that for the single chamber as Schindler<sup>5</sup> and Evans<sup>8</sup> have noted. However, the same statistical error is obtained by increasing the number of observations to 2n-1, where n is the number of observations on a single chamber and with automatic registration this is easily accomplished.

### THE APPARATUS

The apparatus is shown schematically in Fig. 1. The two chambers A and B are constructed identically, having a volume of 2500 cc. The chambers are grounded and the collecting voltage applied to a net placed at a distance of 0.6 cm from the walls and made of 40-mesh copper gauze. One end of each of the copper chambers is sealed with a steel block and lead washer in such a way that no lead is exposed to the chamber. The  $\frac{1}{8}$ -inch brass electrode leads are coned into amber plugs in turn coned into brass guard rings (made of the same brass stock as the electrodes) which are packed into the steel heads. Similar leads without guard rings are provided for the collecting voltage to the nets. Two packed leads to each chamber provide pumping and filling facilities. The chamber nets are charged to + and -200 volts with regard to the center ground tap on a potentiometer across a center 6-volt storage battery. This variable center tap is adjusted as described by Schindler<sup>5</sup> until  $E_A C_A = -E_B C_B$  whereupon battery fluctuations should show no effect on the electrometer. In the head of the 2-inch diameter lead casing is arranged a small ring condenser C. A remote control switch allows a platinum to platinum contact directly with the electrometer lead whereby charges of either sign can be applied to the electrodes and electrometer, or the same grounded. Two potentiometers supply voltages to the remote control switch and the ring condenser C. These voltages can be accurately read by throw-over switches to a Leeds and Northrup potentiometer. The electrode lead casing and shielding to the electrometer is hermetically sealed and any water vapor removed with a P<sub>2</sub>O<sub>5</sub> drying tube. The Compton electrometer E (sputtered quartz fiber suspension) is operated for

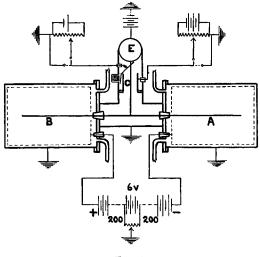
<sup>7</sup> R. D. Evans, Phys. Rev. 39, 1014 (1932), Rev. Sci. Inst. 6, 99 (1935).

G. Halledauer, Ber. Wien Akad. 134, 39 (1925).
 F. Paneth and W. Koeck, Zeits. f. physik. Chemie, Bodenstein-Festband, 145 (1931).

<sup>&</sup>lt;sup>4</sup> E. Steinke, Physik. Zeits. **31**, 1019 (1930). <sup>5</sup> H. Schindler, Zeits. f. Physik **72**, 625 (1931).

<sup>&</sup>lt;sup>6</sup> Publication deferred. I am indebted to Professor F. Paneth for his kind assent to the portion of this article relating to the electrical apparatus.

<sup>&</sup>lt;sup>8</sup> R. D. Evans, Phys. Rev. **45**, 144 (1934).



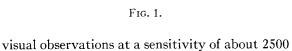


Fig. 2 shows the flask used for storing the solution<sup>9</sup> containing the radium. The flask is of 150 cc capacity fitted with a condenser for use when boiling and passing air through the solution to remove the emanation. With the magnetic break seal A and the tip B sealed the solution is deemanated through C and D which are then sealed off. The ground glass joint E is lubricated over the upper quarter with P<sub>2</sub>O<sub>5</sub>. This design of storage flask avoids any possible adsorption of radon by grease. The period of storing from the time of sealing off C and D to the time of introduction into the chamber gives the fraction of the equilibrium amount of radon generated, accurately known from the tables of Meyer and Schweidler.<sup>10</sup> In most cases sufficient radon has accumulated in fifteen to twenty days (0.934-0.973).

mm per volt at 1 meter distance.

Likewise the introduction train shown in Fig. 3 is designed to avoid all contact with possible adsorbers of emanation. The spiral and charcoal A immersed in liquid air removes the emanation from the background gas—air—drawn through a drying train from outside the laboratory. The air passes through a sulphuric acid trap B as a flow indicator. Connection to the vacuum pump

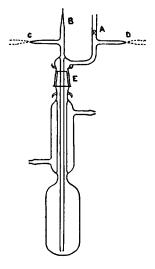
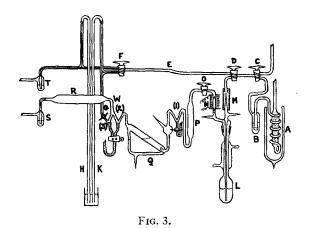


Fig. 2.

or air supply is made through stopcock C. This vacuum connection serves to pump out the connecting lines only. Stopcock D splits the air line to the solution flask and the line E. Stopcock F further splits the line E to the compensating chamber and the flush lead through the stopcock G. The two manometer columns H and K indicate the pressure in the chambers and are used to balance this pressure at a few mm below atmospheric pressure. The storage flask L when ready for measurement is connected at M with rubber pressure tubing and sealed to the line at N with the magnetic break system installed. The only stopcock O (necessary to control the streaming rate) in the emanation train is lubricated with P<sub>2</sub>O<sub>5</sub>. To O is sealed a soda-lime tube P, to absorb most of the HCl gas, which is then connected to the first mercury valve 1. To this is sealed the saturated NaOH bubbler Q, completing the HCl absorption. To Q is connected the mercury valves 2 and 3 with a common lead to the CaCl<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> drying tube R. The leads to the emanation and compensating chamber pass through the mercury backstops S and T. The portion of the train through which the emanation passes is thus seen to be free from any organic adsorbing matter. The adsorption of emanation in the various chemicals used has been shown to be negligible. After considerable use the NaOH solution showed only a very slight trace of chloride and has been left out in the

<sup>&</sup>lt;sup>9</sup> See Urry, "Determination of the Thorium Content of Rocks," preceding article, for the preparation of the solution.

<sup>&</sup>lt;sup>10</sup> St. Meyer and E. v. Schweidler, *Radioactivität*, second edition (Teubner, Leipzig, 1927).



later work. It is significant that the standardization remained the same.

#### OPERATION

A is immersed in liquid air for one hour. The air lines as far as F and M are evacuated through C and filled with emanation-free air. With 0, 1, 2, 3 and G open the chamber and line as far as the magnetic break bulb is evacuated through the emanation-chamber pump lead. G is then closed and 3 run up to prevent contact of the emanation with the greased stopcock G. The pump lead to the chamber and O are closed. The magnetic break-off is brought into action, O carefully opened to start the air out of L into the train and the tip B (Fig. 2) broken off inside M. C is opened to D in turn opened to M, and the solution brought to a temperature slightly below boiling and maintained there. The introduction time of the radon into the chamber is taken as fifteen minutes after starting streaming. When the pressure in the chamber reaches about 73 cm D and O are closed and 2 run up. 3 is lowered and the train from W on flushed through line E and stopcocks F and G until the manometer K is nearly level with the mercury in the reservoir. The valve 1 serves to prevent back diffusion of water vapor from Q to P while not in use. The compensating chamber is then filled through the line E and the stopcock F, until the same pressure in the two chambers is indicated by Hand K. Electrometer readings are commenced immediately after the filling process in order to follow the build-up curve of the decay products in the chamber. This affords a check on the

presence of spurious ionization by a comparison of the build-up curve with the theoretical.

#### ELECTRICAL MEASUREMENTS

With the circuit given in Fig. 1 three methods of measurement, all of which have here been employed, are possible.

- Measurement of the rate of charge starting from the electrical null point.
- (2) Measurement of the rate of charge starting from a predetermined charge on the electrometer system imparted through the remote control switch such that the time of drift in a given observation interval is approximately equal on either side of the null point. Leakage errors if constant with regard to corresponding points on either side of the null point should then cancel out.
- (3) Compensation of the charge on the electrometer system by application of a potential to the ring condenser C with the electrometer as a null instrument. The electrical symmetry of the system permits this method of operation whereas in the single chamber induced effects will make the standardization doubtful. By this method the apparatus is calibrated in terms of volts applied to C per unit of radon or radium. Since the capacity of the system remains constant and the electrometer calibration does not enter, this method is the most direct, but does not lend itself readily to automatic control.

The correspondence of all three methods (observations by each method over many intervals) within 2 percent and random with respect to sign is indicative of the very low losses and absence of spurious effects with this type of electrometer when guard rings of exactly the same material or plating are used at all insulated leads and a thoroughly dry system is maintained. Consequently methods 1 and 2 have been mostly employed in the routine work, 2 more particularly when the observational interval is long.

#### Electrical capacity of the system

The apparatus has been calibrated with standard solutions of radium but a rough check is afforded by the Duane and Laborde<sup>11</sup> equation. This requires a knowledge of the electrometer system capacity to convert e.s. units of current into electrometer volts per hour. The capacity of the ring condenser *C* was determined by Steinke's<sup>12</sup> method to be 0.61 cm. On setting up

<sup>&</sup>lt;sup>f1</sup> Reference 10, p. 305.

<sup>&</sup>lt;sup>12</sup> E. Steinke, Zeits. f. Physik 48, 650 (1928).

the capacity relations for the circuit given in Fig. 1 it is found that, by maintaining all other values constant

$$dV_e/dV_r = -c_r/C_e, (1)$$

where the subscripts e and r refer respectively to the electrometer system and the ring condenser and  $C_e$  is the total capacity of the electrometer, leads and electrodes. The capacity of the electrometer system at zero deflection was determined from Eq. (1). With a series of voltages applied to the electrometer system, the voltage that must be applied to the ring condenser to return the electrometer to zero in each case was determined. The average value of  $C_{e0}$  (zero deflection) was found to be  $34.8\pm0.3$  cm. The change of capacity with deflection was determined by finding the value of  $dV_e$  for a given deflection and of  $dV_r$  for the same deflection. The capacity varied from  $C_{e0} = 34.8$  cm to 32.5 cm for a deflection of 150 mm nearly linearly. In practice the electrometer is calibrated after each observational interval over the same deflection as was obtained in that interval. The length of the observational interval varies from 15 minutes to two hours according to the amount of radon present and the required accuracy of the determination. Observations last over at least nine intervals.

#### STANDARDIZATION

From the equation of Duane and Laborde, the saturation current per 10<sup>-13</sup> curie of radon in equilibrium with its decay products to Ra C' is found to be  $4.72 \times 10^{-7}$  e.s.u. From the average volumetric field intensity (16.3 volts/cm for a collecting voltage of 200 v in the chambers used) the ionization saturation parallel to the field is given by Moulin<sup>13</sup> as 76 percent and perpendicular to the field as 88 percent, averaging 82 percent. Assuming a uniform volumetric distribution of the ions, 16 percent are captured between the net and the wall leaving 84 percent collected within the net (total volume of the chamber 2494 cc, volume inside the net 2113 cc). The saturation current is therefore  $0.82 \times 0.84 \times 4.72 \times 10^{-7} = 3.23$  $\times 10^{-7}$  e.s.u per  $10^{-13}$  gram radium. With the value of the capacity  $C_{e0}$  previously given this

corresponds to 0.010 v per hour per 10<sup>-13</sup> gram Ra = K. Values of K from standard radium solutions<sup>14</sup> varying in strength from 2 to 62.6×10<sup>-13</sup> gram radium were found as follows: 0.009506, 0.009441, 0.009447, 0.009406 mean 0.00945 v per hour. A comparison of the calibrations with standards and the Duane and Laborde formula agrees with the work of other authors on similar chambers in the direction and approximate difference found. The value of *K* as found from the standard solutions has been taken as the calibration. The radium content of an unknown solution is found as follows: Let m be the deflection (mm), less the net background difference in the two chambers if any, in a given observational interval reduced to an hour unit of time and s the sensitivity of the electrometer in volts per mm. If

$$U = \frac{\text{radon generated in the storing period}}{\text{equilibrium radon}}$$

(from the duration of the storing period and the aforementioned tables), and

 $u = \frac{\text{radon in the chamber during the observational interval}}{\text{radon at the time of introduction into the chamber}}$ 

(from the same tables) then the charge rate reduced to equilibrium amount of radon and zero time of the radon in the chamber is given by ms/Uu. The readings used are those for t>3 hours to allow the establishment of equilibrium with the decay products. The n observations reduced in like manner to this standard state can now be averaged. If W is the weight of the original rock sample and R the radium per gram in units of  $10^{-13}$  gram

$$R = \left[\frac{ms}{Uu}\right]_{Av} \times \frac{1}{WK}.$$
 (2)

Any difference in the background ionization between the two chambers is determined by averaging a like number of observational intervals after removing the radon and refilling with emanation free air, allowing sufficient time for

<sup>&</sup>lt;sup>13</sup> Moulin, Ann. chim. phys. 21, 550 (1910); 22, 26 (1911).

<sup>&</sup>lt;sup>14</sup> The standard stock radium solution was kindly supplied by S. C. Lind and was diluted from the main stock used for a radium-uranium ratio determination. See Lind and Roberts, J. Am. Chem. Soc. 42, 1170 (1920). A correction for the decay of radium since the date of standardization following the preparation (1919) has been applied.

the radon decay products to disintegrate. The average background difference is nearly always negligible corresponding to <0.003 v per hour and may be of either sign showing that it is due to the statistical fluctuation residual since  $n \neq \infty$ . The individual background observations, however, are quite readable and enable an analysis of the background ionization to be made. The computation in the case of the null method is similar, substituting in Eq. (2)  $V_r$ , the voltage applied to the ring condenser to maintain zero charge on the electrometer system less any background difference, in place of ms, and  $K_r$  the calibration in ring condenser volts for K. The ionization in the 2-cc quadrant box of the electrometer even assuming as high a value as 12 ions per cc per sec. contributes a negligible charge to the quadrants connected to the electrodes.

#### THE PROBABLE ERROR

Let  $x_1$  be the number of contamination alphaparticles per hour in the one chamber of specific effect, a electrometer volts per particle and  $y_1$  the number of betas, gammas and cosmics per hour of specific effect b in the same units. (The last three sources of ionization are grouped together since the contribution to the fluctuations is found to be negligible compared with that due to the alpha-particles and the specific effect of each source is not greatly different.) Let the subscript  $_2$  refer to the second chamber and  $_3$  to the radon measurement. If E is the electrometer reading in v per hour,

$$E_1 = ax_1 + by_1 \tag{3}$$

and

$$E_2 = ax_2 + by_2 \tag{4}$$

and

$$E_1 - E_2 = (ax_1 + by_1) - (ax_2 + by_2).$$
 (5)

From measurements on each chamber in turn it is found that  $E_1=E_2$  and on the reasonable assumption that  $y_1=y_2$  we have

$$E = E_1 = E_2 = ax_1 + by_1 \tag{6}$$

and hence

$$E_1 - E_2 = (ax_1 + by_1) - (ax_1 + by_1). \tag{7}$$

The nature of statistical fluctuations has been

treated in full by Evans.<sup>15</sup> From Evans' Eq. (4) the Gaussian mean deviation  $D_B$  for the background  $E_1-E_2$  in Eq. (7) is given by

$$D_B^2 = 2a^2x_1 + 2b^2y_1. (8)$$

Now the actual quantity measured is given by

$$E_3 + (E_1 - E_2) = ax_3 + by_3 + (ax_1 + by_1) - (ax_1 + by_1)$$
 (9)

and the mean Gaussian deviation of this sum of effects  $D_S$  is given by

$$D_S^2 = 2a^2x_1 + a^2x_3 + 2b^2y_1 + b^2y_3.$$
 (10)

To derive  $E_3$  Eq. (7) is subtracted from Eq. (9) and by neglecting  $b^2$  terms compared with  $a^2$ , since the specific effect of the alpha-particle greatly exceeds that of the other sources of ionization, by the principle of propagation of errors the mean deviation of  $E_3$  is given by the sum of (8) and (10):

$$D^{2}_{S-B} = 4a^{2}x_{1} + a^{2}x_{3}. {11}$$

Now  $4a^2x_1 = 2D_B^2$  from Eq. (8) by neglecting  $b^2$  terms and since r = 0.6745D (Evans' Eq. (7) where r is the probable error of a single observation)

$$r_{S-B} = 0.6745 \left[ (2D_B^2 + a^2 x_3)/n - 1 \right]^{\frac{1}{2}}$$
 (12)

for *n* observations.  $D_B$  has the value  $8.08 \times 10^{-3}$  v per hour (1-hour intervals) from the residuals of over 300 observations on the background difference from the relation

$$0.6745D_B = r_B = 0.6745 \left[ \sum v_B^2 / (n-1) \right]^{\frac{1}{2}} \quad (13)$$

where v is the observed variation from the arithmetic average. a having the value  $5.25 \times 10^{-4}$  volt per alpha-particle with due regard to the ionization saturation, Eq. (12) reduces to

$$r_{S-B} = 0.6745 \left[ \frac{1.306 \times 10^{-4} + 5.25 \times 10^{-4} ax_3}{n-1} \right]^{\frac{1}{2}} (14)$$

for 1-hour intervals and the probable error is calculated by substituting the average value of ms/Uu from n observations for  $ax_3$ . The value of  $D_B$  appropriate to the observational interval in use must be substituted for intervals other than one hour. One point of practical importance

<sup>16</sup> R. D. Evans, Phys. Rev. 45, 144 (1934).

TABLE I. Ages of the Keweenawan trap rock
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Sp. No.	LOCATION	$\frac{\text{He} \times 10^5}{(\text{cc/g})}$ $3.27 \pm 0.06$		Ra×10 <sup>13</sup> (g/g) 0.90±0.08		$\frac{U \times 10^7}{(g/g)}$	$\frac{\text{Th} \times 10^8}{(g/g)}$ $0.98 \pm 0.12$		Th/U	$\frac{\text{Age}}{(10^6 \text{ years})}$ $520 \pm 25$	
3											
3 5		8.09	.16	2.62	.09	7.70	1.30	.12	1.69	600	15
6L		5.55	.28	1.79	.08	5.26	1.24	.19	2.36	540	30
8		7.80	.31	3.23	.07	9.50	1.01	.15	1.06	535	20
12	Normal lower mine levels	9.28	.19	4.16	.06	12.23	2.00	.24	1.64	450	15
14		11.23	.34	3.21	.06	9.44	2.40	.22	2.54	585	20
18		2.42	.10	0.57	.07	1.66	0.81	.12	4.88	530	35
19		1.94	.04	0.57	.06	1.68	0.65	.08	3.87	480	25
20		2.47	.05	0.74	.06	2.18	0.68	.12	3.12	520	30
										530	
17	Conglomerate felsite pebble	23.54	.70	7.23	.07	21.26	6.75	.40	3.17	500	15
23		20.00	.40	0.79	.05	2.32	3.68	.22	15.86	1290	45
24	Abnormal lower mine levels	20.20	.70	1.29	.08	3.79	3.63	.23	9.58	1190	45
25		1.69	.03	4.71	.05	13.85	11.0	.4	7.94	32	1
1		1.36	.03	0.33	.06	0.97	0.70	.20	7.22	405	50
16	Surface and upper levels with	2.99	.15	1.10	.08	3.23	1.14	.17	3.53	405	20
28	exposure to waters	3.40	.07	1.54	.07	4.53	1.79	.45	3.95	310	25
7		5.45	.22	3.73	.07	10.97	1.00	.15	0.91	340	20
9		1.50	.02	0.71	.02	2.09	< 0.40		< 1.91	>400 <	< 630
11	Surface and upper levels, no	6.82	.27	2.44	.09	7.17	1.67 ±	.21	2.33	490 ∃	
$\hat{2}\hat{2}$	apparent exposure to cir-	3.16	.16	0.97	.06	2.85	1.10	.15	3.86	460	30
29	culating waters	1.87	.04	1.22	.10	3.59		_		440	
31		1.45	.10	0.87	.03	2.56	0.10	.04	0.39	435	60
26		5.36	.22	1.15	.06	3.38	1.73	.15	5.12	555	25
27Ph	Freshly dumped rock	2.30	,16	0.58	.09	1.71	0.63	.16	3.68	565	60

arising out of the foregoing analysis is that the  $b^2y$  term is negligible compared with the  $a^2x$  term unless there is a very large extraneous source of radiation in the neighborhood of the apparatus. In order to reduce the probable error and the observational limit the alpha-particle contamination must be reduced and shielding precautions will have little effect, an important observation first pointed out by Evans. The specific effect of these wall particles can be reduced by the introduction of the net but adjustment must be made between the reduction of probable error on decreasing the residual ioniza-

tion of such contamination particles and the loss of ionization between the net and the wall. The net was finally placed at a distance of 0.6 cm from the wall. For alpha-particles of 4-cm range in air the fractional absorption is therefore 0.15 and from Evans<sup>16</sup> the fractional ionization appearing inside the net is about 0.62. The mean deviation  $D_B$  from Eq. (8) is therefore 0.62 of the mean deviation with no net. From Eq. (12) we obtain the following expression for the ratio of the percentage probable error with and without the net (0.84 of the total ionization available when the net is present).

$$\frac{r \text{ with net}}{r \text{ without net}} = \frac{\left[2D_B^2 + a(ax_3)\right]^{\frac{1}{2}}/ax_3}{(2\left[D_B/0.62\right]^2 + a\left[ax_3/0.84\right]^2)^{\frac{1}{2}}/ax_5/0.84}.$$
(15)

For small values of  $ax_3$  (0.01 v per hour) this ratio is about 0.7 whereas for large values (1.00 v per hour) the ratio is sensibly 1. The probable error is therefore more likely to be diminished by the further removal of contamination sources than by the use of nets. For this reason the following analysis of the background ionization has

been made. Solving Eqs. (6) and (8) for  $x_1$  we have

$$x_1 = (D_B^2 - 2bE)/2a(a - b)$$
, but since  $a \gg b$ ,  
 $x_1 = (D_B^2 - 2bE)/2a^2$ , (16)

where a is here the specific effect of the fractional  $\overline{}^{16}$  R. D. Evans, Phys. Rev. **45**, 29 (1934).

TABLE II. Geological time scale by the helium method.

Horizon	Rock and Source		He×10 <sup>5</sup> (cc/g)		Ra × 10 <sup>13</sup> (g/g)		U×10 <sup>7</sup> (g/g)	${ m Th}  imes 10^6 \ ({ m g/g})$		Th/U	AGE (106 YEARS)	
Miocene	Basalt, Douglas Creek Washington. • Columbia River, Ore.	(1) (2)	$0.23 \pm 0.21 \\ 0.27$	.0.03 .02 .03	2.17 ± 2.16 2.20	-0.06 .04 .07	6.40 6.38 6.45	2.02± 2.10 2.52	-0.20 .23 .23	3.17 3.30 3.88		± 1.3 5 1.0 1.4
Early Eocene?	Tinguaite, Montreal		6.44	.26	20.40	.17	59.98	14.5	.29	2.42	57	1.5
Early Cretaceous	Porphyrite Dike, Cal.		1.17	.09	1.68	.08	4.93	1.58	.16	3.2	110	7
Jurassic	Diabase, N. Star Mine, Cal.		1.76	.11	1.65	.08	4.82	1.98	.16	4.1	150	8
Triassic	West Rock Sill, Conn. Buttress Dike, Conn.	(1) (2) (1) (2) (3)	1.82 1.88 1.52	.13 .13 .09	1.96 2.13 1.55	.15 .16 .07	5.76 6.26 4.56	1.30 1.21 1.06	.38 .35 .11	2.26 1.93 2.28	170 170 175	12 12 9
	Palisade Intrusive, King's Bluff, Weehawken, N. J.		1.60 1.66 1.68	.10 .10 .10	1.44 1.30 1.38	.08 .07 .07	4.23 3.81 4.05	1.79 1.77 1.80	.12 .14 .12	4.24 4.64 4.45	155 165 165	8 9 8
	Basalt Watchung, Mt. Clifton, N. Y. Cape Spencer Flow, N. S.,		1.13	.08	1.00	.06	2.94	0.90	.10	3.06	180	11
	Can.		1.33	.08	1.05	.07	3.08	1.53	.11	5.00	160	8
Ordovician	Stark's Knob, Adirondack M Basalt flow,* Martinsburg shale, Penn. Diabase in above shale	(1) (2) (1) (2)	0.485 1.90 1.15 3.88 2.61	.04 .11 .08 .17 .13	0.34 2.25 1.16 1.30 1.29	.06 .09 .06 .06 .07	1.00 6.6 3.41 3.81 3.78	<.08 1.98± 1.27 1.83 0.91	.18 .11 .12 .10	<0.80 3.0 3.71 4.80 2.40	<340 > 140 = 145 375 355	
Cambrian	Basalt, Unicoi formation, Tenn.	(1) (2)	1.62 1.51	.11 .10	0.87 0.85	.08 .08	$\frac{2.56}{2.50}$	0.15 0.15		$0.59 \\ 0.60$	$\begin{array}{c} 465 \\ 440 \end{array}$	30 30
Pre-cambrian Keweenawan	Mean from Table I Diabase Dike, Noranda Horne Mine, Quebec	(1) (2) (3)	6.00 6.40 6.34	.24 .25 .25	1.26 1.13 1.13	.08 .07 .07	3.70 3.32 3.32	2.50 2.57 2.57	.20 .20 .20	6.76 7.74 7.74	530 485 525 520	20 25 25
Latest Huronian?	Diabase Dike, Gogebic Iron Range, Wis.	(1) (2) (3) (4)	6.50 21.14 21.20 14.81	.26 .64 .64 .44	2.17 2.02 2.44 3.50	.08 .08 .09 .09	6.38 5.94 7.18 10.29	1.30 9.56 8.60 4.28	.19 .33 .30 .25	2.04 16.09 12.0 4.16	550 560 580 570	25 15 25 15
?	Woollen Mill gabbro, N. Y.		2.09	.13	0.19	.09	0.86	0.75	.15	8.75	670	85
Algorian?	Diabase Dike, Great Bear Lake, Can.		11.01	.34	1.71	.07	5.05	1.80	.18	3.55	900	35

<sup>\*</sup> Metamorphosed.

ionization appearing inside the net. 2bE is a second-order term and b need not be accurately known. It was computed from the average path of a beta, etc., through the chamber at 100 ion pairs per cm. E was found to be 0.2002 v per hour. From  $(16) x_1 = 116$  alpha-particles per hour = 11.1 alpha-particles per 100 cm² per hour and  $ax_1 = 0.0609$  v per hour or 1.88 ions/cc/sec. From Eq. (6) the background from the beta, gamma and cosmic-radiation =  $by_1 = 0.1393$  v per hour or 4.29 ions/cc/sec. Not until the alpha-particle background is reduced by special cleaning precautions to 1.6 alphas per hour per 100 cm² does the  $b^2y_1$  term come within 10 percent of the term  $a^2x_1$  although  $by_1$  is now contributing 94 percent

of the total background ionization. If the alphabackground can be so far suppressed, shielding must be used for a further diminution of  $D_B$ . The observational limit is also dependent upon the value of  $x_1$  being given by  $0.36 \times 10^{-14} [2x_1/n]^{\frac{1}{2}}$  gram radium for one-hour intervals and n readings with the differential apparatus.

### RESULTS

The "helium method" for the determination of the geological age of rocks has been dealt with elsewhere. <sup>17</sup> A full discussion of the results given in Table I for the Keweenaw Point, Upper

<sup>&</sup>lt;sup>17</sup> Wm. D. Urry, Chem. Rev. **13**, 2 (1933).

Michigan, basaltic flows is in course of publication by the Geological Society of America. The undue variations of certain results are owing to the inclusion of obviously unsuited material, to determine the influence of geological and physical factors on the result. Table II shows the progress in the present project of building a geological time scale by the examination of authenticated basic rocks from all geological horizons. The advantage of the helium method when once substantiated lies in the wealth of suitable material available. The results recorded here, interdigitate well with lead ratios in radioactive minerals. The helium determination has been described previously.<sup>18</sup> The thorium measurements are described in the immediately preceding article.9 The age result probable error is calculated from the usual differentiation of Eq. (1) for t in the same article. 9 The uranium content is calculated from the equilibrium factor, uranium =  $2.94 \times 10^6$ Ra. The average radium content of all the basic rocks in the two tables is  $1.65 \times 10^{-13}$  g per g. This value may be somewhat low for a general basic rock average since the Keweenawan basalts

are low compared to material from other sources. Thus the average Keweenaw content (27 specimens) is  $1.60 \times 10^{-13}$  g per g, somewhat higher than was given in the preliminary Keweenawan report—15 specimens averaging 1.3×10<sup>-13</sup> g per  $g^{19}$ —but lower than an average of  $1.9 \times 10^{-13}$  g per g for 20 non-Keweenawan basic rocks. The average thorium content of all the basic rocks is  $2.0 \times 10^{-6}$  g per g and the mean Th/U ratio 4.1. The individual ratios are often higher than has previously been supposed, a finding in agreement with the results of R. D. Evans (private communication). As a comparison, the radium contents of various suites of granites as given in the literature vary from 9 to  $17 \times 10^{-13}$  g per g.<sup>20</sup> Individual measurements with the present apparatus give results from 5 to  $20 \times 10^{-13}$  g per g for granites.

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19 Urry, "Radioactivity Measurements. I," Proc. Am. Acad. 68, 125 (1933).
20 Urry, "Radioactivity Measurements. II," Proc. Am. Acad. 68, 137 (1933). See also Evans and Williams, Am. J. Sci. 22, 441 (1935).

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## Rotatory Dispersion of Aliphatic Aldehydes

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Rotatory dispersion curves of configurationally related aldehydes of the type

$$\begin{array}{c|c}
CH_3 & O \\
 & | \\
H-C-(CH_2)_nC \\
 & | \\
C_0H_5 & H
\end{array}$$

(n being equal to 0, 1, 2, or 3) have been determined in the visible and the ultraviolet regions of the spectrum. Their analysis has shown first, that the band of the aldehydic group at  $\lambda 2950$ is rotatory active and that the sign of its contribution in the first member (n=0) is opposite to that of the higher members and second, that the magnitude of that contribution varies periodically with the number of carbon atoms located between the aldehydic group and the asymmetric carbon atom.

<sup>18</sup> Paneth and Urry, Zeits. f. physik. Chemie A152, 110 (1931).