Determination of the Thorium Content of Rocks

Wm. D. Urry

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Determination of the Thorium Content of Rocks*

WM. D. URRY,[1] *Massachusetts Institute of Technology*

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A new method for the determination of thorium in quantities of the order of 10^{-5} to 10^{-6} g is employed to complete the data necessary for the calculation of the age of geological material. The alpha-particle activity of thoron in a streaming gas is measured with a counter, a procedure which is shown to be superior to the usual ionization measurements on the thoron deposit. Simultaneously, the Pa/Ra ratio in common rocks can be determined.

WHILE the determination of radium in ordinary rocks has received considerable attention,[2] the related problem of thorium determination has been almost neglected.[3] From his valuable treatment of the natural alpha-particles ejected from solids, R. D. Evans has developed a method of measuring the total alpha-particle emission from the surface of solids.[4] By deducting the emission due to the uranium and actinium series, determined by a separate radium measurement, the contribution from the thorium series can be computed and the amount of thorium determined. This differential method has given reliable results with granites. The present interest in the accurate determination of thorium is in connection with the calculation of the age of rocks by the helium method which has been found to yield reliable results with certain types of material. A detailed account of the method has been published elsewhere.[5] To illustrate the necessary determinations, the equation for the age of a rock in terms of He (cc), Ra and Th (grams per gram) is given.

$$\text{Age (in years)} = 1.515\times10^{10}\log_{10}\left[1+\frac{4.518\times10^{-10}\text{He}}{\text{Ra}+9.17\times10^{-8}\text{Th}}\right]. \quad (1)$$

Although the thorium series usually contributes much less to the helium content than the uranium series, the thorium series in certain cases may become the chief contributor with a high Th/U ratio. Methods must be devised so that all the necessary determinations can be made on the same sample even in a small hand specimen.

In all but the most recent rocks the radioactive series have long since reached equilibrium, hence it is possible to measure any member of a given series and calculate the amount of any other member present or substitute the measured member in Eq. (1) by using the appropriate constants. The most convenient member of either the uranium or thorium series to measure is the emanation. Because of the short half-life (54.5 sec.) of thoron a constant streaming method is employed by renewing the ionization chamber with fresh thoron from a solution containing its parent Th X. The thoron disintegration in the chamber may be measured directly, or the thoron active deposit measured after an appropriate streaming time. The latter process employed by most investigators is very inefficient as is shown later. Previous measurements have always been made on the total ionization with some type of electrometer, but an alpha-particle counter of the type used here has certain advantages over the total ionization method especially when applied to a streaming gas. Although the total ionization is affected by the various stopping powers of the carrier gases the alpha-particle count is not and HCl and water vapor absorbers can be dispensed with under certain conditions of operation. The alpha-particle counter can be built to register only alphas, passing by the usual sources of background ionization. Since the volume and hence the surface of the chamber can be much smaller than in ionization measurements the

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[1] Contribution No. 355 from the Research Laboratory of Physical Chemistry.

[2] See Urry, "Determination of the Radium Content of Rocks," following article.

[3] Joly, Phil. Mag. **18**, 146 (1909); Poole, Phil. Mag. **3**, 1246 (1927). Other papers by these authors are mainly results obtained by the method outlined in the above references. Mache and Bamberger, Akad. Wiss. Wien **123** (2A), 325 (1914); Hirschi, Vierteljahrsschrift d. Naturf. (Ges. Zürich) **65**, 545 (1920); Gräven and Kirsch, Akad. d. Wiss. Wien **141** (2A), 8, 521 (1932). This method has been justly criticised by R. D. Evans, Phys. Rev. **45**, 38 (1934).

[4] Evans, Phys. Rev. **45**, 29, 38 (1934).

[5] Urry, Chem. Rev. **13**, 2 (1933).

background alpha-particle count can be greatly reduced. The following consideration is important in the construction of the apparatus.

Fraction of thoron atoms disintegrating in the count chamber

The solution to be measured (reduced to as small a bulk as possible, see E in Fig. 2) contains the parent of the thoron—Th X separated from its parent radiothorium. The volume of the solution is kept constant and its temperature roughly controlled. Let f be the fraction of thoron atoms leaving the solution in a given time. Both rock and standard solutions are kept at approximately the same salt and HCl concentration but this may be varied appreciably without affecting f. Let A_0 be the number of Tn atoms leaving the solution surface, then the number entering the chamber

$$A = A_0 e^{-\lambda \quad \tau} \tag{2}$$

and the number leaving the chamber

$$A_1 = A_0 e^{-\lambda_{Tn} T} \tag{3}$$

where τ sec. is the time to reach the chamber from the solution surface and T sec. is the time in the chamber. Then the fraction of Tn atoms disintegrating in the chamber is given by:

$$(A - A_1)/A_0 = e^{-\lambda_{Tn}\tau} \cdot (1 - e^{-\lambda_{Tn} T}) = \alpha. \tag{4}$$

Fig. 1 gives the curves of this function α against T which is inversely proportional to the rate of streaming for a given apparatus. For each value of τ/T = the ratio of the dead space volume to the volume of the chamber, there is a maximum for α at some given streaming rate which rises

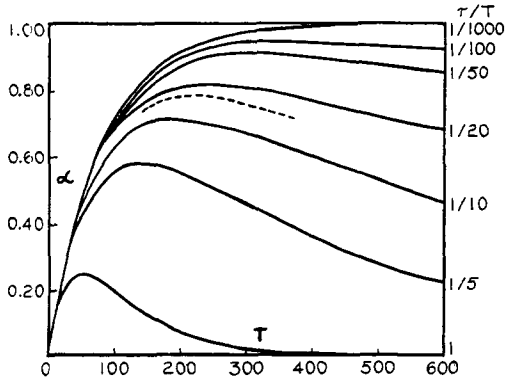

FIG. 1.

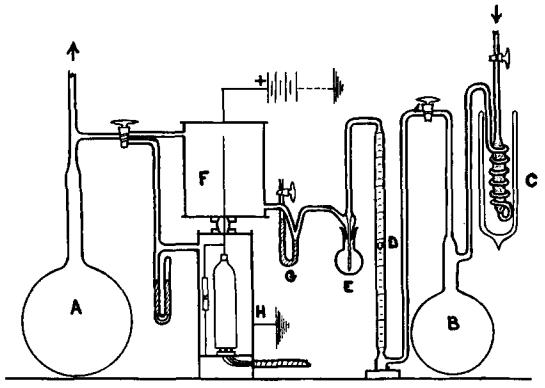

FIG. 2.

with decreasing value of τ/T. Since the count will be $f \cdot \alpha \cdot Q$ where Q is the theoretical count, it is important to construct the apparatus according to these curves and other considerations mentioned later. The dotted curve in Fig. 1 was experimentally determined for a particular apparatus with a solution equivalent to 2×10^{-5} g Th.

APPARATUS

The apparatus is shown in Fig. 2. The Pliotron FP-54 vacuum tube circuit is described by DuBridge.[6] The galvanometer alpha-particle deflections are photographically recorded over a period of several hours (usually about ten) for the measurements and an equal period for the background count. With ion collecting conditions of atmospheric pressure and 45 to 200 volts the deflection is proportional to the original ions produced (collision ionization negligible) and only alpha-particles and rare larger cosmic-ray bursts will be recorded. The large volumes A and B smooth out any streaming fluctuations. The air, drawn from outside the laboratory, passes through a drying train, a spiral and a charcoal immersed in liquid air C, which effectively removes any emanation in the air at even higher velocities than were employed. It then passes through a sensitive rotameter flowmeter, through the solution to be measured in the glass bulb E, whose volume is maintained as small as possible (30 cc), and into the ionization chamber F whence it is pumped away through A. Since the volume above the surface of the solution in

[6] DuBridge, Rev. Sci. Inst. 4, 532 (1933).

E up to the entrance to F is the determining factor in τ (Eq. (4)) it should be kept as small as possible. The upper quarter of the ground glass joint of the container E is lubricated with P_2O_5 since grease is not permitted because of the large adsorption of the emanations. G is a mercury seal to close off the chamber during background counts. The ionization chamber F is insulated from the evacuated housing H of the FP-54 by a $1\frac{1}{2}$-inch round hard rubber block, coned into the steel base of F and the steel head of H, which carries a grounded brass guard ring, a coned amber plug and the electrode made from the same piece of brass as was the guard ring to avoid battery currents across the amber surface. The housing H is maintained at a pressure of 5 mm or less to prevent ionization by alpha-particle contamination in H. Since alpha-particles having a residual range of 1 cm or less can be detected, a large ionization chamber is unnecessary and the increased surface only tends to increase the background count, but a lower limit is set by the fact that decreasing the volume of F decreases T and hence increases τ/T which is the controlling factor in the constant α. It is inadvisable to increase τ/T much more than 1/20 and hence the chamber has volume of 600 cc. The present chamber is constructed of steel having regard to Bearden's[7] extensive tests on the contamination of various materials. All inside faces were machined, carefully sand-papered and immediately put together giving a background count of 3–4 alpha-particles per hour per 100 cm², in good agreement with Bearden's result. Brass chambers have also been built giving a somewhat higher count but by coating all the metal surfaces with a thick layer of carbon by direct deposition from a yellow gas flame, the background count could be suppressed to that of steel. Such a coating has the added advantage of protecting the metal from corrosion due to acid vapors from the solution. The chamber parts were machined to fit tight, not soldered, but sealed with beeswax externally. In soldering it was found impossible to prevent a marked increase in the background caused by exposure of traces of solder to the interior.

[7] Bearden, Rev. Sci. Inst. 4, 271 (1933).

Chemical Procedure

In determining the helium content a carbonate flux containing about 5 g of the original rock is left. This flux is treated as follows:

(1) The rock flux to which barium carbonate was originally added is dissolved in a minimum of warm water to maintain a concentrated solution but not boiled. Under these conditions the radiothorium carbonate is retained in solution.

(2) The carbonate solution is filtered from the residue which is washed with 15 percent Na_2CO_3 solution. The residue contains in particular barium (carrier), Th X, radium and Ac X.

(3) The residue is dissolved in HCl and dried to render the silica insoluble, dilute HCl is again added and the silica filtered off with a thorough washing with dilute HCl and finally hot water. The resulting clear solution is evaporated to convenient bulk maintaining sufficient acidity to prevent precipitation of radium and its isotopes on the walls as sulphate and is ready for measurement.

(4) The silica from (3) is added to the carbonate solution from (2) and dissolved by prolonged boiling. Barium chloride is added and any Ra, Th X or Ac X carbonate filtered off, dissoved in HCl and measured. In all cases so tested no Th X or Ra was found. It is important that the final solutions be free from suspended silica or other material to avoid adsorption of the emanations.

The addition of standard solutions of Th X and Ra to known rock solutions in the initial stages of the chemical work increased the amount of Th and Ra found by the amount of the standard added to within an accuracy of 3 percent. This is additional evidence of no adsorption losses in the chemical processes. After the thorium measurement the solution is transferred to a suitable container and the radon measured in the same solution.

Theoretical

Distribution of the thorium series below Th X at any given time

Suppose the solution to contain X_0 atoms of Th X separated from its parent Ra Th. By applying the equations constituting Case I in Rutherford, Chadwick and Ellis[8] the relative number of Th X, Tn, Th A, Th B, Th C, and Th D (stable) atoms at any given time can be determined. With the very short half-life of Th A (0.145 sec.) the number of Th A atoms will be practically zero except when considering intervals of a fraction of a second. For the same reason the terms in Th A and Tn may be omitted from the equations

[8] Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances* (The Macmillan Co., New York, 1930), p. 11.

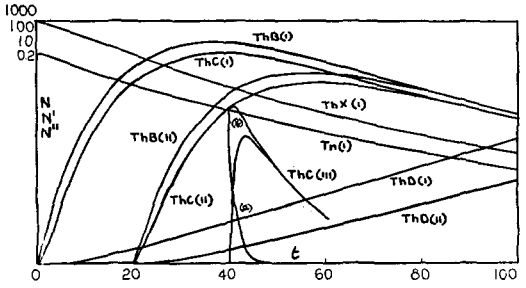

FIG. 3. Ordinate scale: 1000 atoms for Th X and Th D, 100 for Th B, 10 for Th C and 0.2 for Tn. t in hours.

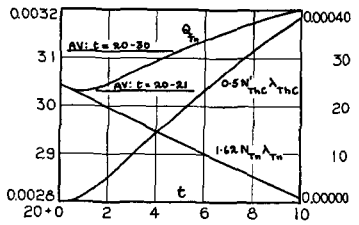

FIG. 4. Ordinate scale in alpha-particles per sec. per 1000 atoms of Th X at $t=0$; left, Q_{Tn} and $1.62\,N_{\mathrm{Tn}}\lambda_{\mathrm{Tn}}$; right, $0.5\,N'_{\mathrm{Th\,C}}\lambda_{\mathrm{Th\,C}}$. t in hours.

giving $N_{\mathrm{Th\,B}}$ and $N_{\mathrm{Th\,C}}$. Using Rutherford's values of λ sec.$^{-1}$ we obtain the following equations (t in sec.):

$$N_{\mathrm{Th\,X}}=X_0e^{-2.20\times10^{-6}t}, \tag{5}$$

$$N_{\mathrm{Tn}}=X_0 1.732\times10^{-4}(e^{-2.20\times10^{-6}t}-e^{-1.27\times10^{-2}t}), \tag{6}$$

$$N_{\mathrm{Th\,B}}=X_0 0.1375(e^{-2.20\times10^{-6}t}-e^{-1.82\times10^{-5}t}), \tag{7}$$

$$N_{\mathrm{Th\,C}}=X_0(0.01324e^{-2.20\times10^{-6}t}-0.1448e^{-1.82\times10^{-5}t}+0.001226e^{-1.91\times10^{-4}t}), \tag{8}$$

$$N_{\mathrm{Th\,D}}=X_0-(N_{\mathrm{Th\,X}}+N_{\mathrm{Tn}}+N_{\mathrm{Th\,B}}+N_{\mathrm{Th\,C}}). \tag{9}$$

In Fig. 3, curves I show the number of atoms of each member present at any time t after the separation of 1000 atoms of Th X from its parent.

The preparation of the solution for measurement however requires at least five hours after the separation of the Th X from the Ra Th. By substituting $N_{\mathrm{Th\,X}}$ for the moment of commencing streaming, for example at $t=20$ hours, in place of $X_0=1000$ in Eqs. (7), (8) and (9) we obtain curves II, Fig. 3, for $N'_{\mathrm{Th\,B}}$, $N'_{\mathrm{Th\,C}}$ and $N'_{\mathrm{Th\,D}}$ accumulating in the chamber. These equations need not be given but will be referred to as Eqs. (7a), (8a) and (9a).

Theoretical alpha-particle count

The alpha-rayers in the chamber will be Tn, Th A, and Th C or Th C'. Whether the disintegration proceeds via Th C' or Th C'' is immaterial on account of the very short half-life of Th C' (*ca.* 10^{-11} sec.). Let a be the fraction of Th A atoms disintegrating before reaching the electrode, then the number of alpha-particles from the thoron and Th A disintegrating in the gas space will be

$$\lambda_{\mathrm{Tn}}N_{\mathrm{Tn}}(1+a). \tag{10}$$

Of the fraction $(1-a)$ Th A atoms reaching the electrode,[9] one-half disintegrate inwards and are lost as counts. Hence the total alpha-count from thoron and Th A is given by

$$\lambda_{\mathrm{Tn}}N_{\mathrm{Tn}}[1+a+(1-a)/2]=\lambda_{\mathrm{Tn}}N_{\mathrm{Tn}}(3+a)/2. \tag{11}$$

The fraction $(1-a)$ Th A atoms reaching the electrode disintegrate through the beta-rayer Th B[10] to $(1-a)$ $N'_{\mathrm{Th\,C}}$ atoms. Of the fraction a all the resulting Th B atoms will be collected. Since half the alphas are again lost in the electrode, the contribution from Th C (or Th C') is given by

$$\lambda_{\mathrm{Th\,C}}N_{\mathrm{Th\,C}}\tfrac{1}{2}[a+(1-a)]=0.50\lambda_{\mathrm{Th\,C}}N'_{\mathrm{Th\,C}}. \tag{12}$$

The sum of (11) and (12) gives the total theoretical count Q_{Tn} alpha-particles per sec.

$$=1.62\lambda_{\mathrm{Tn}}N_{\mathrm{Tn}}+0.50\lambda_{\mathrm{Th\,C}}N'_{\mathrm{Th\,C}}. \tag{13}$$

In Fig. 4 the terms in (13) have been separately plotted for the case of starting streaming at $t=20$ hr. and a 10-hour period of streaming to $t=30$ hr. The alpha-particle emission from the Th C is at first barely sufficient to balance the decay of the supply of thoron and Th A, namely, the Th X, but after two hours the accumulation of the Th C and the consequent Th C alpha-emission is more than sufficient to balance the decay. The average value of Q_{Tn} for $t=20$–21st hr. is 0.9756 times the

[9] The calculation of the fraction reaching the electrode $(1-a)$ is given by Evans, Rev. Sci. Inst. **6**, 99 (1935), and has the value 0.76 for the particular chamber and conditions. Under the same conditions this fraction for Th B and Th C = 1 and recoils from the electrode will be recaptured. The mobility of these atoms is of the order of 1000 times the linear streaming velocity and hence there is no loss from the chamber.

[10] Recoils of Th B or Th C atoms into the electrode will lengthen the path within the electrode of the alpha-particle later ejected but insufficiently to prevent a count. This effect must be considered, however, in total ionization measurements.

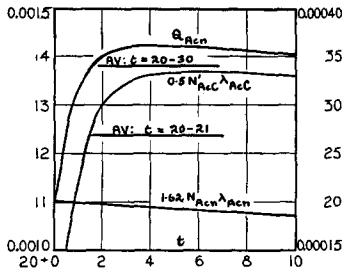

FIG. 5. Ordinate scale in alpha-particles per sec. per 1000 atoms of Ac X at $t=0$; left, Q_{Acn} and $1.62\ N_{Acn}\lambda_{Acn}$; right, $0.5\ N'_{Ac\ C}\lambda_{Ac\ C}$. t in hours.

average of the ten hourly recordings. This factor is independent of the time of commencing streaming and dependent only on the duration of the streaming. In practice the mean of the n hourly consecutive recordings is reduced to the mean for the first hour of streaming with the appropriate factor. The same functions for actinon and Ac C are given in Fig. 5. The mean of ten hourly consecutive runs is here 10.9 percent greater than for the first hour owing to the shorter half-life of Ac B (36 min.).

Thoron deposit

In measurements of the thoron deposit the procedure is to aspirate for about 20 hours, cut off the streaming, and measure the activity of the Th B and Th C or in the case of counting that of Th C. Curve III, Fig. 3, shows the number of Th C atoms $N''_{Th\ C}$ present at any time after streaming from $t=20$ to 40 hours and then cutting off the thoron supply to the chamber. It is the sum of the decay curve (a) for the Th C already present and the build-up curve (b) of the Th C from the Th B present at the moment of cutting off. The measured activity is decaying with the half-life of Th B (10.6 hr.) instead of Th X (3.64 days) and it is difficult to obtain a sufficient number of recordings to reduce the statistical error to a reasonable quantity. The relative efficiency of this method compared to the direct measurement of the thoron is quite low. For a comparison of collecting the deposit from $t=20$–40 hr. with a direct measurement on the thoron at $t=20$ hr., the relative efficiency is given by $(0.50\lambda_{Th\ C}N''_{Th\ C\ 40})/(1.62\lambda_{Tn}N_{Tn\ 20})$, equals 0.205 and requires twenty hours longer. If streaming is continued to $t=60$ hr. to reach peak Th C this rises only to 0.235, the maximum relative efficiency independent of the time of commencing streaming.

The presence of actinon

The solution contains in addition to Th X, the isotopes Ra and Ac X. It is required to determine the contribution of the resulting radon and actinon to the chamber count. $Z=f\cdot\alpha\cdot Q$ where Z is the count per sec. due to given emanation and the other symbols have the significance previously given. The fraction f can be taken the same for all three isotopes Acn, Tn and Rn (masses 219, 220 and 222). $\alpha_{Rn}=4.2\times10^{-4}$ and $\alpha_{Acn}=0.094$ from Eq. (4) for the same experimental conditions as in the routine thoron measurements where $\alpha_{Tn}=0.78$. If we take as an example a rock analysis: $Ra=2\times10^{-13}$ g per g ($U=5.88\times10^{-7}$ g per g.) $Th=1.5\times10^{-6}$ g per g and hence $Th/U=2.55$; assuming von Grosse's value for the half-life of protactinium and the isotope theory of the origin of the actinium series[11] the ratio of Pa to Ra should be the same in all rocks at the present geological time, namely, 0.8 g Pa to 1 g Ra, hence $Pa=1.6\times10^{-13}$ g per g. From these figures the number of Ra, Th X and Ac X atoms in the solution can be computed. With the small value of α_{Rn} and the long half-life of radon compared to thoron and actinon, the radon contribution is negligible for the Th/U ratio in rocks. Table I shows the method of determining the correction for actinon. From Eqs. (5), (6), (8a) and (13) and the analogous expressions for the actinium series (see Fig. 5) the theoretical counts Q_{Tn} and Q_{Acn} are calculated and an average for the period in question determined (column 3). For this particular example column 6 shows that at $t=20$–21st hour, 0.0219 of the total count is due to actinon and its products. In practice this correction factor must be computed after the Ra determination since the Pa is a function of the Ra. The half-lives of Th X (3.64 days) and Ac X (11.2 days) differ appreciably; the fraction due to actinon, etc., at time 240–241 hours is therefore considerably different (column 8), and the correction will depend upon the time of commencing streaming. This difference in ratio with time makes it possible, from two counts, one shortly after separation, the second ten to eleven days later,

[11] A. V. Grosse, Phys. Rev. **42**, 565 (1932).

TABLE I.

CONTENT PER g ROCK	ATOMS AT $t=0$	Q, α-PARTICLES PER SEC. FOR $t=20$–21ST HR.	α	COUNT Z PER SEC. $Z=f\cdot\alpha\cdot Q$	$\frac{Z_{Acn}}{Z_{Tn}}$	Z FOR $t=240$–241ST HR.	$\frac{Z_{Acn}}{Z_{Tn}}$
Th $1.5\times10^{-6}\cdot$g	Th X 2354	0.007144	0.78	0.00557f	0.0219	0.00097f	0.071
Pa $1.6\times10^{-13}\cdot$g	Ac X 1049	0.001299	0.094	0.00012f		0.00007f	
	Th X 2354	0.007144	0.90	0.00643f	0.1414	0.00113f	0.458
	Ac X 1049	0.001299	0.70	0.00091f		0.00052f	

to compute separate values of Q_{Tn} and Q_{Acn} and so find Pa and Th separately with no assumptions as to the Pa/Ra ratio. With the above values of α the apparatus is arranged to favor the thoron to cut down the correction which is one of the considerations in not making τ/T too small. By reducing the dead space volume so that τ/T is 1/100 and maintaining the same streaming velocity, values of α in the lower half of Table I are obtained and the ratio Z_{Acn}/Z_{Tn} rises as shown. It is important in verifying the isotope theory of the origin of the actinium series, based at present on a few Pa/Ra ratios in radioactive minerals, to determine the Pa/Ra ratio in rocks. The procedure is therefore outlined in the following equations. Let Z' be the average count (less the background) at time t' and Z'' at time t''. Then

$$Z'=\bar{Z}'_{Tn}+\bar{Z}'_{Acn} \tag{14}$$

and

$$Z''=\bar{Z}''_{Tn}+\bar{Z}''_{Acn}, \tag{15}$$

where $\bar{Z}'_{Tn}$ is the mean of the hourly readings for Tn and its products at time t' and $\bar{Z}''_{Tn}$ at time t''. $\bar{Z}'_{Acn}$ etc., the same for Acn and its products. In addition

$$\bar{Z}''_{Tn}=K_{Tn}\bar{Z}'_{Tn} \tag{16}$$

and

$$\bar{Z}''_{Acn}=K_{Acn}\bar{Z}'_{Acn}, \tag{17}$$

where

$$K_{Tn}=e^{\lambda_{ThX}(t'-t'')} \quad \text{and} \quad K_{Acn}=e^{\lambda_{AcX}(t'-t'')}.$$

The solution of Eqs. (14) to (17) is given by

$$\bar{Z}'_{Tn}=(K_{Acn}Z'-Z'')/(K_{Acn}-K_{Tn}) \tag{18}$$

and

$$\bar{Z}'_{Acn}=(Z''-K_{Tn}Z')/(K_{Acn}-K_{Tn}). \tag{19}$$

These means of n hourly recordings are now corrected to the mean at the first hour of streaming:

$$Z'_{Tn}=k_{Tn}\bar{Z}'_{Tn} \tag{20}$$

and

$$Z'_{Acn}=k_{Acn}\bar{Z}'_{Acn}, \tag{21}$$

where $k_{Tn}=0.9756$ and $k_{Acn}=0.891$ for $n=10$ (see Figs. 4 and 5). Then $Z'_{Tn}=\alpha_{Tn}\cdot f\cdot Q'_{Tn}$ and $Z'_{Acn}=\alpha_{Acn}\cdot f\cdot Q'_{Acn}$ and the amounts of Th X and Ac X at time $t=0$ or the corresponding equilibrium amounts of any other member of each series, e.g., Th and Pa, can be computed from Q'_{Tn} and Q'_{Acn} as shown below. The radium determination which always follows gives the Pa/Ra ratio.

STANDARDIZATION

From the relation $Z=f\cdot\alpha\cdot Q$, the factor $f\cdot\alpha$ for the apparatus described was determined with several solutions of Th X of known strengths, prepared in an analogous manner to the unknown solutions from a carefully analyzed 3.4 percent Th monazite and a 42.8 percent Th thorite, and ranging from thorium equivalents of 2 to 30×10^{-6} g. The calibrations from the two sources being in good agreement it is assumed that radioactive equilibrium has been established in these geological specimens. $f\cdot\alpha$ was found to be 0.42 independent of Th concentration. α having the value 0.78 from Eq. (4), by knowing the volumetric distribution of the apparatus and the streaming rate (maintained constant at the value giving the maximum of the function α), $f=0.54$ at the room temperature 20°C.

Computation of Th in unknown solutions

Z is the mean of n hourly recordings, corrected for background count, reduced to the mean for the first hour of streaming, corrected for the

presence of actinon, and expressed in alpha-particles per sec. The average value of Q_{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_{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 $N_{Th\ X_0}/N_{Th\ X_t}=e^{\lambda_{Th\ X}t}$ 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_{Acn}.

Probable Error

The nature of statistical fluctuations in counting experiments has been dealt with in detail by Evans and Neher.[12] 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

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

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*.[2]

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

[12] Evans and Neher, Phys. Rev. **45**, 144 (1934).

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Determination of the Radium Content of Rocks*

Wm. D. Urry,[1] *Massachusetts Institute of Technology*
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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 $5.5\times10^{-14}\times n^{-\frac{1}{2}}$ 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.

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