

THE CALCULATION OF GEOLOGICAL AGE.

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ABSTRACT.

New equations are developed by conventional methods for computing the age of rocks and minerals from radioactivity data, and errors in some of the past work are pointed out. By a suitable choice of equations, any desired degree of accuracy in calculation of the age can be obtained for all methods involving the accumulation of lead and helium from the thorium, uranium, and actino-uranium series. At low ages, the simple equation with constants dictated by recently improved values of the disintegration constants is satisfactory, and at higher ages a new equation, which corrects the age by means of a constant involving the thorium uranium ratio, can be generally applied. It is pointed out that if an average value of 3 is assumed for this ratio, the errors introduced into the calculated ages for ordinary rocks are less than those involved in experimental measurements and in changes in the rock since consolidation.

INTRODUCTION.

With the increasing interest in the determination of geological ages by radioactive methods, and the development of improved techniques, it is appropriate to consider the methods used in the calculation of the age from the experimentally determined parameters. It is important to realize the limitations in the use of certain equations, and to bring all methods of computation to a common basis. An approximate formula may give a value 625 ± 25 million years (M.y.), the correct solution¹ being 600 ± 25 M.y., and while the assigned error may cover the discrepancy, it is nevertheless incorrect to report the age as 625 ± 25 , unless the method of computation is made clear.

The simple equation, which has been written²

$$t(\text{M.y.}) = \frac{8.8 \text{ He}}{\text{U} + 0.27 \text{ Th}} \dots\dots\dots (1)$$

$$= \frac{7600 \text{ Pb}}{\text{U} + 0.36 \text{ Th}} \dots\dots\dots (1a)$$

yields a result close to the true age for young rocks, but it can be improved by the inclusion of the actino-uranium series, and

¹ When reference is made to the correct solution, or the true age, it is generally implied that the accepted ultimate reactions of the radioactive series, and the values of the disintegration constants are correct. Small changes that may occur in the future may be incorporated into the equations without changing the arguments appreciably. It is assumed throughout this paper that there has been no loss or addition of helium or lead since crystallization as questions bearing on this point are beyond the present scope.

² Holmes, Arthur: *The Age of the Earth*, Thomas Nelson and Sons, Ltd., 1937.

by introducing more recent values of the radioactive disintegration constants.

Equations of the logarithmic form, when properly employed, are capable of giving exact ages in certain instances, but are not applicable to rocks, which invariably contain the uranium and actino-uranium series, as well as the thorium series. One of these equations commonly used³ for such materials,

$$t \text{ yrs.} = \frac{2.303}{\lambda_U} \log_{10} \left[1 + \frac{4.518 \times 10^{-10} \text{ He}}{\text{Ra} + 9.17 \times 10^{-8} \text{ Th}} \right] \dots (2)$$

and often referred to as the "exact equation,"^{2, 3} has no sound mathematical basis, and its use is not recommended. The thorium cannot be exactly expressed in terms of a member of another series, and be used in conjunction with another disintegration constant, as is done in Eq. 2 for obtaining the integrated effect over geological time. Its apparent application is due to the fact that the disintegration constants of thorium and uranium are not widely different, and that the partial cancellation of errors is such as to give approximately the correct result for many rocks. In other cases, as will be shown later, the discrepancies between the true age and that calculated by the erroneous equation may be large. Furthermore, the equation neglects the actino-uranium series altogether, which limits its supposed application to about the same range as the simple formula, Eq. 1. The methods outlined by Kovarik⁴ were more rigorously developed but have been little used. Others have suggested certain simplifications, and considerable discussion has revolved around the methods of correcting for the decay of the parent elements in old rocks, and the question of the best values of the disintegration constants to use.^{3, 4, 5}

In this paper, a set of equations will be developed which will satisfy all present purposes; these will be expressed in simple forms in which they may be applied directly, using the most recent values for the several constants involved. Details are given to facilitate their use by the geological readers to

³ Lane, A. C., and Urry, W. D.: *Bull. G. S. A.* 46, 1101-1120, 1935. Urry, W. D.: *Chem. Rev.* 13, 305-343, 1933, *Bull. G. S. A.* 47, 1217-1234, 1936, *J. Chem. Phys.* 4, 34-48, 1936.

⁴ Kovarik, A. F.: Part III, *The Age of the Earth*, *Bull.* 80, National Research Council, 1931.

⁵ Holmes, A., and Lawson, R. W.: *This Jour.* 5, B, 327-344 (1927). Kirsch, G., and Lane, A. C.: *Proc. Am. Acad. of Arts and Sci.* 66, 357-379, (1931).

Foye, W. S., and Lane, A. C.: *This Jour.* 28, 136-138 (1934).

Lane, A. C.: *Am. Min.* 19, 3-8, (1934).

whom the results are of greatest interest. No innovations are introduced, but some interesting observations result from carrying the simple, logical procedure sufficiently far. The final equations are simpler, more accurate, and of more general application than the equations previously used, and the relations between the existing equations and methods are shown most clearly by the present treatment. The time is considered appropriate for such a treatment because of improvement within the last year in our knowledge of the constants of disintegration of thorium, uranium, and actino-uranium.⁶

GENERAL EQUATIONS.

The number of atoms, N , of stable end products of radioactive disintegration formed in any interval of time greater than that required for equilibrium to be established* is given by:

$$N = n_1 (N_{UI_0} - N_{UI}) + n_2 (N_{Th_0} - N_{Th}) + n_3 (N_{AcU_0} - N_{AcU}) + n_4 \dots (3)$$

where n_1 = the number of atoms of end product resulting from the disintegration of one uranium atom after equilibrium is reached in the series, that is, the number of atoms of end-product formed after the chain of radioactive disintegrations has ended.

n_2 = similarly, the number of atoms arising from the disintegration of one thorium atom.

n_3 = similarly, the number arising from the disintegration of one actino-uranium atom.

n_4 = the number of atoms of end product due to other

⁶ Nier, A. O.: *Phys. Rev.* 53, 922 (1938).

—: *Phys. Rev.* 55, 150-163 (1939).

Kovarik, A. F., and Adams, N. I.: *Phys. Rev.* 54, 413-421 (1938).

* In all but some post-Pleistocene formations, equilibrium has been established in all of the series. The longest period is for the uranium series which requires several thousand years. After this time it is assumed that there is secular equilibrium between the successive products of transformation. While the amount of the parent element is decreasing with time, no sensible error is introduced for any of these elements (UI, AcU and Th) since they are transformed so slowly that the change in their concentration in the time required for secular equilibrium to be reached is negligible. This is because the rates of disintegration of the intermediate atoms are many thousands of times faster than the parent atoms which have half-lives of more than a billion years. At equilibrium, the ratio of the concentration of one member of a series to another is constant, that to the parent being small, e.g. $Ra/UI = 3.5 \times 10^{-7}$. In rocks, then, the number of atoms of daughter elements disintegrating in a given time is the same as the number formed from the parent, in other words, the rate of formation of one lead and n helium atoms is equal to the rate of disintegration of the parent atom of the series.

radioactive series; it is quite negligible compared to the other terms and need not be considered.

N_{UI_0} = the number of atoms of uranium I at the time t_0 .

This is taken as the time when accumulation of the end product commenced, so that $t_0 = 0$. In the case of helium, it is most probable that this represents the time of solidification, but with lead, it may represent some time before crystallization.

N_{Th_0} = similarly, the number of thorium atoms at time, t_0 .

N_{AcU_0} = similarly, the number of atoms of actino-uranium at time, t_0 .

N_{UI} = the number of atoms of uranium I at the present time, t .

N_{Th} = the number of atoms of thorium after time t .

N_{AcU} = the number of atoms of actino-uranium after time, t .

The law of radioactive disintegration may be written:

$$N_{UI_0} = N_{UI} e^{\lambda_{UI}t} \dots \dots \dots (4)$$

$$N_{Th_0} = N_{Th} e^{\lambda_{Th}t} \dots \dots \dots (4a)$$

$$N_{AcU_0} = N_{AcU} e^{\lambda_{AcU}t} \dots \dots \dots (4b)$$

where λ_{UI} = the disintegration constant of uranium

λ_{Th} = the disintegration constant of thorium

λ_{AcU} = the disintegration constant of actino-uranium

Equation 3, then becomes

$$N = n_1 N_{UI} [e^{\lambda_{UI}t} - 1] + n_2 N_{Th} (e^{\lambda_{Th}t} - 1) + n_3 N_{AcU} (e^{\lambda_{AcU}t} - 1) \dots (5)$$

Exact Solutions for t.

Equation 5 can be solved explicitly for t only in two cases; the first, when only the thorium series is present, since uranium is always associated with its isotope, actino-uranium, and the second, when a quantitative analysis of one or more of the individual lead isotopes is made.

The thorium series alone is present in radioactive minerals containing no uranium (neglecting n_4). Then,

$$e^{\lambda_{Th}t} = 1 + \frac{N}{n_2 N_{Th}} \dots \dots \dots (6)$$

and solving for t ,

$$t = \frac{2.303}{\lambda_{Th}} \log_{10} \left(1 + \frac{N}{n_2 N_{Th}} \right) \dots \dots \dots (7)$$

When the end product considered is lead (Pb^{208}), $n_2 = 1$, but for helium, $n_2 = 6$, so that the equations giving t in years in these two cases are:

$$t \text{ years} = 4.62 \times 10^{10} \log_{10} \left(1 + 1.116 \frac{\text{Pb}^{208}}{\text{Th}} \right) \dots \dots \dots (7a)$$

$$t \text{ years} = 4.62 \times 10^{10} \log_{10} \left(1 + 1.726 \times 10^{-3} \frac{\text{He}}{\text{Th}} \right) \dots \dots (7b)$$

where Pb^{208} is the weight of the 208 isotope in grams,* Th = the thorium content in grams, and He = the helium content in c.c. at standard temperature and pressure.

The second condition for using the explicit solution for t is applicable only to the lead method. Determinations of the amounts of the lead isotopes can be carried out by an analysis for the total lead combined with an isotopic analysis, preferably by the physical method. In the future it may be possible to determine by means of the mass spectrograph the amounts of the lead isotopes in the sample, in addition to their relative abundances. The difficulty with the application of these methods to geology is in limiting the amount of the particular lead isotope used in the age equation to that of radiogenic origin formed since crystallization.

When analyses of the individual lead isotopes of radiogenic origin are available, the following equations also may be used⁷:

$$t \text{ yrs.} = \frac{2.303}{\lambda_{\text{UI}}} \log_{10} \left(1 + \frac{N_{\text{Pb}^{206}}}{N_{\text{UI}}} \right) \dots \dots \dots (8)$$

$$= 1.515 \times 10^{10} \log_{10} \left(1 + \frac{1.15 \text{ Pb}^{206}}{\text{UI}} \right) \dots \dots \dots (8a)$$

$$t \text{ yrs.} = \frac{2.303}{\lambda_{\text{AcU}}} \log_{10} \left(1 + \frac{N_{\text{Pb}^{207}}}{N_{\text{AcU}}} \right) \dots \dots \dots (9)$$

$$= 2.37 \times 10^9 \log_{10} \left(1 + \frac{1.14 \text{ Pb}^{207}}{\text{AcU}} \right) \dots \dots \dots (9a)$$

$$= 2.37 \times 10^9 \log_{10} \left(1 + \frac{158 \text{ Pb}^{207}}{\text{UI}} \right) \dots \dots \dots (9b)$$

* Through the paper the symbols of the elements will refer to the weight in grams, except for helium which is expressed in c.c. The quantities of the elements in any single equation, of course, refer to the amounts from equivalent masses of sample, usually per gram.

⁷ Equation 8 may be used for pure uranium minerals, when the error due to the neglect of actino-uranium is small compared to the experimental errors.

When t is known from some relation other than Eq. 9b, a means is offered of checking the activity ratio r , defined as

$$r = \left(\frac{N_{\text{AcU}}}{N_{\text{UI}}} \right) \left(\frac{\lambda_{\text{AcU}}}{\lambda_{\text{UI}}} \right) \dots \dots \dots (10)$$

The first factor in Eq. 10 is known from isotopic analyses⁸

$$\frac{N_{\text{UI}}}{N_{\text{AcU}}} = 139 \pm 1.0 \dots \dots \dots (11)$$

Combining equations 9, 10, and 11 and introducing numerical constants gives:

$$r = \frac{1.09 \times 10^8}{t \text{ years}} \log_{10} \left(1 + \frac{158 \text{ Pb}^{207}}{\text{UI}} \right) \dots \dots \dots (12)$$

TABLE I.

Numerical Values of Constants
Disintegration Constants^a

$$\begin{aligned} \lambda_{\text{UI}} &= 4.82 \times 10^{-18} \text{ sec.}^{-1} = 1.52 \times 10^{-10} \text{ yr.}^{-1}; T = 4.56 \times 10^9 \text{ yr.} \\ \lambda_{\text{AcU}} &= 3.06 \times 10^{-17} \text{ sec.}^{-1} = 9.72 \times 10^{-10} \text{ yr.}^{-1}; T = 7.14 \times 10^8 \text{ yr.} \\ \lambda_{\text{Th}} &= 1.581 \times 10^{-18} \text{ sec.}^{-1} = 4.99 \times 10^{-11} \text{ yr.}^{-1}; T = 1.39 \times 10^{10} \text{ yr.} \\ \lambda_{\text{Ra}} &= 1.30 \times 10^{-11} \text{ sec.}^{-1} = 4.1 \times 10^{-4} \text{ yr.}^{-1}; T = 1690 \text{ yr.} \end{aligned}$$

Ratios

$$r = \frac{N_{\text{AcU}} \cdot \lambda_{\text{AcU}}}{N_{\text{UI}} \cdot \lambda_{\text{UI}}} = 0.046 \pm 0.002$$

$$\frac{N_{\text{UI}}}{N_{\text{AcU}}} = 139.0 \pm 1.0$$

$$\frac{N_{\text{UI}}}{N_{\text{Ra}}} = 2.70 \times 10^6 = 0.95 \frac{\text{UI}}{\text{Ra}}$$

$$\frac{N_{\text{Th}}}{N_{\text{UI}}} = 1.026 \frac{\text{Th}}{\text{UI}}$$

Atomic Weights

$$\begin{aligned} \text{UI} &= 238.1 \\ \text{AcU} &= 235 \\ \text{Th} &= 232.12 \\ \text{Ra} &= 225.97 \\ \text{Pb} &= 207.2 \\ \text{He} &= 4.002 \end{aligned}$$

$$\begin{aligned} \text{Molecular Volume He, } &22,420 \text{ cc.} \\ \text{Avogadro's Number, } &6.02 \times 10^{23} \end{aligned}$$

^a Nier, A. O.: Phys. Rev. 53, 922, 1938.

Solution by Expansion of the Exponentials.

An exponential may be evaluated to any desired degree of accuracy by means of the familiar series:

$$e^x = (1 + x) + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (13)$$

and the problem is merely to decide how many terms are required in the expansion of each of the exponentials in Eq. 5 to give the desired degree of accuracy. In Table II, values are given for x and e^x involving λ_{UI} , λ_{Th} and λ_{AcU} , and several values of t over the span of geological time, and for convenience, the accuracy of the first, second, and third approximations for several values of the exponent are given in Table III. The values in these tables can, of course, be obtained simply from the values of the constants and a table of exponentials by making the necessary substitutions; they are tabulated here merely for convenience in reference and immediate use by those interested in geological age calculations.

TABLE II.

(a) Values of Exponents and Exponentials in the age equation.

Age in million years	100	400	700	1000	1500	2000	2500	3000
$X = \lambda_{UI}t$	0.0152	0.0608	0.1064	0.152	0.228	0.304	0.380	0.456
e^x	1.015	1.063	1.106	1.164	1.254	1.355	1.462	1.578
$X = \lambda_{Th}t$	0.00499	0.01995	0.0349	0.0499	0.0748	0.0997	0.1245	0.1496
e^x	1.005	1.020	1.036	1.051	1.077	1.105	1.133	1.161
$X = \lambda_{AcU}t$	0.0972	0.389	0.680	0.972	1.458	1.943	2.43	2.91
e^x	1.102	1.475	1.974	2.643	4.29	6.97	11.36	18.36

(b) The variation of $\frac{N_{Th}}{N_{UI}}$ and $\frac{N_{UI}}{N_{AcU}}$ ratios in the past, assuming present values: 3.5 and 139 respectively.

$\frac{N_{Th}}{N_{UI}}$	3.47	3.35	3.28	3.16	3.00	2.85	2.71	2.58
$\frac{N_{UI}}{N_{AcU}}$	128	100	78	61	41	27	18	12

TABLE III.

Accuracy of expansion of e^x for several values of x .

exponent	exponential	1st approximation	2nd approximation	3rd approximation
x	e^x	$1 + x$	$1 + x + \frac{x^2}{2}$	$1 + x + \frac{x^2}{2} + \frac{x^3}{6}$
0.01	1.01005	1.01	1.01005	
0.04	1.0408	1.04	1.0408	
0.08	1.0833	1.08	1.0832	1.0833
0.10	1.1052	1.10	1.105	1.10517
0.25	1.2840	1.25	1.281	1.2836
0.50	1.6487	1.50	1.625	1.6458
1.0	2.7183	2.0	2.500	2.667
1.5	4.4817	2.5	3.625	4.188
2.0	7.3891	3.0	5.00	6.33
3.0	20.086	4.0	8.5	13.0

From these tables, it is evident that the expansion to $(1 + x)$ alone is sufficiently accurate when t is small, and the range of application can be extended when it is remembered that the coefficient before the exponential involving λ_{AcU} is small compared to the others. Furthermore the expansion to the second term in $\times$ will give better than one per cent accuracy for the exponentials involving λ_{UI} and λ_{Th} over the whole range of geologic time. The error in carrying out the expansion of $e^{\lambda_{AcU}t}$ only to the second term, does not exceed one per cent until t is greater than 5×10^8 years. The resulting error in the calculated age of a rock is considerably less, since the abundance of actino-uranium with respect to thorium and uranium is small, being only 0.002 at the present day, assuming a thorium-uranium ratio⁹ of 3. Actually, as shown later, the error does not reach one per cent until the age is one and a half billion years. The changes in the relative amounts of thorium, uranium and actino-uranium in the past are shown in Table IIb.

Age Equations for Young Rocks and Minerals

For rocks younger than a third of a billion years, a single expansion of the exponentials in Eq. 5 to the first term is satisfactory, giving,

$$N = n_1 N_{UI} \lambda_{UI} t + n_2 N_{Th} \lambda_{Th} t + n_3 N_{AcU} \lambda_{AcU} t \dots \dots \dots (14)$$

So that,

$$t = \frac{N}{n_1 \lambda_{UI} N_{UI} + n_2 \lambda_{Th} N_{Th} + n_3 \lambda_{AcU} N_{AcU}} \dots \dots \dots (15)$$

⁹ Keevil, N. B.: *Econ. Geol.* 33, 685-696, 1938.

Introducing numerical constants, the age in years is given by

$$t \text{ years} = \frac{7.23 \times 10^9 \text{ Pb}_R}{\text{UI} + 0.322 \text{ Th}} \dots\dots\dots (15a)$$

where $\text{Pb}_R = \text{Pb} - \text{Pb}_c$, Pb being the total lead content in grams and Pb_c the correction for common lead. The correction to the constant in the numerator of Eq. 15a, $\frac{207.2}{A_R}$, (due to taking the atomic weight as 207.2) may be neglected ordinarily; A_R is the atomic weight of the radiogenic lead. When helium is the end product considered,

$$t \text{ years} = \frac{8.40 \times 10^6 \text{ He}}{\text{UI} + 0.243 \text{ Th}} \dots\dots\dots (15b)$$

or when the radium¹⁰ is the member of the uranium series determined,

$$t \text{ years} = \frac{2.96 \text{ He}}{\text{Ra} + 8.54 \times 10^{-8} \text{ Th}} \dots\dots\dots (15c)$$

The physical meaning of the simple approximation made above is merely that the age is effectively computed from the ultimate reactions,



assuming that the concentrations of the reactants are constant. The errors involved in thus neglecting the decay of the parent atoms is ordinarily less than one per cent for rocks younger than 250 M.y., or for minerals containing no thorium, 150 M.y.

A glance at the denominator of Eq. 15 will reveal that it represents the total number of radioactive atoms disintegrating per unit of time, or where $n_1 = 8$, $n_2 = 6$ and $n_3 = 7$, and the disintegration constants are expressed in units of hr.^{-1} , it is the rate of production of helium atoms in the sample in atoms per hour, a_3 , at the present time.

When the helium is measured in cc., the age is given by,

$$t \text{ years} = \frac{3.065 \times 10^{15} \text{ He}}{a} \dots\dots\dots (17)$$

¹⁰ Usually determined by measuring the ionization due to the radon.

Where,

$$a = 3.65 \times 10^8 \text{ UI} + 8.86 \times 10^7 \text{ Th atoms per hr.} \dots (18)$$

$$a = 1.037 \times 10^{15} \text{ Ra} + 8.86 \times 10^7 \text{ Th atoms per hr.} \dots (18a)$$

This rate of production of helium from a rock sample has been defined as the "activity index," which is the total alpha particle emission per milligram of sample.^{11,12} When the radium is expressed in units of 10^{-12} grams per gram, and the thorium in units of 10^{-6} grams per gram of sample, the activity index, I, is given by,

$$I = 1.037 \text{ Ra} + 0.0886 \text{ Th} = \text{Alpha particles per mg. per hour.} \dots (19)$$

Age Equations for Older Rocks

For rocks and minerals more than a third of a billion years old, an equation obtained by the expansion of the exponentials to the second term can be applied.

Equation (5) then becomes,

$$N = n_1 N_{\text{UI}} \left(\lambda_{\text{UI}} t + \frac{\lambda_{\text{UI}}^2 t^2}{2} \right) + n_2 N_{\text{Th}} \left(\lambda_{\text{Th}} t + \frac{\lambda_{\text{Th}}^2 t^2}{2} \right) + n_3 N_{\text{AcU}} \left(\lambda_{\text{AcU}} t + \frac{\lambda_{\text{AcU}}^2 t^2}{2} \right) \dots (20)$$

and after rearranging,

$$\frac{t^2}{2} (n_1 N_{\text{UI}} \lambda_{\text{UI}}^2 + n_2 N_{\text{Th}} \lambda_{\text{Th}}^2 + n_3 N_{\text{AcU}} \lambda_{\text{AcU}}^2) + t (n_1 N_{\text{UI}} \lambda_{\text{UI}} + n_2 N_{\text{Th}} \lambda_{\text{Th}} + n_3 N_{\text{AcU}} \lambda_{\text{AcU}}) - N = 0 \dots (21)$$

$$\text{Letting } x = n_1 \lambda_{\text{UI}}^2 N_{\text{UI}} + n_2 \lambda_{\text{Th}}^2 N_{\text{Th}} + n_3 \lambda_{\text{AcU}}^2 N_{\text{AcU}} \dots (22)$$

$$\text{and } y = n_1 \lambda_{\text{UI}} N_{\text{UI}} + n_2 \lambda_{\text{Th}} N_{\text{Th}} + n_3 \lambda_{\text{AcU}} N_{\text{AcU}} \dots (23)$$

t is given by,

$$t = \frac{-y + [y^2 + 2xN]^{1/2}}{x} \dots (24)$$

Expressing N in terms of grams of Pb, or cc. of He, this becomes,

$$t = \frac{-y + [y^2 + 5.81 \times 10^{21} \text{ Pb. } x]^{1/2}}{x} \dots (24a)$$

$$t = \frac{-y + [y^2 + 5.37 \times 10^{19} \text{ He. } x]^{1/2}}{x} \dots (24b)$$

¹¹ Evans, R. D., Goodman, C., Keevil, N. B., Lane, A. C., and Urry, W. D.: in preparation.

¹² Keevil, N. B.: Trans. Roy. Soc. Canada, Vol. 32, Third Series, Sec. IV, pp. 123-150, 1938.

Where N is the number of lead atoms produced in time t ,

$$x_{\text{Pb}} = 2.990 \times 10^{-20} N_{\text{UI}} + 2.486 \times 10^{-21} N_{\text{Th}} \dots\dots (25)$$

$$= 75.6 \text{ UI} + 6.45 \text{ Th} \dots\dots\dots (25a)$$

and,

$$y_{\text{Pb}} = 1.59 \times 10^{-10} N_{\text{UI}} + 4.99 \times 10^{-11} N_{\text{Th}} \dots\dots (26)$$

$$= 4.02 \times 10^{11} \text{ UI} + 1.294 \times 10^{11} \text{ Th} \dots\dots\dots (26a)$$

and where N is the number of helium atoms produced in time t ,

$$x_{\text{He}} = 2.324 \times 10^{-19} N_{\text{UI}} + 1.492 \times 10^{-20} N_{\text{Th}} \dots\dots (27)$$

$$= 5.88 \times 10^2 \text{ UI} + 38.7 \text{ Th} \dots\dots\dots (27a)$$

$$= 1.670 \times 10^9 \text{ Ra} + 38.7 \text{ Th} \dots\dots\dots (27b)$$

and,

$$y_{\text{He}} = 1.265 \times 10^{-9} N_{\text{UI}} + 2.992 \times 10^{-10} N_{\text{Th}} \dots\dots (28)$$

$$= 3.198 \times 10^{12} \text{ UI} + 7.760 \times 10^{11} \text{ Th} \dots\dots\dots (28a)$$

$$= 9.092 \times 10^{18} \text{ Ra} + 7.760 \times 10^{11} \text{ Th} \dots\dots\dots (28b)$$

There are some advantages in changing the form of Equation 22, so as to have a more general application.

The constant, y , is again the present rate of production of helium, or (when expressed in the proper units) the activity index. The age obtained by the approximate equation (15) is given by N/y , x being an additional term which takes into account the decay of the parent elements.

As actino-uranium is an isotope of uranium, and the following constants are known,

$$k_1 = \frac{N_{\text{AcU}}}{N_{\text{UI}}} = 0.0072$$

$$k_2 = \frac{\lambda_{\text{AcU}}}{\lambda_{\text{UI}}} = 6.396$$

x and y may be simplified to,

$$x = (n_1 + n_3 k_1 k_2^2) \lambda_{\text{UI}}^2 N_{\text{UI}} + n_2 \lambda_{\text{Th}}^2 N_{\text{Th}} \dots\dots\dots (29)$$

$$y = (n_1 + n_3 k_1 k_2) \lambda_{\text{UI}} N_{\text{UI}} + n_2 \lambda_{\text{Th}} N_{\text{Th}} \dots\dots\dots (29a)$$

If we let,

$$\frac{N_{\text{Th}}}{N_{\text{UI}}} = k_3 = 1.026 \frac{\text{Th}}{\text{UI}} \dots\dots\dots (30)$$

then, by substituting $k_3 N_{UI}$ for N_{Th} in Eqs. 22 and 23, and introducing k_1 and k_2 ,

$$N_{UI} = y [(n_1 + n_3 k_1 k_2) \lambda_{UI} + n_2 k_3 \lambda_{Th}]^{-1} \dots\dots\dots (31)$$

$$N_{Th} = k_3 y [(n_1 + n_3 k_1 k_2) \lambda_{UI} + n_2 k_3 \lambda_{Th}]^{-1} \dots\dots\dots (31a)$$

Substituting these values in Eqs. 29 and 29a

$$x = \frac{y [(n_1 + n_3 k_1 k_2^2) \lambda_{UI}^2 + n_2 \lambda_{Th}^2 k_3]}{(n_1 + n_3 k_1 k_2) \lambda_{UI} + n_2 \lambda_{Th} k_3} = Ky \dots\dots\dots (32)$$

$$\text{where } K = \frac{(n_1 + n_3 k_1 k_2^2) \lambda_{UI}^2 + n_2 \lambda_{Th}^2 k_3}{(n_1 + n_3 k_1 k_2) \lambda_{UI} + n_2 \lambda_{Th} k_3} = f\left(\frac{Th}{UI}\right) \dots\dots (33)$$

Equation 24, may now be transformed into,

$$t = \frac{-y + (y^2 + 2NKy)^{1/2}}{Ky} \dots\dots\dots (34)$$

$$= \frac{\sqrt{1 + 2Kt_1} - 1}{K} \dots\dots\dots (34a)$$

Where $t_1 = \frac{N}{y}$, the approximate value of t calculated by one of the simple formulas, Eq. 15 to 15c or Eq. 17.

This may be further simplified by expanding the square root term by means of the binomial theorem as far as the quadratic term, then,

$$t = t_1 - \frac{1}{2} K t_1^2 \dots\dots\dots (34b)$$

a simpler equation to use, and one which has certain advantages at high ages. The use of equation 34b with a constant $K = 1.27 \times 10^{10}$ results in errors less than six per cent, even at two and a half billion years, over a Th/UI range from zero to ten. When $\frac{1}{2} K t_1^2$ is small compared to t_1 , $t = t_1 = \frac{N}{y}$.

After introducing numerical constants K becomes, for the lead method:

$$K_{Pb} = \frac{2.990 \times 10^{-10} + 2.486 \times 10^{-11} k_3}{1.531 + 0.4986 k_3} \dots\dots\dots (35)$$

$$= \frac{1.953 \times 10^{-10} + 1.624 \times 10^{-11} Th/UI}{1 + 0.334 Th/UI} \dots\dots\dots (35a)$$

and for the helium method:

$$K_{\text{He}} = \frac{2.324 \times 10^{-19} + 1.492 \times 10^{-20} k_s}{1.265 \times 10^{-9} + 2.992 \times 10^{-10} k_s} \dots\dots\dots (36)$$

$$= \frac{1.837 \times 10^{-10} + 1.210 \times 10^{-11} \text{Th/UI}}{1 + 0.2427 \text{Th/UI}} \dots\dots (36a)$$

In Fig. 1 are plotted values of K_{He} and K_{Pb} as a function of the thorium uranium ratio. For present purposes, this graph may be used directly to obtain K , for use in calculating the age of old rocks.

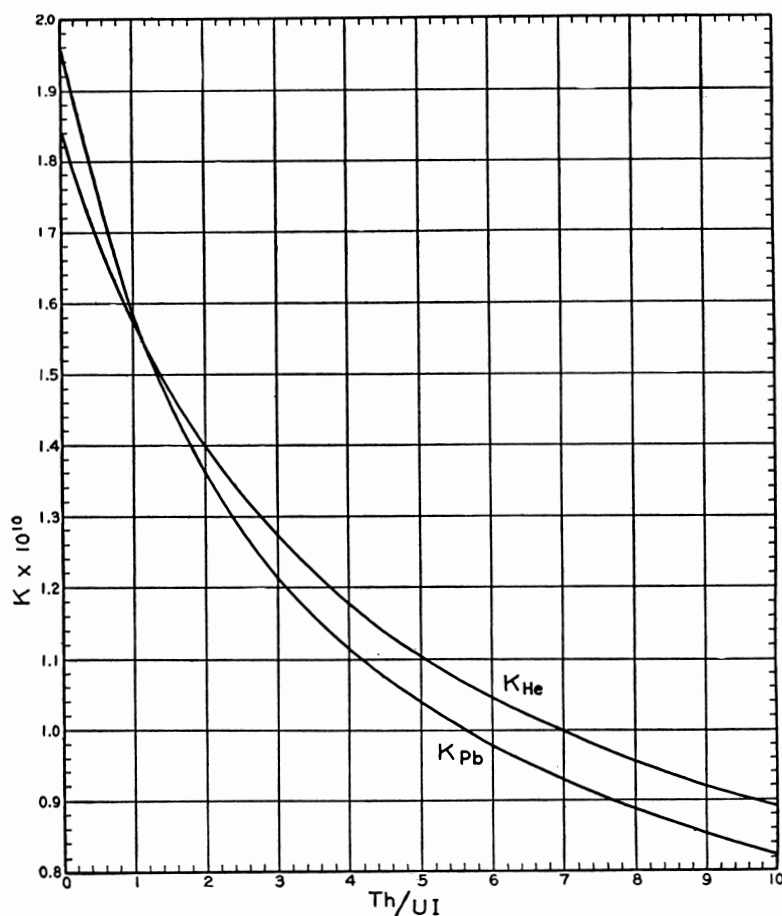


Fig. 1. Values of constant, K , used in the age equations, as a function of the thorium-uranium ratio, for both the lead (K_{Pb}) and the helium (K_{He}) methods.

Equations 34a and 34b are useful in that the age of any old mineral or rock can be easily computed from the approximate age, t_1 , once the thorium-uranium ratio is known. It can be used for either the lead or the helium methods.

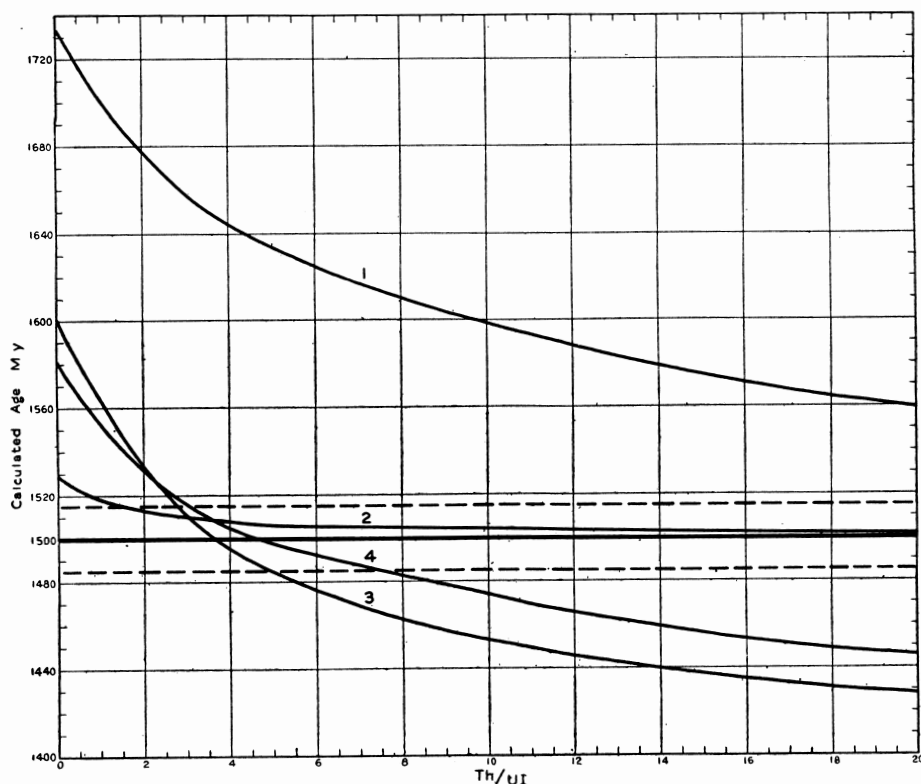


Fig. 2. Test of Different Equations at 1500 Million Years

1. Simple equation (15-15c, 17).
2. More exact equation (24, 34, 34a).
3. Old logarithmic formula (Eq. 2).
4. Ages calculated by Eq. 34a and the assumption of $\text{Th/UI} = 3.5$.

The dotted lines show the 1% error limit.

There is an increasing amount of evidence that wide fluctuations in the Th/UI ratio are not as common as earlier work indicated. The most recent determinations of radium and thorium for a number of rocks¹² of various types have shown that the average is about 3, and the results of isotopic analyses of lead minerals by the mass spectrograph,¹³ and indirect evi-

¹³ Nier, A. O.: J. Am. Chem. Soc., 60, 1571, 1938.

dence from lead ore-genesis indicates that the average value of the ratio⁹ is between 3 and 4.

Assuming a value of $\text{Th/UI} = 3.5$, calculations were made with Eq. 34a, at $t = 1500$ M.y., over a wide range of values of the activity index, and with true Th/UI values ranging from zero to one hundred. The results are plotted in Fig. 2, curve 4. It is important to note that the calculated age is within $3\frac{1}{2}$ per cent of the true value, over the range from $\text{Th/UI} = 1$ to $\text{Th/UI} = 20$, less than the present experimental errors of measurement. This is a valuable observation, for it means that the geologic age of any rock can be obtained within narrow limits, merely by measuring

- a) the volume of helium in the sample.
- b) the total alpha particle emission from the sample.¹⁴

Since past work indicates that there is a greater chance of the thorium-uranium ratio being below 1 than above 10, it is suggested that the assumed value for Th/UI be taken as 2.5 or 3.0, rather than 3.5, when Eq. 34a is used. Less error will result from the choice of a lower rather than a higher value, because at higher Th/UI ratios, the approximate age, t_1 , is closer to the true age, and also the error due to the actino-uranium series at very high ages is in the opposite direction.

When Eq. 34b is used the approximation made in obtaining it from Eq. 34a more than compensates for the error due to previously neglecting higher terms in the expansion of $e^{\lambda_{\text{Ac}} t}$ (Fig. 3) so that the assumption of $\text{Th/UI} = 3.5$ is satisfactory. When this is done, curve 4, Fig. 2, is lowered by about 30 M.y., so that the error varies from $+3\frac{1}{3}\%$ to $-3\frac{1}{3}\%$ as the true Th/UI ratio changes from 0 to 10.

Fig. 2 shows the behavior of various equations at an age of fifteen hundred million years when used to calculate ages from samples with different thorium-uranium ratios. This may be used to test the validity of the equations. At 1500 M.y. the simple equation is obviously not applicable, and the more exact equations will tend to give a little too high an age because of the limited number of terms to which the expansions are carried. Since Tables II and III show that the expansion to $(1 + x)$ is satisfactory for the thorium term in Eq. 5, increasing thorium-uranium ratios should cause the calculated ages to approach the true value uniformly.

This is indeed true with the simple equation (15), curve 1, and with the more exact equation (24, 34), curve 2, but it is

¹⁴ Goodman, C., and Evans, R. D.: Phys. Rev. 53, p. 916, 1938.

not the case with the old logarithmic formula,¹⁵ Eq. 2, curve 3. With no thorium, the error due to the neglect of the actino-uranium series in Eq. 2 is one hundred million years, while at high values of $\frac{\text{Th}}{\text{UI}}$, the inaccurate treatment of the thorium

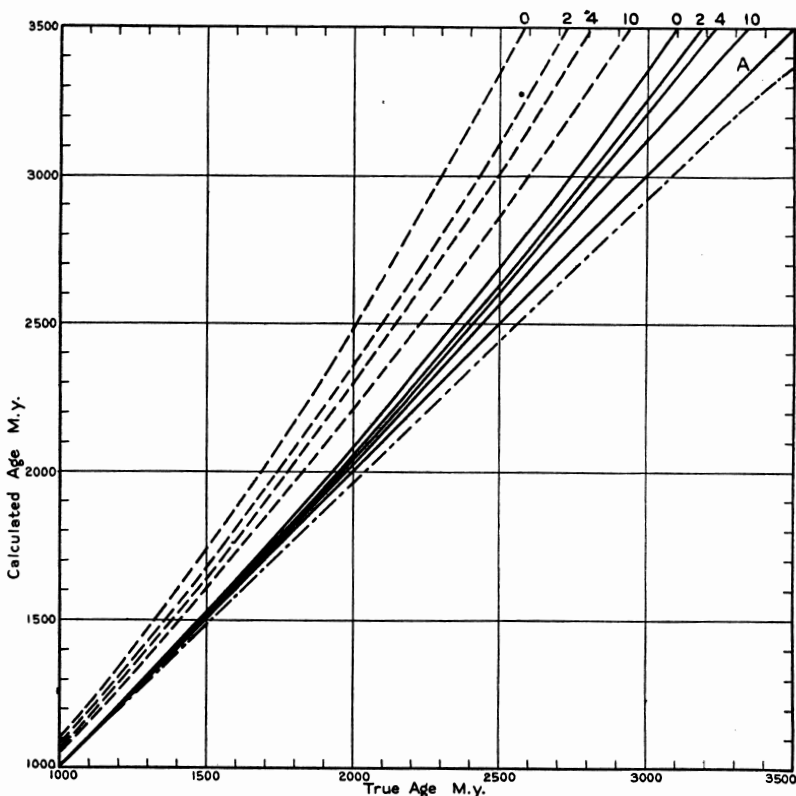


Fig. 3. Deviations of Calculated Ages from the True Values, A (Eq. 40).

Dashed curves: Eq. 15-15c, 17.

Solid curves: Eq. 24, 34, 34a.

Dot and dash curve: Eq. 34b.

The numbers at the top of the curves refer to the Th/UI ratio.

series causes as large an error in the opposite direction. It so happens that the two errors cancel at $\frac{\text{Th}}{\text{UI}} = 3.5$, in this instance. It is interesting to note that curve 4, showing the effect of assuming a constant value of 3.5 for purposes of approximation only, yields a result closer to the true age than the old logarithmic equation.

¹⁵ Using the new values of the disintegration constants.

Corrections at Ages Greater Than 1500 M.y.

The effect of neglecting higher terms in the expansion of the exponential involving λ_{AcU} begins to cause errors greater than one per cent after about one and a half billion years (the extent of the error depending upon Th/U). The value of the exponent increases so rapidly after this age, that the inclusion of one or two more terms is insufficient, and further expansion is not feasible because of the high powers of t that would be introduced.

The deviations of the calculated "ages" from the true age are illustrated in Fig. 3. The dashed lines give values of t_1 calculated by the simple formula (Eq. 15) for $\frac{N_{Th}}{N_{UI}}$ ratios of 0, 2, 4 and 10. The solid curves show the deviations at high ages of equations 24, 34 and 34a from the true age (Curve A) for several $\frac{Th}{UI}$ ratios.

Ages obtained with Eq. 34b (dot-and-dash curve) show smaller deviations at high ages than those calculated by means of Eq. 34a because of the approximate cancellation of the actino-uranium error mentioned above. The effect of variations in the Th/UI ratio on the size of the discrepancy is also much smaller, so that only one curve is shown which represents closely the age calculated for Th/UI ratios varying from 2 to 10.

The simplest way to correct the "ages" computed from Eq. 24, 34 or 34a, is by means of a curve or tables. Actually, such a correction is seldom necessary at the present time, because the experimental errors are seldom less than five per cent, and also because such old minerals and rocks appear to be rare. When necessary, corrections can be applied for high ages by interpolation from the curves in Fig. 4. For convenience, the broken line is included to show the point at which the error amounts to five per cent.

A General Substitution Method for Obtaining the Exact Age.

It is possible, by substitution methods similar to those described by Kovarik,⁴ to obtain the age as accurately as may be desired. Such a method, which is perfectly general, is described below.

The number of operations may be reduced to a minimum if a good guess of the age can be made. This is possible by computing the approximate age, t_1 using Eq. 15 or 17 or even Eq. 34, and improving the guess by referring to Fig. 3 and Fig. 4.

If the trial value of the age is t_0 , the true age, t , is given by

$$t = t_0 + t^1 \dots\dots\dots (37)$$

where t^1 is relatively small compared to t and t_0 . (It is preferable to have t^1 positive, because of the way in which the series converge.) If t^1 is small enough a simple expansion of the exponentials to the first term is sufficient.

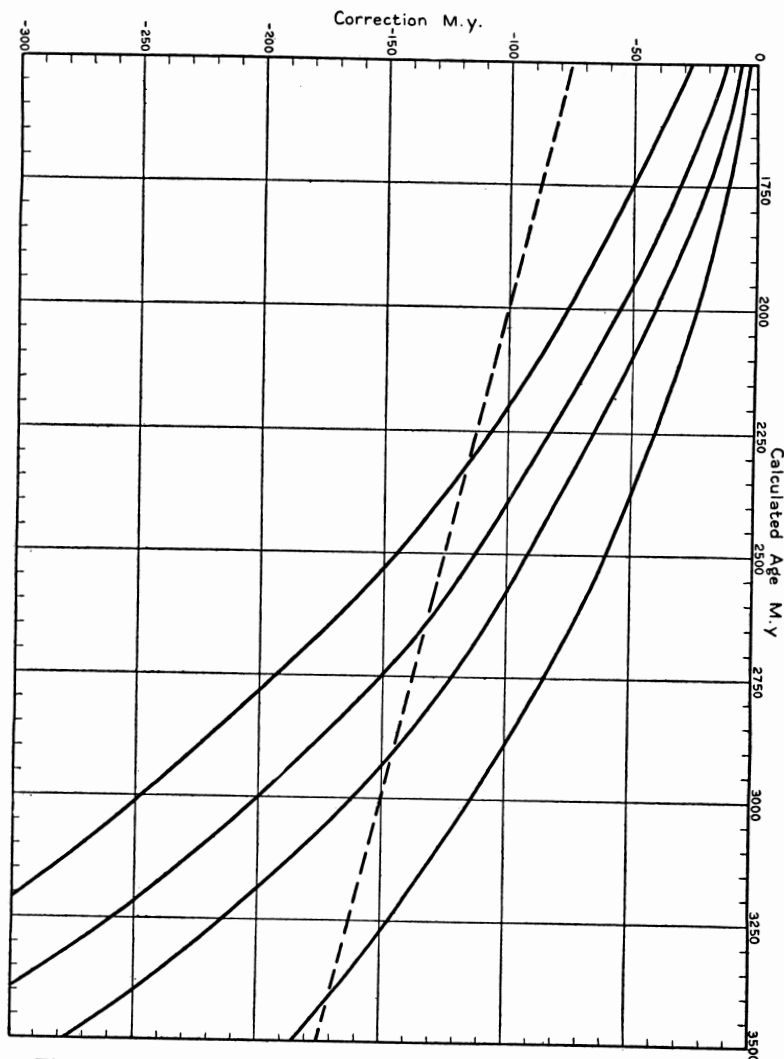


Fig. 4. Corrections to be applied to "ages" calculated by Eq. 24, 34 or 34a, with Th/UI ratios of 0, 2, 4 and 10, respectively, reading from the left to the right curve. The dashed line shows the 5% error limit.

Equation 5 may be rewritten to include t_0 and t^1 in place of t ; then,

$$N = n_1 N_{UI} (e^{\lambda_{UI} t_0} e^{\lambda_{UI} t^1} - 1) + n_2 N_{Th} (e^{\lambda_{Th} t_0} e^{\lambda_{Th} t^1} - 1) \\ + n_3 N_{AcU} (e^{\lambda_{AcU} t_0} e^{\lambda_{AcU} t^1} - 1) \dots \dots \dots (38)$$

which becomes, after a simple expansion,

$$N = n_1 N_{UI} e^{\lambda_{UI} t_0} (1 + \lambda_{UI} t^1) - n_1 N_{UI} + \\ n_2 N_{Th} e^{\lambda_{Th} t_0} (1 + \lambda_{Th} t^1) - n_2 N_{Th} + \\ n_3 N_{AcU} e^{\lambda_{AcU} t_0} (1 + \lambda_{AcU} t^1) - n_3 N_{AcU} \dots \dots \dots (39)$$

This may be rewritten

$$N + n_1 N_{UI} + n_2 N_{Th} + n_3 N_{AcU} = n_1 N_{UI} e^{\lambda_{UI} t_0} + n_2 N_{Th} e^{\lambda_{Th} t_0} \\ + n_3 N_{AcU} e^{\lambda_{AcU} t_0} + t^1 (n_1 N_{UI} \lambda_{UI} e^{\lambda_{UI} t_0} + n_2 N_{Th} \lambda_{Th} e^{\lambda_{Th} t_0} \\ + n_3 N_{AcU} \lambda_{AcU} e^{\lambda_{AcU} t_0}) \dots \dots \dots (39a)$$

After grouping and introducing values for n_1 , n_2 , n_3 and N for the two end products, t^1 is given by

$$t^1 = \left(\frac{Pb_R}{A} + 4.23 \times 10^{-3} UI + 4.31 \times 10^{-3} Th \right) - [4.20 \times 10^{-3} UI (\dots \\ \frac{(e^{0.152 t_0} + 0.0072 e^{0.972 t_0}) + 4.31 \times 10^{-3} Th e^{0.0499 t_0}}{6.383 \times 10^{-4} UI (e^{0.152 t_0} + 0.0460 e^{0.972 t_0}) + 2.15 \times 10^{-4} Th e^{0.0499 t_0}}] \dots \dots \dots (40)$$

where A is the atomic weight of the lead, t_0 and t^1 are in units of one billion years, and the disintegration constants in billion years $^{-1}$.

$$t^1 = 4.46 \times 10^{-5} He + 3.38 \times 10^{-2} UI + 2.586 \times 10^{-2} Th - \dots \\ \frac{[3.36 \times 10^{-2} UI (e^{0.152 t_0} + 0.0063 e^{0.972 t_0}) + 2.586 \times 10^{-2} Th e^{0.0499 t_0}]}{5.10 \times 10^{-3} UI (e^{0.152 t_0} + 0.0403 e^{0.972 t_0}) + 1.29 \times 10^{-3} Th e^{0.0499 t_0}} \dots \dots \dots (40a)$$

If t^1 is too large, or if greater accuracy is desired, a second substitution may be made, replacing t_0 with the new value of t , and so on. Ordinarily it should be possible to select a trial value of t , which is not more than one hundred million years from the true value. When this is so, only one substitution is necessary, and with a table of exponentials, the whole computation can be carried out within a few minutes.

This method is applicable also to the calculation of the age from the knowledge of the $\frac{Pb^{207}}{Pb^{206}}$ ratio obtained either from

pleochroic halos, or from isotopic analyses as Nier has done.⁶ If the ratio is called R , then from equations 4 and 11,

$$139R = \frac{e^{\lambda_{Ac}t} - 1}{e^{\lambda_{UI}t} - 1} \dots \dots \dots (41)$$

and applying Eq. 37.

$$139R = \frac{e^{\lambda_{Ac}t_0} \cdot e^{\lambda_{Ac}t^1} - 1}{e^{\lambda_{UI}t_0} \cdot e^{\lambda_{UI}t^1} - 1} \dots \dots \dots (42)$$

After expanding to the first term, and rearranging as before,

$$t^1 = \frac{139R e^{\lambda_{UI}t_0} - e^{\lambda_{Ac}t_0} - 139R + 1}{e^{\lambda_{Ac}t_0} \lambda_{Ac} - 139R \lambda_{UI} e^{\lambda_{UI}t_0}} \dots \dots \dots (43)$$

and introducing numerical constants,

$$t^1 = \frac{139R e^{0.152t_0} - e^{0.972t_0} - 139R + 1}{0.972 e^{0.972t_0} + 21.1R e^{0.152t_0}} \dots \dots \dots (43a)$$

where t_0 and t^1 are in units of billion years, and λ_{UI} and λ_{Ac} in billion years⁻¹.

Summary.

The age equation can be solved exactly by one of the logarithmic equations (7 to 9) when only the thorium series is present or when the amounts of the radiogenic lead isotopes are known. When all of the radioactive series are present, the true age can be obtained with any desired degree of accuracy by successive substitution methods (Eqs. 39-40, and 43).

It is satisfactory for present purposes to use one of the approximation formulas (Eqs. 15, 24 and 34) which may be summarized as follows:

$$t \text{ yrs.} = \frac{(1 + 2 K t_1)^{1/2} - 1}{K} \cong t_1 - 1/2 K t_1^2 \sim t_1$$

$$t_1 = \frac{2.96 \text{ He}}{\text{Ra} + 8.54 \times 10^{-8} \text{ Th}} = \frac{3.065 \times 10^{15} \text{ He}}{a} = \frac{7.23 \times 10^9 \text{ Pb}_R}{\text{UI} + 0.322 \text{ Th}}$$

where K is obtained from Fig. 1, or for many purposes may be assumed to be 1.25×10^{10} without introducing significant errors.

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