QUARTERLY REVIEWS

THE DETERMINATION OF GEOLOGICAL AGE BY MEANS OF RADIOACTIVITY

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Early Difficulties.—In the last century scientists were in considerable difficulty in attempting to reconcile different estimates of the age of mineral deposits and of the earth itself. This difficulty was aggravated by the conflict with a considerable body of religious opinion based on the erroneous conclusions of Archbishop Ussher. From certain interpretations of ancient documents he had concluded that the earth was about 6000 years old. The purely scientific discrepancies arose in two different fields. Thus Kelvin, from calculations which assumed that the earth had been a molten mass which was gradually cooling, reached a value of some 40×10^6 yr. This conclusion of the distinguished physicist was in sharp contrast with the rough estimates based on the geological examination of such processes as the rate of deposition of sediments or the accumulation of salt. These estimates exceeded Kelvin's figure by a factor of at least 10.

Near the close of the century the phenomenon of radioactivity was discovered and this obviously invalidated the work of Kelvin. He had assumed that the earth was cooling without the additional complication of an internal source of heat, but in the decay of the various naturally occurring radioactive substances we have, of course, precisely such an energy source. Although the magnitude of such internal sources is even now uncertain it was clear to Rutherford and others that it could be very large and so result in a considerable decrease in Kelvin's rate of cooling. More reliance was placed on the geological methods for a time, till in fact the radioactive elements themselves provided the most reliable methods so far discovered of determining the ages of mineral deposits or indeed that of the earth itself. The " age of the earth " is a term which must be defined in an adequate way and most physicists regard it as the period of time that has elapsed since some catastrophic event soon after which the earth had a form not very unlike that which we know today. This point will be explained in more detail below. Meanwhile we shall follow the more general practice of considering the age of the earth as the period during which it passed from a molten state to its present-day form.

Radioactivity as a Timekeeper.—In view of the inapplicability of Kelvin's method it was indeed fortunate that we had in the various radioactive substances found on the surface of the earth a system of timekeepers of great stability. The principle of the method is inherent in the statement of the law of radioactive decay as put forward by Rutherford and Soddy in 1902, *viz.*, " the probability of an atom breaking up is independent of its age ". It had been shown very early in the study of the decay of radioactive materials that the rate of decay was completely unaffected by the most violent physical and chemical changes. Extremes of pressure and temperature or states of chemical combination were found to have no detectable influence. In actual fact, although the point is entirely academic, so far at least as the present discussion is concerned, very recent studies of a few carefully selected cases have shown that changes in the decay rate can be produced by essentially chemical means.[1]

The decay law stated above can be expressed as follows. If a number N_0 of atoms of a radioelement decreases to a number N in time t, then

$$N = N_0 e^{-\lambda t} \qquad (1)$$

Here λ is a constant for any particular substance, being the probability that any one atom of the substance decays in one second. It is zero for a completely stable element. This decay constant λ is related to the half-life T of the element by the relation

$$\lambda = 0{\cdot}69/T \qquad (2)$$

Equations (1) and (2) yield a useful form of the decay law, namely,

$$t = 1{\cdot}45 T \ln(N_0/N) \qquad (3)$$

It is more pertinent to consider the number of parent and daughter atoms present in a certain mass of a mineral. The number of stable daughter atoms D present after time t is $N_0 - N$ and, if we denote by P the number N of parent atoms remaining after time t, then since $N_0 = D + N = D + P$ we have, for equation 3,

$$t = 1{\cdot}45 T \ln[(D + P)/P] \qquad (4)$$

We can now see very clearly the method of age estimation. If we find T for a certain radioactive substance (a typical method is described later) and if a given mass of material contains P parent atoms together with D daughter atoms resulting from the transmutations of the parent during the time t, then the time t corresponds to the interval during which the material has remained undisturbed. In practice, chemical analysis of a mass M of a mineral may yield, say, a mass m_1 of parent and a mass m_2 of daughter. Then, conversion of m_1 and m_2 into numbers of atoms gives P and D. With the known T value for the radioactive change $P \longrightarrow D$ we have from equation (4) the age t of the specimen. Many variations of this process are adopted but all have a common principle. The useful elements are all of long half-life T, since otherwise the mass of the parent is too small to be measured. On the other hand, T must not be so large that the parent element is effectively stable. This situation frequently results in two major difficulties: (*a*) the experimental evaluation of T for weakly radioactive

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[1] Bainbridge, Goldhaber, and Wilson, *Phys. Review*, 1951, **84**, 1260.

elements is somewhat uncertain, and (*b*) the mass of daughter element is usually small and this complicates the task of determining D.

Some elements which have been or could be employed are listed, together with the corresponding T values,[2] in Table 1. We do not include in this table intermediate elements such as radium, a member of the uranium series and constantly formed by the decay of parent elements. Its own relatively short life does not therefore result in its complete disappearance.

TABLE 1. *Half-lives of natural sources*

Element . .	^{238}U	^{235}U	^{232}Th	^{87}Rb	^{40}K
T (yr.) . .	$4{\cdot}4 \times 10^{9}$	7×10^{8}	$1{\cdot}8 \times 10^{10}$	$6{\cdot}1 \times 10^{10}$	$1{\cdot}3 \times 10^{9}$
Element		^{14}C	^{138}La	^{176}Lu	^{187}Re
T (yr.)		$5{\cdot}6 \times 10^{3}$	$\sim 10^{11}$	$\sim 3 \times 10^{10}$	4×10^{12}

Again some elements may be formed in certain circumstances at an effectively constant rate, giving an equilibrium amount, and then allowed to decay. This situation arises in the case of radiocarbon ^{14}C and we shall see that its relatively short life does not prevent its application to age studies.

The Methods of Measurement.—The more important methods are as follows: (1) Determination of the uranium–lead content of uranium-bearing minerals; likewise for thorium minerals. (2) Measurement of the helium content of minerals (the helium formed from α-particles emitted in radioactive decay). (3) Photometric examination of pleochroic haloes due to α-rays. (4) The rubidium–strontium content of minerals. (5) The potassium–calcium and/or the potassium–argon content of minerals. (6) The radiocarbon content of substances.

An excellent survey of methods 1, 2, and 3 has been given by Hevesy and Paneth.[3] Recently, methods (4), (5), and (6) have been studied in detail and results of considerable accuracy achieved. We shall therefore review somewhat briefly the first group and consider more closely the interesting developments in the second group, occurring largely during the last six years.

The uranium–lead content. Uranium consists mainly of two isotopes ^{238}U and ^{235}U, of percentage abundances 99·3 : 0·7. Both of these isotopes give rise to a series of radioelements and the successive disintegrations of these elements result in the formation of the stable isotopes of lead, ^{206}Pb (Ra-G) and ^{207}Pb (actinium-lead). The series may be expressed in abbreviated form, neglecting the emission of β-rays,

$$^{238}U \longrightarrow 8\,^{4}He + {}^{206}Pb \quad . \quad . \quad . \quad . \qquad (5)$$

$$^{235}U \longrightarrow 7\,^{4}He + {}^{207}Pb \quad . \quad . \quad . \quad . \qquad (6)$$

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[2] "Nuclear Data", Nat. Bur. Stand., circular no. 499.

[3] Hevesy and Paneth, "Radioactivity", Oxford Univ. Press, 1938.

Hence, in long periods of time measurable amounts of helium and lead are formed by the decay of uranium. If we find in a mass of some suitable mineral a mass W_U of uranium (neglecting isotopic abundances for the moment) and a mass W_L of lead, then from equation (4) we have

$$t = 1{\cdot}45T\ln[(W_U + W_L 238/(206/W_U] \tag{7}$$

for the process (5) above. Here the ratio 238/206 effectively converts numbers of atoms into masses. Usually W_L is very small compared with W_U. For example, in 10^8 years a mass of 1 g. of ^{238}U yields less than 0·014 g. of ^{206}Pb. Hence, expanding the log term and taking the first approximation, we have

$$t = 1{\cdot}45T(238W_L)/(206W_U) \tag{8}$$

or, more briefly,

$$\text{Age} = 7{\cdot}12 \times 10^9(W_L/W_U)\ \text{yr.} \tag{9}$$

This equation makes clear the simplicity in principle of the method, but in practice very considerable caution must be exercised. Frequently thorium is present in the minerals and this gives rise to lead (^{208}Pb) in its decay and again " ordinary " lead as distinct from radiogenic lead (^{206}Pb in the case of ^{238}U) may invalidate the findings. It is generally essential that a straightforward check on the atomic weight of lead obtained in the analysis should be made. This is a safeguard against both of these hazards.

Thorium (^{232}Th) gives rise to ^{208}Pb and the thorium–lead ratio can be used. The results are generally less reliable and of course both methods are limited in scope since ordinary rocks, containing very minute amounts of uranium or thorium, cannot be analysed satisfactorily.

Perhaps the principal source of error in this type of analysis (and in most others) is to be traced to the various leaching-out processes that may occur in the long periods of time involved. Here the mineral specimen is not allowed to remain undisturbed and its composition is changed by the removal of some fraction of certain elements and by the addition of others. There is a variation of the uranium method which reduces markedly the errors introduced in this manner. Such processes as are in question affect the two isotopes of uranium and lead almost equally and hence the ratio of the radiogenic lead isotopes is much less subject to error. Then we have [4]

$$\frac{N(^{207}\text{Pb})}{N(^{206}\text{Pb})} = \frac{N(^{235}\text{U})\{\exp \lambda(^{235}\text{U})t - 1\}}{N(^{238}\text{U})\{\exp \lambda(^{238}\text{U})t - 1\}} \tag{10}$$

where $N(^{207}Pb)$, etc., refer to the numbers of atoms of the isotopes in the sample, $\lambda(^{235}U)$, etc., are the decay constants, and t is the time.

As an example of these techniques we refer to the work of Ahrens [5] who analysed both uraninite and monazite from S.E. Manitoba. His results are in the nature of a good check on the methods since the age of the specimens has been found in addition by the rubidium–strontium ratio. In Table 2 the superiority of the lead ratio technique is apparent (see Nier [6]) and Ahrens himself regards the $^{207}Pb/^{206}Pb$ ratio as the most trustworthy.

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[4] Collins, Freeman, and Wilson, *Phys. Review*, 1951, **82**, 966.

[5] *Nature*, 1947, **160**, 874.

[6] *Phys. Review*, 1941, **60**, 112.

TABLE 2. *Ages (in 10^9 yr.) obtained from various ratios*

Ratio	$^{206}Pb/^{238}U$	$^{208}Pb/^{232}Th$	$^{207}Pb/^{206}Pb$
Uraninite	1·57	1·25	2·20
Monazite	3·18	1·83	2·57

Helium content. The ratio of helium to uranium can obviously be employed as alternative to the lead–uranium ratio. In old mineral deposits ($t > 10^5$ yr., say) the uranium is in equilibrium with the radium which has a relatively short half-life ($T = 1620$ yr.) and the helium–radium ratio is usually determined. If the helium content is expressed in c.c. and the radium in g., then it can be shown that

$$\text{Age (yr.)} = 1{\cdot}47 \times 10^{10} \ln(1 + 4{\cdot}42 \times 10^{-10}\text{He/Ra}) \quad . \quad (11)$$

If there is thorium contamination, we may apply the approximate formula

$$\text{Age (yr.)} = \text{He}/(0{\cdot}35\text{Ra} + 3{\cdot}0 \times 10^{-8}\text{Th}) \quad . \quad . \quad (12)$$

There is one major source of uncertainty in the helium analysis. It can be shown that in periods of $\sim 10^8$ yr., each c.c. of a nearly pure uranium mineral may contain the equivalent of about 100 c.c. of helium (measured at N.T.P.). Thus pressures $\sim 10^2$ atmospheres or more can be created internally and a very real possibility of escape of the radiogenic gas arises. Extreme caution is necessary in choosing samples for analysis and when possible fine-grained smooth specimens should be used. The method is properly applied to all types of rock (where of course the pressure hazard is nearly always negligible) and it is not necessary to restrict its application to uranium minerals as such. The extreme sensitivity of the beautiful techniques developed for the measurement of very small quantities of helium widens greatly the field of research and permits age estimation of minerals which contain what are really impurity traces of the radioactive substances such as uranium. Paneth and his co-workers [7] have applied the method with skill and success to the study of meteorites. More will be said below on this subject.

Pleochroic haloes. Spherically symmetrical colorations are found in materials such as mica, quartz, and glass. Rutherford showed that similar haloes can be produced artificially by the inclusion of minute specks of radioactive substances within the volume of the materials. Indeed the technique is employed for calibration of samples of the mineral. A known weight of a suitable radioactive substance which emits α-rays is used and the colour produced in a definite period of time is measured. Photometric analysis is generally useful and uranium in equilibrium with all its daughter elements is the obvious calibrator. From the analysis the number of α-rays involved is deduced and hence D of equation (4) is known. The value of P, the number of parent atoms remaining in the nucleus of the halo, is required and this is the main task because of the minuteness of the mass of material.

[7] *Nature*, 1942, **149**, 235.

Usually, however, the weight can be found approximately and when D and P are found equation (4) yields t.

The ring-like structure of the halo is characteristic of the effects produced by the various members of a family which includes several α-emitting elements. The elements each release α-rays of a specific energy and range within the mineral. The photochemical action of α-particles is strongest towards the end of the range and so regions of maximum density result, with zones of greater clearness between. The radii of the rings correspond fairly closely with the ranges of the various α-rays and microphotometry of a slice of material yields a pattern with a set of peaks. Fig. 1 illustrates schematically the ring structure of a halo and a typical photomicrograph.

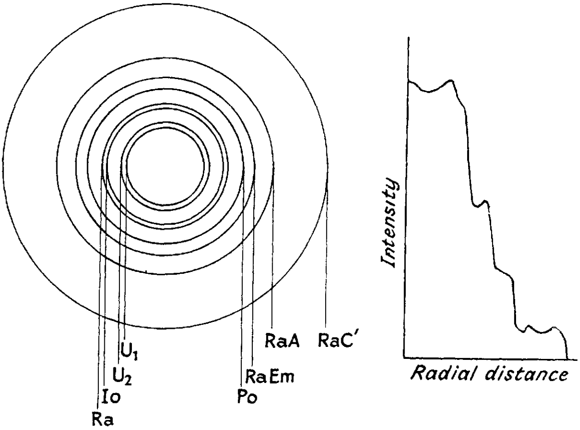

FIG. 1

Schematic representation of a halo and the form of a typical photometric analysis. The circles correspond approximately with the ranges of the α-particles from the various radioelements indicated.

Once again a comparative method gives an increased accuracy in the estimation. Since ^{235}U decays more rapidly than ^{238}U the ratio of the blackening due to α-rays from ^{235}U to that due to α-rays from ^{238}U increases with increasing time interval. The value of the ratio can be found fairly precisely and the age so estimated.

Before passing to consider more recent developments it is interesting to note the extraordinary sensitivity of the technique. As little as 10^{-19} g. of radium suffices to produce measurable blackening in the long times involved. This remarkable result is due of course to the integrating action of the mineral.

The rubidium–strontium method. The natural activity of rubidium was discovered by J. J. Thomson [8] in 1905 but only recently has the mode of decay been clarified. The β-decay of the rubidium isotope ^{87}Rb yields radiogenic strontium :

$$^{87}Rb \longrightarrow {}^{87}Sr + \beta \qquad . \quad . \quad . \quad . \quad (13)$$

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[8] *Phil. Mag.*, 1905, **10**, 584.

and the process gives a thoroughly practical means of estimating the ages of deposits, although the types of deposit are clearly severely restricted. In regard to the elucidation of the decay itself the first main step [9] consisted in establishing that the unstable isotope of rubidium was ^{87}Rb. There was some uncertainty in the value of T for ^{87}Rb in 1948 and Haxel and Houtermans [10] regarded 6×10^{10} yr. as the best average of the more reliable results. Recent studies by Curran *et al.*[11] at Glasgow, involving a new method, give $T = (6{\cdot}15 \pm 0{\cdot}30) \times 10^{10}$ yr. The work was carried out with a shielded proportional counter and in addition to giving the T value showed the decay to be simple and established the form of the energy spectrum of the β-rays. This made the position of the Rb–Sr method of age determination secure. The apparatus employed is readily applied to various studies of weak radioactivities and will be described briefly.

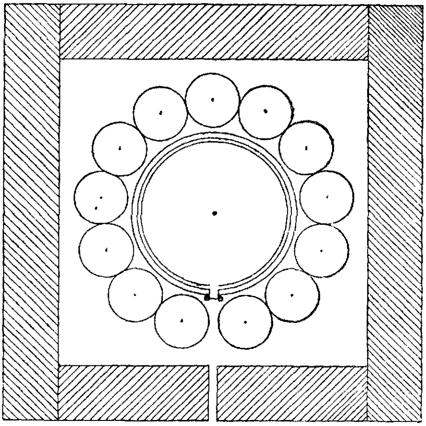

FIG. 2

Experimental apparatus for studying ^{87}Rb. *A large proportional counter is shielded from cosmic rays by a ring of Geiger counters, connected in anti-coincidence with it. Thick lead shielding surrounds the assembly. An aperture permits the passage of calibrating radiation. The source is mounted on the inner wall of the proportional tube.*

In Fig. 2 the cross-section of a large proportional counter (diameter 14 cm., useful length 25 cm.) is shown. This main counter is surrounded with a shielding system of long counters of the Geiger type and these act in anti-coincidence with the proportional tube so that all pulses due to cosmic rays are eliminated.[12] A thick shield of lead surrounds the assembly of counters thereby reducing considerably the effect of external γ-ray sources (laboratory contamination, etc.). When these shielding techniques are

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[9] Hemmendinger, and Smythe, *Phys. Review*, 1937, **51,** 1052 ; Hahn, Strassman, and Walling, *Naturwiss.*, 1937, **25,** 189 ; Mattauch, *ibid.*, p. 189 ; *Physikal. Z.*, 1937, **38,** 951.

[10] *Z. Physik*, 1948, **124,** 705 ; *Phys. Review*, 1948, **74,** 1886.

[11] Curran, Dixon, and Wilson, *ibid.*, 1951, **84,** 151.

[12] Korff, " Electron and Nuclear Counters ", Van Nostrand, 1946, and Curran and Craggs, " Counting Tubes ", Butterworths, 1949, provide general information on counters.

vigorously prosecuted the counting rate (in the absence of a source) of the central counter can be greatly reduced. Serious efforts along such lines have been expended in dealing with ^{14}C estimations, considered below, and large counters of 2·5″ diameter and 8″ working length have been found to count at a rate as low as 2 counts per minute. Such a successful reduction can be a factor of major importance in the success of age estimation.

When the apparatus is used to examine a natural source such as rubidium the inner wall of the proportional tube is coated with a thin layer of the element or suitable compound. The available area of wall is $\sim 10^3$ cm.^{2} and even very weakly active sources can be spread thinly so that the uncertainties due to self-absorption of the β-rays (or other radiations) are reduced to a minimum or rendered negligible. The shape of the energy spectrum of the radiation can in fact be explored and any error due to self-absorption fairly accurately calculated and removed. This was done in the Glasgow experiments. Before these experiments there was considerable uncertainty regarding the nature of the rays and their energies. The work of Ollano [13] had suggested that conversion electrons as well as primary β-particles were emitted and Haxel *et al.* thought that the conversion electrons might be the most energetic of the particle radiations. The Glasgow experiments proved that only primary β-rays were emitted and that their energy limit was close to 280 Kev. The T value remained almost unchanged since Haxel *et al.* cleverly avoided the difficulty in understanding the decay process.

As an example of the magnitude of the effects observed a total mass of 0·10075 g. of RbCl spread as a layer of thickness 0·12 mg./cm.^{2} gave an increase in the counting rate of 1477 per minute. Corrected for self-absorption and reflection this corresponded to $T = 6{\cdot}15 \times 10^{10}$ yr. for ^{87}Rb.

With T known the age analysis amounts to a chemical analysis. The rubidium method has been applied to some of the mineral samples from the oldest deposit yet discovered—in S.E. Manitoba. It appears to have about the same age as a mineral deposit in Karelia. Disagreement in results obtained by uranium–lead and rubidium–strontium methods for the Manitoba minerals had given rise to speculation concerning the possibility of modification of the radioactive decay processes during the early history of the earth but the two techniques are now in fairly close agreement. For instance, the work of Strassman and Walling [14] showed that 1012 g. of lepidolite from the area contained 7·16 g. of ^{87}Rb (the percentage abundance of ^{87}Rb in natural rubidium is 27·2) and 0·156 g. of presumably radiogenic strontium, ^{87}Sr. Then since

$$\mathrm{d}N = (0{\cdot}69/T)N\mathrm{d}t,$$

$$T\mathrm{d}W = 0{\cdot}69W\mathrm{d}t$$

weights being substituted for numbers of atoms. Thus

$$0{\cdot}156 \times 6{\cdot}15 \times 10^{10} = 0{\cdot}69 \times 7{\cdot}16\mathrm{d}t$$

or

$$\mathrm{d}t = 2 \times 10^9 \text{ yr.}$$

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[13] *Nuovo Cimento*, 1941, **18**, 11.

[14] *Ber.*, 1938, **71**, 1.

This result for the age d*t* of the mineral is fairly close to those found by the uranium method as given in Table 2 above and reassuring evidence of the reliability of the procedures. Indeed, a third independent method of spectrochemical analysis introduced by Ahrens and applied to the same minerals gave ages of 2·20, 2·30, 2·10, and 2·35 (accuracy ±15%), all $\times 10^9$ yr., all consistent with the other techniques.

The rubidium technique applies to a relatively limited variety of minerals and, of the methods so far discussed, that involving helium is widely applicable. Recent studies of the radioactivity of potassium (^{40}K) suggest that a second procedure capable of wide exploitation may be available.

Potassium–calcium and potassium–argon ratios. The radioactivity of potassium has been examined by many workers on account of its major geophysical interest. The difficulties inherent in these studies left much uncertainty but recently there has been nearly complete agreement among the most reliable observations. There is good reason to consider the decay scheme shown in Fig. 3 as well established. The isotope ^{40}K disintegrates in two ways, by *K*-electron capture in some 12% of the disintegrations and by β-ray emission (88%), yielding ^{40}A and ^{40}Ca respectively. The *K*-capture process leads to an excited state of ^{40}A, so that the *K*-radiation (the *X*-rays are those of ^{40}A) is followed by the emission of γ-rays of energy 1·46Mev. The *X*-rays and γ-rays can both be used to detect the branching activity. The two decay processes give us two partial decay constants and corresponding half-lives T_K and T_β, say, where the overall half-life T_{tot} is given by $1/T_{\text{tot}} = 1/T_\beta + 1/T_K$. These T values are now fairly accurately known, as seen from a selection of results[15] in Table 3. The values in parentheses have been calculated by the Reviewer from the data supplied.

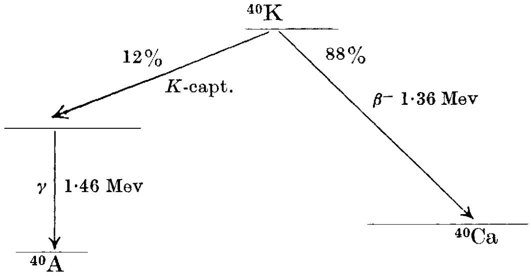

FIG. 3

TABLE 3. *Half-period of* ^{40}K *(in* 10^9 *yr.)*

Author	T_β	T_K	T_{tot}
Graf	1·50 ± 0·07	—	—
Inghram *et al.*	(1·50 ± 0·09)	(11·0)	1·33 ± 0·08
Sawyer and Wiedenbeck . .	(1·44 ± 0·06)	(10·6)	1·27 ± 0·05

[15] Graf, *Arkiv Fysik*, 1951, **3,** 171 ; Inghram, Brown, Patterson, and Hess, *Phys. Review*, 1950, **80,** 916 ; Sawyer and Wiedenbeck, *ibid.*, 1950, **79,** 490.

The decay processes :

$$^{40}\mathrm{K} + e_K \rightarrow {}^{40}\mathrm{A} \quad . \quad . \quad . \quad . \quad (14)$$

$$^{40}\mathrm{K} \rightarrow {}^{40}\mathrm{Ca} + \beta \quad . \quad . \quad . \quad . \quad (15)$$

show us that both ^{40}Ca and ^{40}A accumulate in potassium-bearing minerals. Unfortunately the content is not high since ^{40}K has a very low abundance in potassium ($0{\cdot}0119 \pm 0{\cdot}0001\%$). None the less the sensitivity of the available methods is high and Aldrich and Nier [16] suggested application of potassium to the estimation of geological time. They examined the amplitudes of the peaks due to isotopes in the region of mass 40 with a mass spectrometer. As usual, comparative measurements were made and the ratio of the masses of the isotopes of argon, for example ^{40}A/^{36}A, was measured both for atmospheric argon, as standard, and for the gas released from a mineral specimen. The general form of their mass spectrograms is illustrated in Fig. 4. Similarly analysis of the calcium content can be made and compared with standard material. There are considerable advantages in using argon since as a gas it is easily handled in the spectrometer. In Fig. 4 it is very obvious that most of the ^{40}A peak in the case of the mineral is radiogenic since its intensity, relative to that of ^{36}A, exceeds that of atmospheric argon by a factor of more than three. This basic work was performed with four different potassium minerals, orthoclase, mycrocline, sylvite, and langbeinite, each being taken in definite amounts and heated in a vacuum furnace, with removal of gaseous impurities by

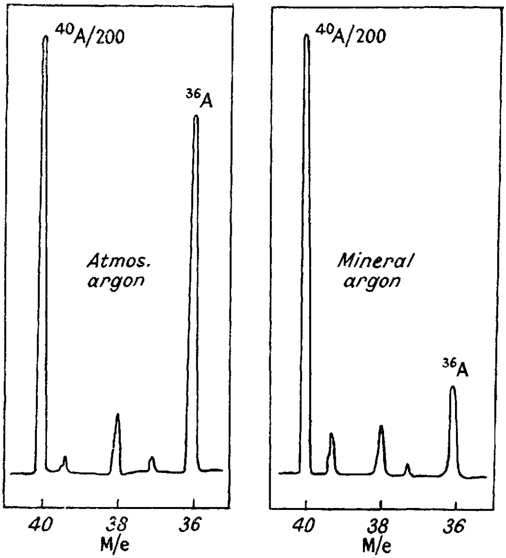

FIG. 4

Form of the mass spectrograms for atmospheric argon and argon released from a potassium mineral.

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[16] *Phys. Review*, 1948, **74**, 876.

suitable means. The ages of the minerals in this case were known and the results were used really to determine the branching ratio of the disintegration of potassium, *i.e.*, the probability of K-capture to the sum of the probabilities of K-capture and β-particle emission. A value not too different from the presently accepted one of 0·127 was derived and it is obvious that with the ratio now established the experimental method can be turned round and used to estimate the age of the minerals.

If we can assume then that the escape of radiogenic argon is not a serious source of error in the use of potassium minerals, there is much in favour of the method. Among the favourable conditions we have (*a*) widespread distribution of potassium deposits, (*b*) relatively straightforward chemistry, and (*c*) ready application of mass spectrometry to the radiogenic gas. It is possible that the method will prove superior to all others in its general ease and scope.

Mass spectrometer isotopic dilution method. A fresh variation of the method of mass spectrometry which offers very interesting possibilities has been employed recently in pile physics. It was first used in measuring the amounts of the products of artificially radioactive elements created in the pile. The potential power of the technique is well stated by Reynolds :[17] " the amount of a decay product . . . even though present only in parts per million can be measured with precision by the use of the mass spectrometer and an isotope dilution technique." Clearly since this is precisely the problem in age estimation the method applies directly and indeed the observations of Inghram and his co-workers [15] on ^{40}K are of great interest.

The aim of the experiments is to measure the mass of an isotope present in quantities which would usually be regarded as sufficient for detection but not for weighing. First, enrichment of the element is carried out with the help of an electromagnetic mass separator (Calutron). The enrichment is in some isotope of the element other than that whose mass is required. For example if we wish to know the mass of ^{40}A in a given sample of a mineral we can enrich atmospheric argon in the isotope ^{36}A. The supply of tracer argon highly enriched in ^{36}A is then used in conjunction with the argon gas released from the mineral. The mass spectrometer is applied to the analysis of the tracer gas and to a defined mixture of tracer and mineral gas. In Table 4 the remarkable results achieved by this two-fold application of spectrometry are shown. They refer to a typical specimen of sylvite (KCl) of known age, 10^8 yr., obtained from the Stassfurt sylvite deposits. We can readily interpret the figures given in this Table. We have inserted data for atmospheric argon for ready comparison. Ratios are determined, namely, ^{40}A/^{36}A and ^{38}A/^{36}A. The second ratio serves an important secondary purpose. It is essential in accurate work to estimate the amount of non-radiogenic argon contamination and the extremely good agreement in the ^{38}A/^{36}A ratios for tracer alone and tracer + sylvite gas assures us that the ^{38}A detected is introduced almost entirely with the tracer gas since otherwise the ratio would tend to move towards 0·195. In other

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[17] Hayden, Reynolds, and Inghram, *Phys. Review*, 1949, **75**, 1500 ; Reynolds, *ibid.*, 1950, **79**, 789.

words, the sylvite gas proves to be free from contamination by atmospheric argon.

TABLE 4. *Argon ratios for sylvite estimation*

Sample	$^{40}A/^{36}A$	$^{38}A/^{36}A$
Tracer alone	$1{\cdot}712 \pm 0{\cdot}001$	$0{\cdot}02242 \pm 0{\cdot}00002$
4·9 c.c. of tracer + gas from 197·8 g. of sylvite . . .	$2{\cdot}633 \pm 0{\cdot}002$	$0{\cdot}02239 \pm 0{\cdot}00002$
Atmos. argon	324	0·195

The $^{40}A/^{36}A$ ratios allow us to calculate the amount of radiogenic ^{40}A created within the sylvite by the decay of the ^{40}K, the mass of which is known. Thus, if W g. of ^{40}A are present in the tracer gas added to the sylvite gas then $(2{\cdot}633 - 1{\cdot}712)W/1{\cdot}712$ g. is the mass of ^{40}A from the sylvite (see Table 3). With this mass for the ^{40}A we get by equation (4) the age t of the sylvite, knowing of course T_K and the mass of ^{40}K.

In the actual experiment 197·8 g. of sylvite were placed in a quartz furnace which was evacuated for 12 hours. Then 4·90 c.c. of tracer argon were added and heating started. A temperature of 1050° C was maintained for 1 hour. The gases from the sylvite, together with the admixed tracer gas, were taken off, treated, and analysed with the spectrometer.

The method is equally successful with ^{40}Ca. Enrichment of the isotope ^{48}Ca was carried through and the two important ratios observed were $^{40}Ca/^{48}Ca$ and $^{44}Ca/^{48}Ca$. Table 5 summarises the results and it is seen that tracer alone and tracer + calcium from sylvite give significantly different values for $^{44}Ca/^{48}Ca$. The difference 0·0204 to 0·02316 allows us to calculate the " impurity " of natural calcium in the sylvite specimens.

TABLE 5. *Analysis of sylvite by calcium ratios*

Sample	$^{40}Ca/^{48}Ca$	$^{44}Ca/^{48}Ca$
Tracer enriched in ^{48}Ca	$0{\cdot}584 \pm 0{\cdot}001$	$0{\cdot}0204 \pm 0{\cdot}00005$
Tracer + calcium from 10·7 g. of sylvite .	$1{\cdot}040 \pm 0{\cdot}002$	$0{\cdot}02316 \pm 0{\cdot}00007$
Normal calcium . . .	510	10·8

The work clearly establishes the method as an elegant and reliable way of finding the age of potassium minerals and incidentally it demonstrates the almost complete retention of the ^{40}A by the mineral (the sylvite analysis shows that $99{\cdot}0 \pm 0{\cdot}5\%$ of the argon is radiogenic) for periods up to at least 10^8 years.

General remarks on pile activation. It appears that the fundamental problem in the various methods of age determination amounts to the reasonably accurate weighing of the very small amounts of the decay product of the radioelement. It is, at least for the methods so far discussed, relatively easy to weigh the parent substance (except possibly for the halo technique). For this reason we note the wide variety of procedures which have been exploited, a good example being Ahrens's spectrochemical analysis. The Reviewer [18] has suggested another possibility. Irradiation of the mineral or, better, of the separated decay product or products (*e.g.*, ^{40}A in the case of potassium minerals), in the neutron flux of a pile, may yield enough of an unstable element, or elements, to permit deduction of the weight of the material involved. Here the great sensitivity of modern techniques in detecting extremely low intensities of radiation of the β-, γ-, or X-ray type is turned to account. For example, suppose that heating a sample of sylvite yielded a little ^{40}A and that this was partly converted into radioactive ^{41}A by neutron capture in the pile. It can be shown that by estimating the amount of ^{41}A through its radioactivity, with counting techniques, then ages as short as 10^4 yr. for the mineral may be determined. Checks against impurities can sometimes be included. However, till practical tests of the method are made it is difficult to assess its value.

The radiocarbon (^{14}C) **method.** An advance of much significance in the science of geological and archæological dating was foreshadowed in a note from Libby [19] in 1946. He considered the interaction of neutrons in the cosmic radiation with nitrogen in the earth's atmosphere. The faster neutrons produce tritium which decays to form the helium isotope ^{3}He while, on the whole, the slow neutrons interact to produce radiocarbon (^{14}C) :

$$^{14}N + n \rightarrow {}^{14}C + p \quad . \quad . \quad . \quad . \quad (16)$$

The cross-section for this process is such that probably at least 97% of the neutrons are so absorbed and of course the ^{14}C formed is soon widely diffused. The ^{14}C atoms burn to carbon dioxide before reaching the earth from about 30,000 ft. We may therefore expect all plant life to be radioactive since it lives on carbon dioxide which contains ^{14}C. Then again, the animals consuming the plants acquire the activity while inorganic carbon in the sea (in such forms as CO_3^{--}, HCO_3^-, and H_2CO_3) will exchange with the carbon in the weakly active carbon dioxide of the atmosphere acquiring in turn the activity. Hence, a dilution of the ^{14}C through terrestrial matter takes place. Later work has shown this dilution occurs in a time much shorter than the half-life T of ^{14}C ($5{\cdot}57 \times 10^3$ yr.). Anderson and Libby [20] have drawn up a carbon inventory, listing the more important sites of the radiocarbon and giving estimates of the total masses of carbon involved in each item of the inventory. This is reproduced in Table 6 and it remains to note that the total inventory fits well with the available data. Thus the neutron flux into the atmosphere is 156 ± 30 per cm.^{2} per minute. When a steady state is reached (after $\sim 10^5$ yr. say) this flux must give rise to the same number of ^{14}C atoms as are lost by decay of ^{14}C. The experimental analysis of the activity of carbon-containing materials shows that the specific activity of living matter (biosphere and organic) is $15{\cdot}3 \pm 0{\cdot}5$ disintegrations per min. per g. of carbon and $16{\cdot}2 \pm 0{\cdot}5$ for inorganic carbonate, yielding an average figure of $16{\cdot}1 \pm 0{\cdot}5$. With a total of 8·3 g.

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[18] *Atomics*, 1952, **3**, 5.

[19] *Phys. Review*, 1946, **69**, 671.

[20] *Ibid.*, 1951, **81**, 64. This paper contains references to earlier work by the Chicago group on the ^{14}C method.

TABLE 6. *Carbon inventory*

Source	Amount (g /cm ^{2})
Ocean " carbonate "	7·25
Ocean, dissolved granite	0·59
Biosphere	0·33
Atmosphere	0·12
Total	8·3

of carbon per cm.^{2} of earth surface (see Table 6), we have $8{\cdot}3 \times 16{\cdot}1 = 134$ disintegrations per min. per cm.^{2} to match the flux of 156 ± 30 cosmic-ray neutrons. The agreement is within the experimental uncertainty.

No significant variation in the ^{14}C content with latitude, longitude, altitude, or depth in the sea has been observed and it would appear that mixing is complete. Such mixing seems to occur well within the average life of a ^{14}C atom. The data for the inventory are an interesting collection of measurements from diverse fields. Paneth [21] contributes the amount of atmospheric carbon dioxide, Schroeder and Riley [22] the contribution of the biosphere, and the work of Bullard [23] is used as evidence that thermal gradients in the oceans are adequate to ensure sufficient circulation to smooth out the ocean contribution. The total amount of ^{14}C distributed over the earth's surface is enormous. The mass of ^{14}C can be calculated as follows. Neutron flux on upper atmosphere = 2·6 per cm.^{2} per sec. Area of earth's surface $= 5{\cdot}1 \times 10^{18}$ cm.^{2}. Hence, total flux of neutrons per sec. $= 5{\cdot}1 \times 10^{18} \times 2{\cdot}6$ and this equals dN/dt, the rate of disintegration of the total mass of ^{14}C on the earth. But as $N = (-T/0{\cdot}69)(dN/dt)$, we have $N = 5570 \times 5{\cdot}1 \times 10^{18} \times 2{\cdot}6/0{\cdot}69$ yr., which corresponds to 77 tons. The wide distribution of the radiocarbon reduces the specific activity of elemental carbon to 16·1 ± 0·5 disintegrations per min. per g. In terms of percentage abundance ^{14}C exists in natural carbon to the extent of only $1{\cdot}85 \times 10^{-10}\%$.

Problem of detection. The low abundance deduced above makes the detection problem one of considerable difficulty. The Chicago team uses the carbon in the form of elementary carbon within a special screen wall counter. Some 6 g. of carbon are spread uniformly over an area of about 300 cm.^{2}, giving an " infinitely " thick layer (the thickness exceeds the range of the β-rays of limiting energy 157Kev). The cathode of the tube is a wire cage inside an outer cylinder on which the source is spread. The outer cylinder is usually at above 100v positive relative to the screen or cage. The layer of carbon can be moved into and out of the counting position without disturbing the counter itself. The counters are operated

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[21] Quoted by Kuiper, " The Atmosphere of the Earth and Planets ", Univ. Chicago Press, 1949, p. 1.

[22] Schroeder, *Naturwiss.*, 1919, **7**, 8, 976 ; Riley, Bull, and Bingham, Oceanographic Coll., 1941, Vol. I, p. 1.

[23] *Nature*, 1945, **156**, 35.

in Geiger–Müller fashion and their efficiency is measured with the help of a separate source containing a known small amount of ^{14}C dispersed through its volume. Some 6% of the total emission of the ^{14}C is registered. The shielding is made as efficient as possible to reduce the " background " to the lowest possible value. Kulp and Tryon [24] have been most successful in this effort. Their counter, 8″ in active length and 2·63″ in diameter, is placed within a mercury cylinder 1″ thick, and Geiger counters round this cylinder act in anti-coincidence as a cosmic-ray shield. This assembly is surrounded with iron to a thickness of 8″. Among the preferred materials for the counter wall is stainless steel, and the insulating substance is Perspex. Thus all contaminated materials such as lead are removed from the system. A " background " of only 2 counts per min. is observed which makes an extension of ^{14}C analysis possible.

Applications. The problem of detecting and measuring the ^{14}C within carbon samples is much facilitated if isotopic enrichment in ^{14}C is secured. Some fine work on methane gas illustrated this point clearly as well as vindicating completely Libby's ideas on the scheme for age determination. Methane from a sewage disposal plant was concentrated in ^{14}C content by the thermal column equipment (made to enrich the gas in ^{13}C), and a similar treatment of petroleum methane followed. Both enriched samples were tested for activity and it was obvious that the biomethane was much more radioactive than the petroleum methane. This difference followed from the fact that living carbonaceous matter must be richer in ^{14}C than identical material which has been buried for a period of the order of the half life of ^{14}C since the activity decays during this period.

Isotopic concentration is an expensive and rather wasteful process and the excellence of modern counting procedures makes it possible to work without enrichment in nearly every instance. With 6 g. of elementary carbon and an overall counting efficiency for β-rays from the thick layer of 6%, a counting rate due to ^{14}C of 5·8 counts per min. is observed. At a " background " of 5 or 2 counts per min. this extra activity is readily measurable, with fair accuracy. If this is regarded as the norm for living carbonaceous matter, then identical material buried for times comparable with or greater than the half-life of ^{14}C will give reduced activity and comparison of this smaller activity with the norm allows us to deduce the period of isolation of the carbon in the sample. In other words the age of the specimen is based on the measured activity and knowledge of T for ^{14}C.

Results obtained by Arnold and Libby [25] are shown in Fig. 5. Specimens of wood carbon, whose origin is denoted on the curve, were examined for specific activity and this was plotted as a function of the known ages. The points lay on a smooth curve and the full-line curve shown corresponds to that of the decay of ^{14}C. Clearly any specimen of unknown age up to more than 10^4 yr. can be analysed in the same way. At a " background " of 2 counts per min., ages up to 3×10^4 yr. can be measured with fair accuracy ($\pm$ 10% say). This work shows without doubt that the inner wood of trees is effectively dead and the ^{14}C activity is decreasing. Botanists

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[24] *Rev. Sci. Instr.*, 1952, **23**, 296.

[25] *Science*, 1949, **110**, 678.

anticipated this finding but here we have clear proof. Among other interesting points emerging from the studies we note that fractionation of carbon (^{14}C and of course ^{13}C) takes place in the many varieties of sea shells which have been tested.[20] The specific activity of the carbon from shells is ~ 5 to 10% higher than the average. Among the archæological findings of interest the estimation of the age of vessels from Stonehenge may be mentioned. An age of 3600 yr. was found and this agreed well with the estimate of the Astronomer Royal, based of course on entirely different data. There is certainly a large field of research opened up by the ^{14}C method and archæological and geological specimens of ages up to some 3×10^4 yr. can undoubtedly be assessed with confidence.

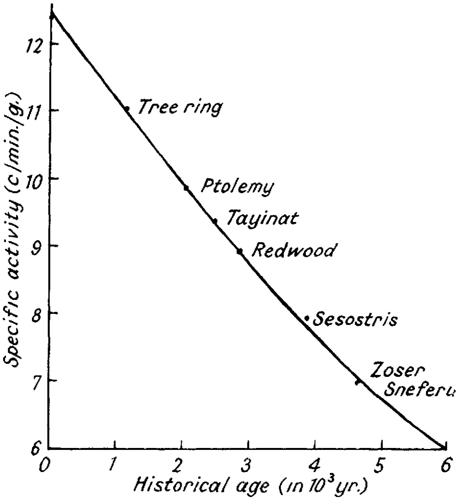

FIG. 5

The known ages of various woods plotted against the measured specific activities. The full curve represents the decay curve for ^{14}C and the points lie close to it.

Some General Considerations.—The oldest mineral samples analysed seem to come from two areas, S.E. Manitoba and Karelia, Russia. Many of the experimental values in each case lie close to 2×10^9 yr. Holmes [26] has applied statistical methods to the examination of the data and come to the conclusion that an age of $3{\cdot}35 \times 10^9$ yr. can be given to the earth itself. Jeffreys [27] has argued that individual measurements of high quality seem to centre round 2×10^9 yr. and that this figure may well correspond closely to that of the earth. Actually, about 2×10^8 yr. must be added to allow for the time the earth took in settling from the molten state to its present form with a solid crust. The choice would then lie between, say, 2·2 and $3{\cdot}35 \times 10^9$ yr. with most other data favouring the second of these values. We should remark here that for some time the estimated energy release

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[26] *Nature*, 1946, **157**, 680; 1947, **159**, 127.
[27] *Ibid.*, 1948, **162**, 822.

from ^{40}K seemed to preclude the existence of a solid crust on the earth some 2 or 3 $\times 10^{9}$ yr. ago. However, the recent work on ^{40}K showed that earlier data were in error and no such difficulty appears in the present-day picture.

Tolman [28] has classified the methods of estimating the age of the earth into three categories : (1) radioactive decay in terrestrial and stellar matter, (2) the consequences of stellar interactions in our own galaxy, and (3) the consequences of nebular recession.

Regarding (1), we note that Paneth and his collaborators [7] estimate the age of meteorites by the helium content and obtain values ranging from about 6×10^{7} to 7×10^{9} yr. Tolman thinks these values are not incompatible with his own view that meteors belong to the solar system and that they separated from the sun at the same time as the earth and planets.

The basic assumption behind method (2) is that the age of the universe, of which the earth is a part, corresponds roughly to the time during which gravitational interaction has persisted among stars with roughly the same distribution as at present observed. Bok [28] estimates on this basis that a time of 3—5 $\times 10^{9}$ yr. has elapsed since the last major event which involved the whole of our own galaxy.

Regarding recession, Tolman and Omer [29] find the time of recession of nebulæ to be $3{\cdot}6 \times 10^{9}$ yr.

It is clear that all of these methods suggest that an " age " of about 3×10^{9} yr. fits most of the facts. It would correspond to the beginning of an expansion possibly preceded by a condensation. In other words, it corresponds to the time during which the present phase of a vast trend has persisted.

Stellar Energy.—Gamow and Critchfield [30] use the estimated age of the

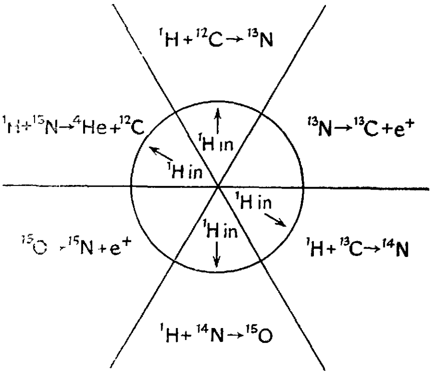

FIG. 6

The carbon cycle leading to the production of helium from hydrogen.

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[28] *Rev. Mod. Physics,* 1949, **21,** 374.

[29] Omer, *Astrophys. J.*, Jan., 1949.

[30] " Theory of Atomic Nucleus and Nuclear Energy Sources ", Oxford Univ. Press, 1949, Chapter 10.

earth in considering the question of energy production in the sun and stars. A total of 24 nuclear reactions could contribute the whole or a part of the energy released but of these only one satisfies the age condition. Thus the interaction of protons with protons

$$^{1}\mathrm{H} + {}^{1}\mathrm{H} \rightarrow {}^{2}\mathrm{He} \rightarrow {}^{2}\mathrm{H} + \mathrm{e}^{+} \quad . \quad . \quad . \quad (17)$$

has a reaction time of $1{\cdot}5 \times 10^{10}$ yr. and an energy production of 1·0 erg $\mathrm{g.}^{-1}$ $\mathrm{sec.}^{-1}$. The mean energy release in the sun is 2 erg $\mathrm{g.}^{-1}$ $\mathrm{sec.}^{-1}$. They conclude that reaction (17) is important in the majority of the stars in our galaxy and that another mechanism which is independent of interaction time is that responsible in a number of brilliant stars. This mechanism is described as the carbon cycle, and the cycle of reactions, as shown in Fig. 6, leads to the production of helium from hydrogen. In these cosmological studies we have an instance in which the age of the earth plays a decisive role in limiting the choice of mechanisms.