

HELIUM AND THE PROBLEM OF GEOLOGICAL TIME¹

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INTRODUCTION

Few branches of science have been developed with such rapidity as that of the phenomena of radioactivity. One would show a decided bias in mentioning any particular investigator or indeed any list of experimenters, which might be compiled in this limited space, who have worked in this field during the thirty-seven years since the discovery of the radioactivity of uranium by Professor Henri Becquerel. For a complete reference to all the literature on this subject the reader is referred to the excellent book on *Radioaktivitaet*, by Professors Stefan Meyer and Egon v. Schweidler (1), or for a brilliant modern discussion and particularly to those interested in the experimental side, *Radiations from Radioactive Substances*, by Rutherford, Chadwick, and Ellis (2). A comprehensive introduction to the subject is afforded by G. v. Hevesy and F. Paneth's *Lehrbuch der Radioaktivitaet* (3).

The first seven years were devoted to the compilation of a mass of facts, the chaotic nature of which was reduced to order by the application of the transformation theory of Rutherford and Soddy in 1903. It must here be assumed that the reader has knowledge of the theory of spontaneous disintegration of the radioelements accompanied by the loss of an α - or β -particle and the subsequent formation of the transformation series, three of which are known today. It was soon shown that such series end in definite stable products and that the time required to produce a given amount

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of the end-product of a given series from a given amount of the parent element is always the same once radioactive equilibrium has been established. Owing to the probability nature of the spontaneous disintegration this statement, however, must be modified so as not to include small intervals of time, measured in seconds and minutes. Stating this in mathematical terms, the disintegration constants of all the radioelements are invariable, at least under the ordinary physical conditions existing on the earth today. Radioactive equilibrium is attained when as many atoms of the "daughter element" disintegrate in a given time as are produced from the "parent element." On scanning the uranium series it will at once be seen from the average life of ionium, that a period of many thousands of years will be necessary for the establishment of equilibrium in the uranium series. In the case of the thorium series a few years is sufficient. With the actinium series in an uncertain state in the initial stages, this necessary period cannot be determined, but it is probably less than that required for the uranium series. The case of very young minerals and rocks will not be discussed here. The next progressive step was to show that one and only one α -particle was ejected on each successive transformation, except in the case of dual disintegrations and branching series. Determinations of the ratio of the charge to the mass of the α -particle by Rutherford and Soddy in 1903 (4) showed that the α -particle was probably a doubly positive charged helium atom. The association of helium with minerals containing uranium and thorium had been noticed previously by Ramsay, and in 1904 Ramsay and Soddy (5) found that helium was present in the gases released by heating or dissolving radium salts. The identity of the α -particle with the helium nucleus has long since been firmly established. It was correctly concluded in the early stages of the history of radioactivity that the β -rays consisted of high speed electrons.

The series

The end-products of the uranium and thorium series having been ascertained as lead, by tracing the various steps in the transformation series with the help of the radioactive displacement law,

it was found that the uranium series should end in the lead isotope 206 and the thorium series in the isotope 208. Recent investigation by Aston (6) on the isotopes of lead would indicate that the isotope 207 is the end-product of the actinium series. It is now possible to draw up a diagram of the end-products of the three known disintegration series which under the condition of the attainment of radioactive equilibrium will illustrate the methods of determining the age of matter containing radioelements simply by reference to the initial radioelement and the final products. This is shown in figure 1.

The method of determining the age of a mineral from the proportion of uranium and lead present was first suggested by Boltwood (7). It has been necessary to modify Boltwood's method

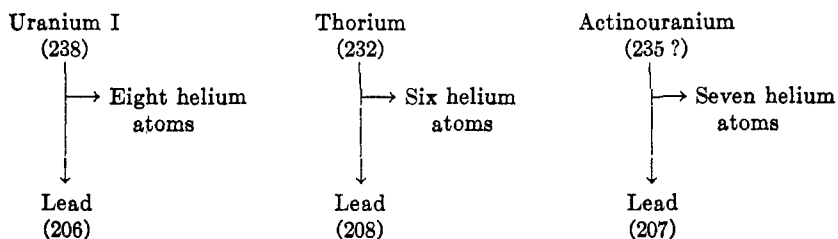


FIG. 1. THE END-PRODUCTS OF THE RADIOACTIVE SERIES

only in so far as he assumed that all the lead was produced by uranium. We now know that in addition to thorium and actinium lead, account must be taken of ordinary lead. Rutherford (8) was the first to draw attention to the helium method of determining the age of a mineral. Between 1905 and 1911 appeared a series of papers by R. J. Strutt (Lord Rayleigh) in which he worked out in detail the relation of the helium to the radioelements. A very complete résumé of these results is given in Bulletin No. 80 of the National Research Council, *The Age of the Earth*, or in Abegg's Handbuch (9).

The fivefold test on the age of a mineral

From figure 1 it will be seen that if the possibility of common lead is excluded, and the amount of uranium, thorium, and ac-

tinium and the respective proportions of the lead isotopes determined, three independent ratios giving the age of the mineral can be obtained. Such determinations at present are very few and do not lead to very accordant results, but this is mainly due to the uncertainty of the constants in the less studied series of thorium and actinium. The accurate determination of the isotopes of lead is now within the range of possibility even on a large scale, as is shown by Aston's recent results (10). The fourth test is given by the ratio of helium to uranium, thorium, and actinium. The fifth test is the oxygen method proposed by A. C. Lane, on which no crucial calculations have been made as yet (see appendix). A sixth test might be added, namely, the study of the pleochroic haloes, which will be mentioned later, were it not that the present methods of determining the quantities to be known place this method far outside of the degree of accuracy with which the other tests can be applied. So far no fivefold test has been applied, with the possible exception of a uraninite (see appendix); the highest is probably a threefold test by the uranium, thorium, and helium ratio, but such tests lead at present to very discordant results, partly on account of the practical difficulties. Thus recent research has shown that the helium method is applicable only when exceedingly minute radioactivity is present, so that although the very small quantities of uranium and helium can still be measured with accuracy, the amount of lead present is far too small for a determination. For the present, therefore, each mineral will have to be treated appropriate to its analysis. Before discussing this problem, however, it may be well to consider the evidence for the constancy of disintegration of the radioelements.

THE SPONTANEOUS DISINTEGRATION OF THE ELEMENTS

Apart from the three series mentioned previously, so far only three other elements of the periodic system have been found to show an activity. Potassium and rubidium exhibit a weak activity, but no series associated with these disintegrations yielding only β -particles has been traced. G. v. Hevesy has lately found samarium to be radioactive, yielding probably an α -particle (11).

Artificial disintegration

Many are the experiments which have been carried out in efforts to alter the rate of disintegration of the radioelements or produce artificial disintegration. The effects of temperatures up to 3000°C. and pressures of 20,000 atmospheres, of very strong fields of electrical, magnetic, and gravitational type, have all failed to show a positive result. That such puny sources of energy would not avail might have been predicted from the quantum theory. Einstein has shown that the emission of radiation may be stimulated by incident radiation. To become effective, however, such incident radiation must closely approach in quantization the emitted radiation. Thus to remove electrons from the outer orbits is an everyday occurrence, but it requires many thousands to even millions of times this incident radiation to effect a nuclear rearrangement. The wave length of the radiation, λ , and the temperature, T , are found to be connected by the relation $\lambda T = 0.2885$ cm. deg. From this relation Jeans (12) has drawn up table 1 showing the mechanical effects of radiation. When some such temperature as 5.8×10^9 °A. is reached, but not before, the nuclei of uranium will commence to rearrange themselves.

The next obvious step to increase artificially the rate of disintegration was to bombard a radioactive element with a source of α -particles. Such a source would have an energy corresponding to about 6×10^{10} degs. in the case of the fastest. This however failed, and its failure is again predicted by the quantum theory on determining the probability of disintegration by α -particle bombardment for heavy elements. Jeans finally concludes that apart from the "white dwarf stars," whose center probably consists of only nuclei and free electrons—their density is enormous compared to matter in the earth—and the spiral nebulae, "No place is known hot enough to have any appreciable effect on the transformation either by synthesis or by disintegration, of the radioactive elements. . . ." It has been suggested that radioactive disintegration is effected by the penetrating or so-called cosmic rays. By measuring the activity of a polonium preparation at the bottom of a mine and at the surface, Maxwell (13)

showed that such an effect must be less than 1 per cent. Another method has suggested itself to the author, namely, that the age of specimens taken from an inclined basaltic flow such as may be traced downwards for some thousands of feet in the Keweenawan copper mines should show differences even though the flow is definitely of uniform age, if the penetrating radiation is effecting

TABLE 1
The mechanical effects of radiation
Sir James Jeans

WAVE LENGTHS	NATURE OF RADIATION	EFFECT ON THE ATOM	TEMPERATURE	WHERE FOUND
<i>cm.</i> 7500 × 10 ⁻⁸ to 3750 × 10 ⁻⁸	Visible light	Disturbs outermost electrons	<i>degrees A.</i> 3850 to 7700	Stellar atmospheres
250 × 10 ⁻⁸ to 1 × 10 ⁻⁸	X-rays	Disturbs inner electrons	115000 to 29,000,000	Stellar interiors
5 × 10 ⁻⁸ to 1 × 10 ⁻⁹	Soft γ-rays	Strip off all or nearly all electrons	58,000,000 to 290,000,000	Central regions of dense stars
4 × 10 ⁻¹⁰	γ-Rays of Radium B	Disturbs the nuclear arrangement	720,000,000	
5 × 10 ⁻¹¹	Shortest γ-rays	—	5,800,000,000	
1.3 × 10 ⁻¹³	Highly penetrating radiation (?)	Annihilation or creation of proton and accompanying electron	2,200,000,000,000	

the disintegration and the specimens are taken so as to have been exposed to the radiation in one set and not exposed in a second set. Some preliminary results which appear to show that no differences are exhibited have been obtained, but on account of their preliminary nature are withheld for future publication.

The recent experiments of Cockcroft and Walton (14) are of

interest in that the disintegration rate of uranium is apparently increased by bombardment with high speed protons. It is difficult to conceive of the presence of such protons in the present physical state of the earth, but such a bombardment might well have occurred in the sun. The process appears to be the reversal of the bombardment of some elements by α -particles, in that the proton is absorbed and an α -particle emitted. The product of the bombardment of UI is therefore an isotope of protoactinium of mass 235. A conceivable initial transformation of the actinium series might then be represented as in figure 2. Moreover on account of the close genetic relation—the head of the actinium series is, however, no longer a uranium isotope—it might be ex-

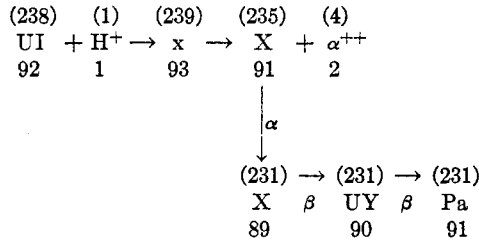


FIG. 2. POSSIBLE MECHANISM OF THE FORMATION OF THE ACTINIUM SERIES

pected to find a reasonably constant proportion at any given time of the uranium series to the actinium series, as is actually observed in a few analyses made. Such a mechanism must have ceased operation when the earth was born, otherwise we must postulate a source of protons of the required energy in the earth today. The necessity of accounting for any excess helium production by this and similar mechanisms, in age determinations, and the question of the large helium content of beryls has been discussed by Urry (15).

Pleochroic haloes

Perhaps the best positive evidence of the constancy of the rate of disintegration of the various radioelements is afforded in observations of the previously mentioned pleochroic haloes. The α -particles have certain characteristic properties, amongst which

is the property to ionize all gases through which they pass and solid bodies in which they are absorbed. In certain minerals this property is exhibited by a permanent visual after-effect in the formation of concentric darkened or colored rings surrounding a minute radioactive inclusion. These darkened rings seen in a thin cross-section are really spheres in the body of the mineral or a succession of shells. The reason for the appearance of the ionization effect in rings and not as circular uniform dark areas lies in the fact that the ionizing power of an α -particle increases rapidly and reaches a maximum very near to the end of its "range," as may be seen from figure 3.

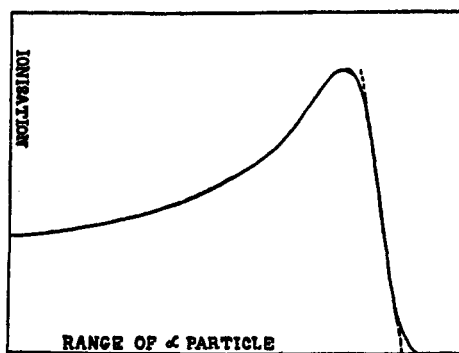


FIG. 3. VARIATION OF THE IONIZING POWER OF AN α -PARTICLE WITH DISTANCE TRAVELLED

The range of an α -particle in a given medium is a perfectly definite quantity for any given radioelement and has been found by Geiger and Nuttall to be connected with the rate of disintegration of the element producing the α -particle by the following relation:

$$\log \lambda = A + B \cdot \log R$$

where λ is the disintegration constant, A and B constants, the first of which depends on the series considered, the second being independent thereof, and R the range. Thus Joly found the maximum radius of the haloes referred to the uranium series in biotite to be about 0.04 mm., which agrees closely with 0.041

mm. found for RaC' in biotite experimentally. The various other rings of smaller radius can be identified, at least in fluor spar, with those due to the other members of the series, but the center of the halo in biotite is usually more or less of even intensity owing to the combined, although small, ionization effect of all the α -particles in their initial excursions. Many observers have made measurements since the pioneer work of Joly, and the constancy of the radii of the various rings in both thorium and uranium haloes in minerals of all geological ages has led to the conclusion that the rates of disintegration of the radioelements have not altered during geological time. A very able summary of our present knowledge of these haloes is given by Arthur Holmes (16).

THE APPLICABILITY AND RELIABILITY OF THE LEAD AND HELIUM METHODS

In order to compare the two methods it is as well to summarize first the required data for a complete solution of the age determination for each case. Kovarik (17), in developing the formula for the exact determination of the age by the lead method, has clearly enunciated the conditions and requirements. He writes, "To be able to attack the problem successfully we must be reasonably sure that the mineral did not change by admixture from outside or by losses from inside and that only such changes have taken place as can be ascribed to radioactive disintegration. In addition we must have a knowledge of the following things:

- (A). The data from the analysis of the mineral, namely, the masses of uranium, thorium, and lead (all isotopes) per given mass of the mineral.
- (B). Atomic weight of the lead (all isotopes) from the same analysis.
- (C). The disintegration constants of the radioactive elements involved.
- (D). The atomic weight of the various lead isotopes, separately.
- (E). The parental lineage of the various isotopes of lead.
- (F). The possibility of the presence of common lead and of each one of the several lead isotopes separately at the time of formation of the mineral."

Minor difficulties present themselves in conditions C, D, and E, such as a lack of accurate knowledge of constants or of the origin of the actinium series, but the errors involved are often less than those in the data under A. Condition B presents difficulties in many of the older analyses, since no determination is available or, if so, probably from some second sample of the material.

Helium method

For the helium method the condition in Kovarik's opening paragraph above must also apply and a knowledge of the following:

- (1). The data from the analysis of the mineral, namely, the masses of uranium and thorium and the volume of helium contained in a given mass of the mineral.
- (2). The disintegration constants of the radioactive elements involved.
- (3). The possibility of the presence of helium at the time of formation of the mineral.

The factors involved in the helium method are therefore but three in number compared to six in the lead method; moreover, condition 3, comparable to condition F in the lead method, is considerably simplified in that the only possibility involved in the helium method is a retention of helium from a previous formation, whereas in the lead method there is the possibility of the original formation containing the end-product isotopes in addition to ordinary lead, in which case the problem is insolvable without the analyses of many minerals of varied content but the same geological age. It has been customary in the past to base reliable age determinations only on specimens in which the lead has been found to have an atomic weight very near to 206 or 208, but this has been shown by Kovarik (17) still insufficient to satisfy condition F, particularly with regard to the common lead possibility, and the method certainly limits the field of application to a very few specimens (18). Now let us examine the evidence which throws light on condition 3 in the helium method. The so-called radioactive minerals containing between 0.01 and 50 per

cent or more uranium may contain anything up to 10 cc. of helium per gram. Wood (19) has investigated the loss of helium from monazite and thorianite and his results are tabulated in table 2. Such minerals, however, are definitely out of the range of the helium method on account of a loss which also occurs merely on grinding and quite certainly occurs to a large extent over the periods of geological time. For reasons to be discussed below, the helium method is at present known to be applicable only to fine-grained rocks and minerals containing the order of 10^{-6} to 10^{-7} gram of uranium, a little more thorium, and hence about 10^{-4} to 10^{-8} cc. of helium. Such rocks and minerals have been found to lose nearly all of these small quantities of helium under the conditions of the formation of the rock, although the helium would appear to be closely held in the physical state of their present existence after the necessary cooling period. It is impossible to conceive of the small quantities of helium in the ordinary rocks as being the retained helium from heated highly radioactive and therefore high helium content minerals, since the radioactivity is infinitesimal compared with minerals which might conceivably retain these small quantities. It then remains only to consider the possibility of absorption of helium by the specimens to be worked with. If helium is absorbed by rocks on cooling and this absorption presupposes a source of helium in the neighborhood of the magma which must be greater than that in the atmosphere at present, then under the experimental conditions of liberating the helium from a rock, allowing it to cool in the atmosphere of its own evolved gases, pumping off these gases and reheating, the amount of absorption can be determined. It was found to be less than the detectable amount of helium, or $<10^{-10}$ cc. Paneth and Peters (20) found that the diffusion of helium through palladium was also less than this minimum detectable quantity at 1000°C . Similar unpublished results of the author are also included in table 2. The very small absorption of helium by potassium chloride is insufficient to support the proposal that absorption accounts for the high helium content of sylvin and carnallite found by Strutt (9). The non-absorption of helium by basalts at room temperature is illustrated in another experi-

TABLE 2
The liberation and absorption of helium

OBSERVER	EXPERIMENT	TEMPERATURE	RESULT
Wood, O. D.	Liberation of helium from monazite containing about 9 cc. per gram	degrees C. 720	68.6 per cent of total
		1000	98.3 per cent
Urry, W. D.	Liberation of helium from a fine-grained Keweenawan basalt. Total content 11.73×10^{-5} cc. The specimen, heated to 1050°C ., was allowed to cool in its own evolved gases, whereupon it was found to give off on isolation and reheating.....	750	62.3 per cent of total
		1000	100.0 per cent
Urry, W. D.	Liberation of helium from a fine-grained Keweenawan basalt. Total content 11.73×10^{-5} cc. The specimen, heated to 1050°C ., was allowed to cool in its own evolved gases, whereupon it was found to give off on isolation and reheating.....	900	78 per cent of total
		1050	91 per cent
Urry, W. D.	Diffusion of helium through bismuth 1 mm. thick; 4 hours	1050	$< 10^{-4}$ per cent of the previous loss
Urry, W. D.	Diffusion of helium through copper 1 mm. thick; 4 hours	125	10^{-9} cc. of helium
Urry, W. D.	Diffusion of helium through iron 1 mm. thick; 4 hours (In the last three experiments the limit of detection was 10^{-9} cc. of helium.)	700	$< 10^{-9}$ cc. of helium
Urry, W. D.	Diffusion of helium through iron 1 mm. thick; 4 hours (In the last three experiments the limit of detection was 10^{-9} cc. of helium.)	850	$< 10^{-9}$ cc. of helium
Urry and Hettich	Potassium chloride was crystallized over a period of several months under one atmosphere of pure helium, removed and evacuated for one hour. Contained.....	18	5.7×10^{-8} cc. per gram
Urry, W. D.	Sliced specimen of Keweenawan basalt. Control half contained..... Analysis of the second half after three months continuous exposure to 200 mm. Hg; pressure of helium during diffusion experiments gave.....	26	11.71×10^{-5} cc. per gram
			11.65×10^{-5} cc. per gram

ment. A fine-grained basalt from Keweenaw Point, Michigan, was sliced and cut into two parts. One part was fused for a helium determination and the second was used in the course of some diffusion experiments. Although quantities of the order of 10^{-4} cc. of helium passed through the rock, an analysis of this second specimen showed almost the same helium content as the first specimen. This experiment is interesting from several angles, for it tends to show that diffusion rates of helium as measured by the helium-mineral-vacuum method do not give us information as to the possible loss of helium from a rock. In this case the law of diffusion through fine capillaries was found to hold, and it is improbable that the diffusing helium entered the solid part of the rock at all. Again it is evidence that the radioactive helium is retained within the crystal structure and therefore that in the fine-grained rocks the radioactive points are not situated along the cracks as has been found for coarser rocks, for if such were so it is unlikely that the two results would have agreed.

Summing up the evidence in table 2 it would appear that there is small likelihood of the presence of helium at zero time of the age determination, namely, the time of solidification. Compared to the apparent ease with which this zero state of affairs is reached, the complete removal at the time of the formation of a mineral of the end-products, uranium and thorium lead, produced in the earlier history of its composite material, must depend upon volatility and chemical separation.

Limitations

Turning to Kovarik's introductory condition, it is obvious that although an age may be determined for a metamorphosed rock it has no particular significance. Metamorphism is the changing of the chemical and mineralogical composition, very often by oxidizing reactions or leaching by water or salt solutions. The proportional loss of the various radioactive elements and their end-products cannot be determined during this period, and the most that can be done is to assume that all the end-products were lost during the change, in which case the age gives us the time of metamorphism. Such an assumption can be made but rarely.

As far as the helium method is concerned, we have already dealt with the possibility of admixture from outside in considering the absorption of helium. It must here be noted that the diffusion rates of helium through glass and similar materials have no bearing on the diffusion of helium through crystalline substances. Thus Piutti (21) found that although he was able to detect with ease the diffusion through silica glass, he was unable to observe a diffusion through crystalline quartz. This experiment has lately been repeated by the author with a sensitivity of 10^4 times that of the above experiment, with the same result. The investigation of the diffusion of helium through glass, employing the most sensitive detecting arrangements so far possible, which has been carried out by Paneth and Peters (22) and lately investigated by Urry (23) in detail, although throwing light on the mechanism of such diffusion cannot tell us anything about the loss of helium from rocks and minerals and will lead to conclusions opposite to those found later to be correct. For this reason an investigation into the loss of helium from rocks etc., has been started by the author, and this will be dealt with under Kovarik's second condition. It has generally been argued, and in many cases correctly, that the inherent failure of the helium method of determining ages is due to a loss of helium from the inside; that helium being a gas cannot be retained throughout geological time in the same manner as lead. The conclusion that the helium method gave only minimum values was chiefly due to attempts to compare the lead and helium ratios. Since all the lead ratios must be of minerals of high radioactive and therefore of high helium content the comparisons are unfair, since it cannot be expected that there will be no loss of helium when the pressure of the generated helium may reach several atmospheres in the mineral.

Reliability

There is one class of substances which has the property of completely retaining the generated helium, namely, the metals. Paneth and Urry (24) have shown that the heating of the iron meteorites to 1000°C . for several hours will remove only the helium corresponding to the surface. The results of such experi-

ments are shown in figure 4. A specimen of the iron meteorite Thunda was obtained from the British Museum, where it had existed for several years in the form of filings. The helium content derived from this sample was practically identical with that found for a compact piece of the same meteorite. It should also be noted that both Mount Ayliff and Thunda are the two meteorites containing the most helium of the forty-two so far investigated. It should be mentioned that the older method of liberating the helium by merely heating is far from sufficient. Thus in the case of the iron meteorite, Staunton, Augusta Co., Strutt recorded only about one-twelfth of the actual helium content

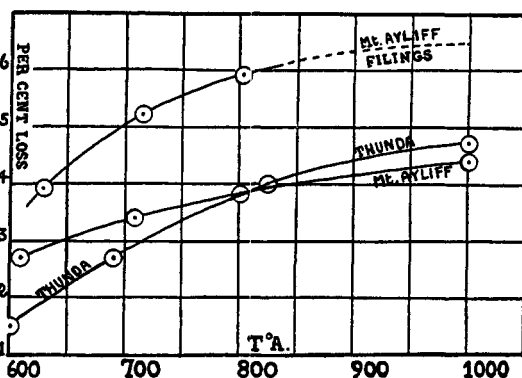


FIG. 4. THE PERCENTAGE LOSS OF HELIUM ON HEATING THE IRON METEORITES²

found on dissolving the meteorite. Even in the case of the minerals, too great an uncertainty is introduced by assuming that a certain fraction of the helium is liberated at a given temperature. Many determinations have been nullified by such assumptions and the spurious results obtained have reflected on the helium method.

The determination of the ages of the meteorites and such native metals as may be found in the earth are decidedly of importance, but the limitations imposed by the rare occurrence of such material would detain us from making anything like a complete survey by this method. A stumblingblock has already been encoun-

² In figure 4, "T°A" should read "T°C".

tered in the case of the native metals, in that at least one has been found to contain an insufficient quantity of radioactivity, but there remains by far the greater proportion of such material for further work, especially in the field of native iron, silver, and gold. There has been found, however, of late another class of material that is likely to prove suitable for determinations by the helium method, namely, the fine-grained basalts, a class which it is highly important to investigate, since such material is abundant in every geological sub-period. The preliminary investigation of this material was undertaken by V. S. Dubey in collaboration with A. Holmes (25). The results are grouped together in table 3 to show the present limits of the applicability of the method in this class of rocks, together with some later determinations by Dubey (26). The helium measurements of these rocks, which necessitated the improvement of the technique to determine the ten to hundred-thousandth part of the helium ordinarily found in the "radioactive minerals," were made in the laboratory of Professor F. Paneth and the uranium and thorium determinations by Professor Mache's methods in Vienna. Owing to possible inhomogeneity of the specimens, all the measurements are now to be made on one sample in the same laboratory, which will remove a certain doubt of the results obtained from measurements of the three required factors on different samples.

In discussing the results, A. Holmes (27) points out that specimens 1 and 2 are of a cryptocrystalline nature, which probably accounts for the apparent loss of helium, the ages being low. No. 3 is a fresh fine-grained rock yielding a value which may be expected to be about correct. No. 4 is definitely younger than No. 3 and the age is consistent with this. No. 5 is also consistent with the known geological period of the Whin Sill but may be 25 per cent low in the light of evidence from the lead ratios. It is interesting to note that the total lead content, including common lead, is about sixty times the expected radioactive lead. In Dubey's later determinations No. 1 is fine-grained and Nos. 2 and 3 progressively coarser, pointing to a reliability only in the case of the fine-grained, where the age is consistent with the lead ratios for the period usually assigned to the Gwalior series, al-

TABLE 3
The age of igneous rocks

GEOLOGICAL AGE	ROCK	LOCALITY	He × 10 ⁴ cc. per gram	Ra × 10 ⁴ grams per gram	Th × 10 ⁶ grams per gram	AGE IN MILLIONS OF YEARS
1. Miocene	Acid Felsite	Mt. Pawagarh plug, 100 ft. below summit, India	11.0	224.4	41.0	5
2. Miocene	Acid Felsite	Mt. Pawagarh plug, summit	10.0	224.4	31.0	5.9
3. Early Eocene	Nonporphyritic basalt, Deccan traps	Mt. Pawagarh, India (about 1400 ft.)	11.6	44.9	5.4	37
4. Oligocene or Miocene	Porphyritic tholeiite of the Cleveland dyke	Bolam, Co. Durham, England	11.0	62.2	6.1	28
5. Late carboniferous	Quartz-dolerite of the Whin Sill	Scordale Beck, Westmoreland, England	36.0	27.5	3.0	196
1. Late Precambrian	Fine-grained basalt flow	Belaki-Bauri, Morar group, Gwalior series, India	55.0	17.4	1.7	500
2. Late Precambrian	Medium-grained dolerite sill	Santowa Temak, Morar group, Gwalior series, India	42.0	17.5	1.5	389
3. Late Precambrian	Coarser grained dolerite sill	Panier, Morar Group, Gwalior series, India	31.0	21.1	2.4	203

TABLE 4
Illustrating the non-loss of helium from the fine-grained basalts
 Part I. Analysis of the gases after sealing up specimens in pure oxygen for three months

SPECIMEN NO.	OXYGEN PRESSURE	LOCALITY OF SPECIMEN	WEIGHT AND SURFACE	ANALYSIS AFTER THREE MONTHS	MAXIMUM HELIUM LOSS FROM ROCK	HELIUM LOSS PER YEAR PER GRAM	LOSS PER 100 YEARS AS PER CENT OF TOTAL CONTENT
11	<i>mm.</i> 453	Fine-grained basalt, Keweenaw	8 grams, about 13 sq. cm.	About 10^{-8} cc. of He + Ne in the air ratio	10 per cent of He in the foregoing mixture = 2.5×10^{-10} cc.	1.1×10^{-10} cc.	0.05
25	671	Mesnard epidote, Felsite	8 grams, about 12 sq. cm.	About 10^{-8} cc. of He + Ne in the air ratio	As above = 2.5×10^{-10} cc.	1.1×10^{-10} cc.	0.03

Part II. Analysis of piece and powdered specimens of a Keweenaw basalt

SPECIMEN NO.	LOCALITY	REMARKS	EXPERIMENT AND NO.	TOTAL HELIUM CONTENT ON FLUOKING
23	91st level of No. 2 shaft, Quincy mine, Keweenaw Point, Michigan	Highest helium content of twenty Keweenaw basalts	1	38.98×10^{-5} cc. per gram
			2	38.90×10^{-5}
			3	39.34×10^{-5}

though no lead ratio for material from this site is available. In the first report of this work (25), Holmes writes, "Clearly there is a large field of geological research now open to investigation by the long-neglected helium method. If our initial hopes are realized—and these preliminary results provide ample encouragement—a method is now available for dating all fresh igneous rocks which have not been heated up or metamorphosed since they came into place. . . . Moreover, since igneous rocks suitable for the helium method are far more abundant and far better distributed in time than are radioactive minerals suitable for the lead method, there is now available a practical means of effecting long distance correlations and of building up a geological time scale which, checked by a few reliable lead ratios here and there, should become far more detailed than could ever be realized by means of the lead method alone."

During the course of an investigation of the Keweenaw series of Michigan, which is still in progress, the writer has found evidence supporting the reliability of the helium method for the fine-grained basalts. Thus one specimen, No. 23 from the bottom of the Quincy mine, was found to give repeatedly the same helium content whether a single piece was taken or a finely powdered specimen, thus exhibiting no loss of helium on grinding. Certain specimens were sealed up in a helium-free, that is, an air-free, oxygen and an analysis made of the gas after three months. Table 4 gives the combined results and the evidence for the retention of helium under the existing conditions. It will be seen that the analysis showed both helium and neon in the proportion in which these two gases are found in the atmosphere. Such sealing up experiments usually give this result, owing to the occlusion of air. This does not invalidate the experiments as a maximum value, for the leakage can still be obtained. The proportion of helium to neon in the atmosphere is approximately 1 to 3. Thus the amount of helium in the analysis above is $< 2.5 \times 10^{-9}$ cc. A variation of 10 per cent of the helium from the proportion in the air could have been detected spectroscopically and thus the maximum amount of helium having its source in the rock must have been 2.5×10^{-10} cc. From the last column it

will be seen that specimens similar to these would yield reliable age determinations even after exposure to the atmosphere for one hundred years or more. The rate of loss of helium from the same rocks *in situ* must be far less than the above determined maximum rates on small samples with exposed surfaces and reduced pressure conditions. In connection with the helium results for specimen No. 23 it is interesting to note that, assuming a complete loss of helium on denudation of the surface rocks, the atmosphere contains today only a fraction of the helium which would have been set free, or, conversely, the denudation required to produce the atmospheric helium is absurdly small. The retention of helium on grinding such rock as the Keweenawen basalt is probably an explanation of this difficulty, since we can now assume that, at the most, only a fraction of 1 per cent is given off in the denudation of a large proportion of the surface rock.

Analytical limitations

Finally we have to consider Kovarik's condition A, namely, the data from the analysis, and with this condition also the fact (B) that the atomic weight of the lead from the same analysis shall be known. The lead method is immediately limited to the radioactive minerals, not on account of the uranium and thorium analyses which can be accomplished even when these elements are present in too small amounts for chemical detection, but on account of the lead determinations and more so since the atomic weight of this lead must be known. Thus to take the example of an iron meteorite which contains on the average 10^{-7} to 10^{-5} cc. of helium (this can be determined with an accuracy of 1 per cent (28)), this amount corresponds to the formation of 10^{-10} to 10^{-8} gram of lead. The radioactive lead, however, must be accompanied by a far greater amount of common lead, for I. and W. Noddack (29) have found on the average 5×10^{-5} gram of lead per gram of meteorite, and for the present it is quite impossible to determine the lead isotopes in such a mixture. As we have seen with the Whin Sill, such a state of affairs also exists in the ordinary rocks, and thus the lead method is limited to minerals

containing sufficient lead for both the ordinary and isotopic analysis and in which all Kovarik's conditions can be satisfied, a limitation which seriously hinders the setting up of a complete geological time scale. On the other hand, analysis leads to no such limitations for the helium method, unless it be that certain minerals contain less than the detectable amounts of radioelements and helium. Only two substances have so far been found limited by this extremity. The Keweenawan copper was found by Paneth and Koeck (30) to contain $< 10^{-15}$ gram of radium per gram, as also was the iron meteorite Savik. With regard to the last it is no longer necessary to account for the absence of helium by assuming a passage near the sun (31), since it is merely due to the absence of radioactivity. The helium method is limited for quite another reason, which was given above. For the present it may be said, aside from the metals, to apply strictly only to the fine-grained lavas containing not more than about 10^{-4} cc. of helium per gram. Unfortunately, on account of the analytical difficulties, there remains a gap between the limits of the two methods, otherwise it would be possible to proceed by the two methods on one and the same suitable sample and thus to reconcile the methods. The lead method is at present limited to specimens containing at least about 0.01 per cent of lead, 0.3 per cent of uranium, and 0.5 per cent of thorium. Herein lies the difficulty of applying the fivefold test previously referred to.

THE DEVELOPMENT OF THE EXPERIMENTAL TECHNIQUE

The measurement of the helium content

In the field of detection and measurement of small quantities of helium, must first be mentioned the work of Soddy (32), who was able to detect 1×10^{-6} cc., followed by the studies of Strutt (Lord Rayleigh) (33), which have previously been mentioned, who was able to detect half this amount. This remained the limit of detection for several years, until the methods of Paneth and Peters (22) were published in 1928. These workers succeeded in detecting quantities of helium or neon as small as 10^{-10} cc. Finally Paneth and Urry (28) devised a method of accurately measuring quantities of helium of the order of 10^{-8} cc. This is

practically the limit of the helium content of any geological material. The final form of the analysis apparatus is represented in figure 5. The principle of the purification process is to remove all the extraneous gases by adsorption on charcoal at liquid air temperature. At the partial pressure of the helium and neon in these experiments the adsorption at this temperature is quite negligible, whilst hydrogen is also incompletely adsorbed, necessitating its removal by chemical means. No attempt is made to separate the helium and neon, as the presence of neon is an excellent indicator of the former presence of air and in fact is made use of in the control experiments to determine qualitatively and quantitatively the possibility of error due to the presence of air and a consequent source of extraneous helium. Neon has a valuable asset in being capable of spectroscopic detection in a helium-neon mixture when present only to the extent of a few thousandths of 1 per cent. When present in greater amount the result is usually rejected. The refinements introduced by Paneth and Peters consist essentially of: (1) obtaining the helium or the helium-neon mixture in a pure state and therefore not having to detect these gases spectroscopically in the presence of other gases; (2) the avoidance of another source of extraneous helium than the presence of air, namely, by diffusion through heated portions of the glass apparatus; (3) producing the best conditions for a spectroscopic analysis by observation of the excited gas (using an external electrode) in the very small capillary attached to the McLeod gauge A.

The first refinement requires the chemical removal of the incompletely adsorbed hydrogen. This is best accomplished when present in large amount by absorption on fine calcium turnings heated to about 350°C. in the calcium oven B. In order to remove very small traces of hydrogen, the calcium oven is shut off from the rest of the apparatus, and after introducing a few millimeters of absolutely air-free electrolytic oxygen these traces are burnt over heated palladium at about 300°C. in the palladium oven C, so constructed that by alternately cooling and warming the charcoal D a to and fro circulation of the gases over the palladium is obtained. The final stage in any analysis is the ad-

sorption for one hour on charcoal D, which is then shut off, and a further adsorption for two hours on charcoal E, whereupon the McLeod gauge is run up and the spectroscopic and quantitative analysis made. The method of vacuum jacketing the heated ovens and further immersing them under water should be noted in figure 5. This is the second important refinement, being the

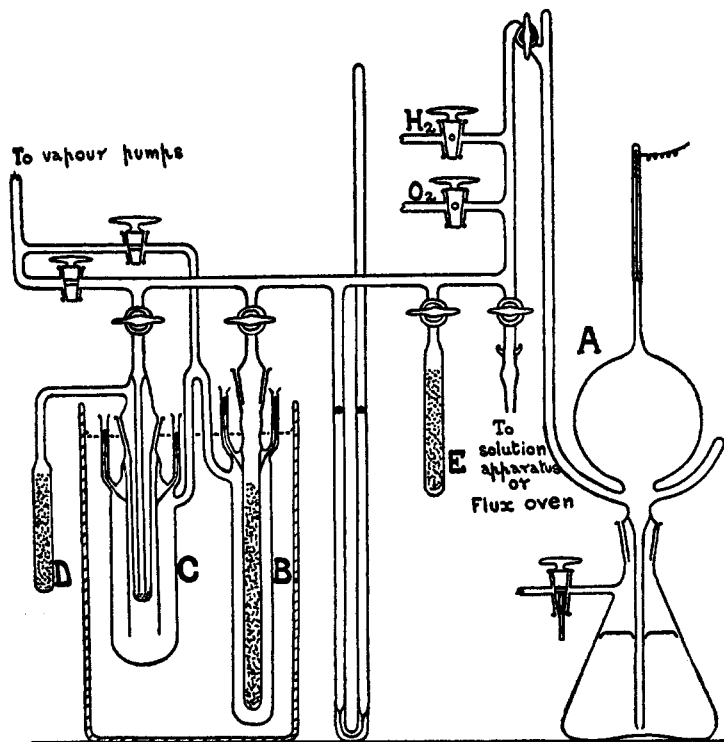


FIG. 5. DIAGRAM OF THE APPARATUS FOR THE DETERMINATION OF HELIUM

method of obviating the diffusion of helium through hot glass (23). The winding of the heating elements on asbestos is also excluded, since such mineral has been found to contain appreciable amounts of helium. The McLeod gauge is constructed to measure directly the volume of helium in the capillary, which is of a diameter chosen according to the amount expected. In dealing with very minute quantities it may be as small as 0.1 mm. The

time for an analysis varies considerably with the mineral under investigation. Thus in the case of the solution of an iron meteorite in hydrochloric acid a large quantity of hydrogen is evolved, which conveniently acts as a carrier gas for the helium but which must be completely absorbed on the calcium. For a description of the apparatus for the solution of such soluble material under completely air-free conditions, the reader is referred to the original publication (24). In the case of insoluble material the usual procedure is to make a flux in a vacuum oven at 1000°C. and either to use the carbon dioxide available from the flux as a carrier gas or to supply air-free carbon dioxide conveniently formed by heating a powdered mixture of potassium dichromate and sodium carbonate. Since the type of vacuum oven is still a matter for further work it will not be depicted here.

The measurement of the uranium and thorium content

In order to determine the age of a rock, two further measurements are necessary,—the uranium and thorium content. Except in the case of the acidic rocks where the radioactive content is high compared to the basalts and meteorites, the difficulties of these measurements are even greater than the determination of the helium. The only practical method for the determination of these very small radioactivities is the emanation method. Thus if radioactive equilibrium has been established the measurement of the amount of any one of the series is sufficient to establish the content in any other of the radioelements of that series, the equilibrium amounts of each being known from their disintegration constants. Practically, the method involves the separation of the parent radioelement of the emanation of that series, the collecting of all the emanation in equilibrium with this separated parent in a suitable ionization chamber and the measurement by a comparison method of the emanation so collected. Figure 6 illustrates one possible series of chemical treatments which has been used, starting from the flux of the rock which may be conveniently carried out for the helium determination. All vessels employed and all reagents are treated previously with barium chloride to remove traces of sulfate which will precipitate the

radium in a form not suitable for the complete recovery of the emanation. In most cases it is also necessary to treat the reagents by various processes to remove a certain activity which they

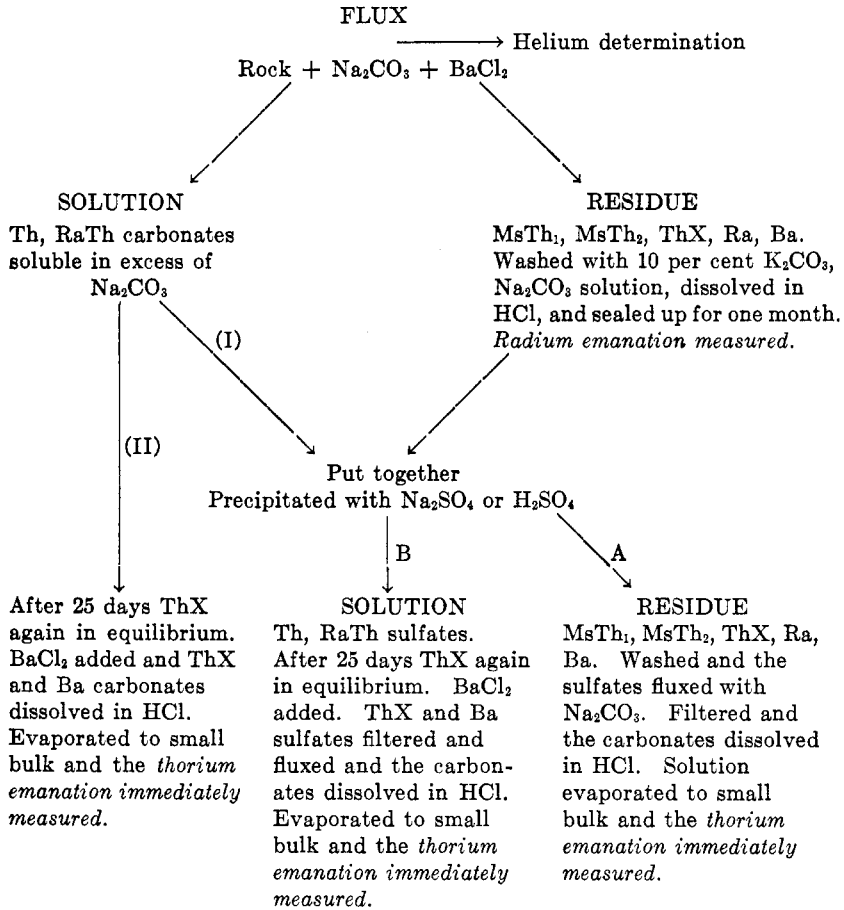


FIG. 6. THE CHEMICAL SCHEME FOR THE HELIUM-RADIUM-THORIUM ANALYSIS OF A ROCK

themselves contain. The separation depends upon the isotopy of the various radioelements. Thus, having obtained the carbonates of the two mesothorium, thorium X, and radium in an excess of barium carbonate as a carrier there remains in solution

the carbonates of thorium and radiothorium, the parent element of thorium X. The diagram explains the method of obtaining the equilibrium amount of emanation. If we are satisfied that the radiothorium went completely into solution, then after about twenty-five days we may proceed to obtain the thorium X, which is the parent of the thorium emanation by route II. The half-period of thorium X is 3.64 days, hence the period of several days required to reach equilibrium again after separation. As a control, however, this solution and that used for the radium determination may be put together, a sulfate added, and the thorium and radiothorium soluble sulfates separated out (route I). After the required period the solution is treated as under B. If, on putting the two solutions together, a time of twenty-five days is allowed to elapse before precipitating, the precipitate will again contain the equilibrium amount of ThX and can be treated as under A. The thorium emanation having a half-life of 54.5 seconds, equilibrium is quickly established, but once having obtained the ThX separated from its parent, the measurement must be made quickly on account of the short life of the ThX itself. If the much more slowly generated radium emanation affects the determination of the thorium emanation, the methods A and B should differ. When an acid solution is obtained after the helium analysis, this may be used directly for the radium determination and further treated in a similar manner as outlined above for the measurement of the thorium. If the radiothorium solutions after separation are kept for several months a correction must be made for the disintegration, since the half-life of this radioelement is 1.90 years.

Measurement of the emanation

The practical methods employed fall roughly into three classes, the order of which also corresponds with the historical order. The first method is that in which one ionization chamber is employed and the charge attained by the needle is progressively followed over a given period with some type of electroscope or electrometer. There is, however, present a natural ionization due to a variety of sources, chief amongst which is the local

gamma radiation and the secondary effects at the walls of the chamber with penetrating radiation playing a small part as well. This natural ionization can be reduced to a minimum by taking various precautions, but there is a practical limit. When the ionization due to the emanation and its disintegration products is of the same order as the natural ionization the determinations become far too uncertain, especially since there is always doubt as to whether the natural ionization has remained the same during the period that must elapse between the control experiment and

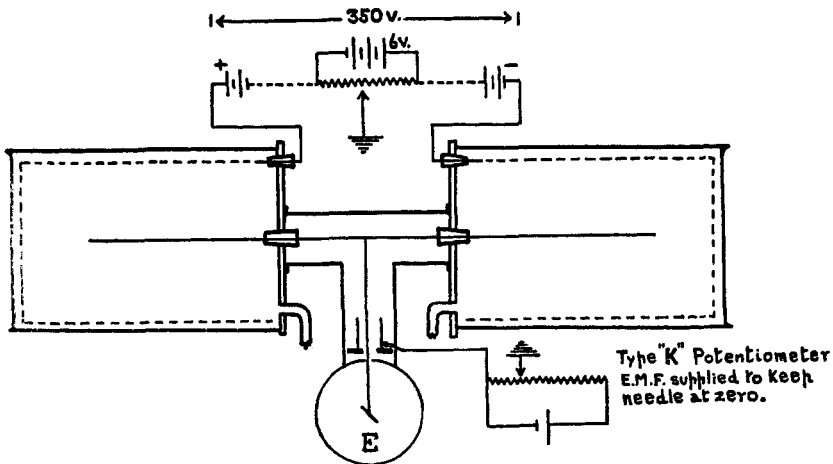


FIG. 7. DIAGRAM OF THE ARRANGEMENT OF THE APPARATUS FOR THE DETERMINATION OF RADIUM

the measurement. In order to overcome this difficulty Halle-dauer (34) set up two identical chambers, the one containing the emanation and the other a control, so operated that the needles of both were allowed to charge up almost simultaneously for a given time, a slight difference in simultaneity being necessary to allow time to take the electrometer reading by the charge-sharing method, using the same electrometer for both chambers. Paneth and Koeck (30) have considerably modified this method, so that with quantities of from five to ten grams they were able to measure with a moderate degree of accuracy the minute radium content of the iron meteorites. The charge-sharing method

has the disadvantage of requiring a very careful distribution of the various mechanical parts and exacting manipulation precautions in order not to change the capacities of the systems. The logical outcome of the above method was the development of the compensated system, which is shown diagrammatically in figure 7. The net arrangement used reduces the secondary effects at the walls, and the method of charging the ionization chambers oppositely cancels out the natural ionization, since the cause of this ionization must act equally on both chambers. This method also has the advantage of being able to apply a known voltage to a small ring condenser sufficient to keep the electrometer always at zero, thus eliminating leak errors.

On account of the very different life-periods of the radium and thorium emanations, different experimental procedures are necessary. Whereas in the case of the radium emanation it is sufficient to collect the whole in the chamber, with the thorium emanation the radioactive deposits of thoron must be collected by streaming through the solution containing the ThX, at a given rate for a given time. The ionization due to the deposits is then determined, the apparatus having been standardized by the same method with the active deposit from a known solution. Unlike the helium investigation, the measurement of radium in rocks has not been confined to a very few investigators, so that quite a detailed study of the distribution of radium can be made, whereas but few results are available for the helium content.

THE CALCULATION OF THE GEOLOGICAL AGE

The disintegration of the radioelements is a spontaneous process and as such may be written mathematically as:

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

where N is the number of atoms left after time t , N_0 being the original number present, and λ the disintegration constant. After a time t let N' be the number of helium atoms produced since zero time. Since there are seven other elements yielding α -particles in equilibrium with uranium, N' is equal to $N''/8$

where N'' is the measured number of helium atoms. Thus we have

$$N' = \frac{N''}{8} = N_0 - N = N_0 (1 - e^{-\lambda t}) \quad (2)$$

From equations 1 and 2 we have

$$e^{\lambda t} = \left[1 + \frac{N''}{8N} \right] \quad (3)$$

or, taking logarithms,

$$t = \frac{2.303}{\lambda} \log_{10} \left[1 + \frac{N''}{8N} \right] \quad (4)$$

The question of the value to be taken for λ_U is not such a matter for discussion as the choice of λ_{Th} treated below, since most of the determinations of the constant for uranium at least, agree fairly well. The value here employed is that chosen by Kovarik in his calculations (17), namely $\lambda_U = 1.52 \times 10^{-10} \text{ yr}^{-1}$. The helium value obtained in cubic centimeters per gram and the uranium in grams per gram must be converted into number of atoms, and the equation may be further reduced to the corresponding expression in terms of radium by including the factor found for radium to uranium of 3.40×10^{-7} under equilibrium conditions. We then obtain:

$$t \text{ (in years)} = 1.515 \times 10^{10} \log_{10} \left[1 + \frac{4.518 \times 10^{-10} \text{ He}}{\text{Ra}} \right] \quad (5)$$

This formula may be reduced to the following approximate equations:

$$t \text{ (in years)} = \frac{\text{He}}{\text{U}} \times 8.8 \times 10^6 = \frac{3 \times \text{He}}{\text{Ra}}$$

All the ages here given have been calculated by the exact formula 5. The above approximate formulas do not take into account the wearing out of the uranium. The ages of the iron meteorites as quoted by Holmes (35) were inadvertently corrected for this wearing out, and since they were originally obtained by the use of

equation 5 the original data are correct. The error introduced by the use of the approximate formulas is usually within the experimental error for material less than about 300 million years old. Unlike some of the minerals used in the lead method, the rocks and minerals suitable for the helium method invariably contain thorium. Thus the age calculated by equation 5 will be a maximum, and to the radium in the denominator of the bracketed portion must be added the uranium equivalent, for the generation of helium, or the thorium present also reduced to terms of radium. Table 5 indicates the necessity for the determination of thorium.

TABLE 5*

The effect of varying proportions of thorium to the uranium present in lowering the age determined from the radium only

$\frac{\text{Th}}{\text{U}}$	AGE IN MILLIONS OF YEARS FROM EQUATION 5		
	550	1296	2174
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.25	4.9	4.5	4.2
0.50	8.9	8.3	8.0
1.00	16.5	15.7	14.9
2.00	28.4	27.2	25.9

* This table was compiled assuming $\lambda_{\text{Th}} = 0.42 \times 10^{-10} \text{ yr}^{-1}$. A revision of the choice of this constant will be discussed below.

A preliminary survey shows that the proportion of thorium to uranium present in the iron meteorites is such that the values given in table 7 may be expected to be at the most about 10 per cent too high through neglecting thorium. In the rocks, however, the ratio is probably between 1.0 and 3.0 and possibly higher, hence to obtain any result even approximating the correct age thorium must be measured. Bearing in mind that the thorium series yields only six helium atoms compared to eight from the uranium series and that the rates of disintegration are different, the equivalent of thorium in terms of radium is given by,

$$\text{Th/Ra} = \frac{6 \times 238.14 \times \lambda_{\text{Th}}}{8 \times 232.15 \times \lambda_{\text{U}}} \times 3.40 \times 10^{-7}$$

The difficulty arises in the choice of λ_{Th} . Rutherford and Geiger (36) by the counting method found $\lambda_{\text{Th}} = 5.33 \times 10^{-11} \text{ yr}^{-1}$. Kirsch (37) by quite another method has found a value of $4.2 \times 10^{-11} \text{ yr}^{-1}$. Kovarik deduces a probable ratio of 3.85 from some of Kirsch's later work. This corresponds to a value of $3.95 \times 10^{-11} \text{ yr}^{-1}$. Taking Rutherford and Geiger's value the equivalent factor becomes $9.17 \times 10^{-8} \text{ Th}$ (expressed in grams per gram), or using Kirsch's result $7.23 \times 10^{-8} \text{ Th}$. The full equation is then:

$$t \text{ (in years)} = 1.515 \times 10^{10} \log_{10} \left[1 + \frac{4.518 \times 10^{-10} \text{He}}{(\text{Ra} + 9.17 \times 10^{-8} \text{Th})} \right] \quad (6)$$

The error involved in this uncertainty of λ_{Th} will naturally increase with increase in the proportion of thorium present. Thus for the ratio $\text{Th}/\text{U} = 1/2$, a difference of 2.2 per cent in the age is found between the above two values of the equivalent factor. This rises to 3.8 per cent for the ratio $\text{Th}/\text{U} = 1$ and to 5.3 per cent for the ratio 2. In most cases this error will be less than the experimental error.

The effect of the inclusion of the actinium series with the uranium series

The work of Aston (6), Fenner and Piggot (18), Rutherford (38), and recently v. Grosse (39) shows that the origin of the actinium series may be not a branching of the uranium series but a start from an isotope of uranium. If this isotope were to disintegrate at a very much greater rate than UI, then we might expect, even though it is present in only a very small amount, a considerable discrepancy in the age. It can be shown that such is not the case, however. The measured uranium will consist of UI and actinouranium. We have then:

$$\text{UI} + \text{AcU} = \text{U} \quad (7)$$

If we designate the helium from UI as H_{U} and from AcU as H_{Ac} then:

$$\text{H}_{\text{U}} + \text{H}_{\text{Ac}} = \text{He (total)} \quad (8)$$

v. Grosse has found that, independent of any variables, the activity ratio of the actinium to the uranium series is 0.04. Thus we have:

$$\frac{\text{AcU}}{\text{UI}} = 0.04 \frac{\lambda_{\text{UI}}}{\lambda_{\text{AcU}}} \quad (9)$$

From equations 7 and 9 we get:

$$\frac{\text{U}}{\text{UI}} = 1 + 0.04 \frac{\lambda_{\text{UI}}}{\lambda_{\text{AcU}}} = 1.0034 \quad (10)$$

From the radioactive law we have:

$$\text{UI} = \text{UI}_0 e^{-\lambda_{\text{UI}} t} \quad (11)$$

$$\text{AcU} = \text{AcU}_0 e^{-\lambda_{\text{AcU}} t} \quad (12)$$

In a similar manner to the derivation of equation 3 and remembering that the uranium series gives eight α -particles to the actinium seven we have:

$$\text{H}_U = 8\text{UI}(e^{\lambda_{\text{UI}} t} - 1) \quad (13)$$

$$\text{H}_{\text{Ac}} = 7\text{AcU}(e^{\lambda_{\text{AcU}} t} - 1) \quad (14)$$

From equations 9, 13, and 14 we have:

$$\frac{\text{H}_{\text{Ac}}}{\text{H}_U} = \left[\frac{7}{8} \times 0.04 \times \frac{\lambda_{\text{UI}}(e^{\lambda_{\text{AcU}} t} - 1)}{\lambda_{\text{AcU}}(e^{\lambda_{\text{UI}} t} - 1)} \right] = r \quad (15)$$

Taking logarithms in equation 13 and combining with equations 15 and 8:

$$t = \frac{2.303}{\lambda_{\text{UI}}} \log_{10} \left[1 + \frac{\text{He (total)}}{8\text{UI} (1+r)} \right] \quad (16)$$

A. C. Lane, in an address to the Annual Meeting of the American Mineralogical Society (1932), has pointed out that the disintegration constant of uranium as measured is that of the sum effect of UI and AcU, they being isotopes. Knowing this value and the tentative value of $\lambda_{\text{AcU}} = 1.73 \times 10^{-9} \text{ yr.}^{-1}$ as found by v. Grosse (39), and the activity ratio of 0.04 we obtain for λ_{UI} a value of $1.466 \times 10^{-10} \text{ yr.}^{-1}$. This value has been used in equation 10 to find $\text{U/UI} = 1.0034$. Putting in this value to

replace the unknown UI by U, the appropriate constants to reduce the uranium and helium to grams and cubic centimeters per gram respectively, and the U/Ra ratio, the final equation is:

$$t = 1.571 \times 10^{10} \log_{10} \left[1 + \frac{4.518 \times 10^{-10} \text{ He}}{\text{Ra} \times 0.9966 (1 + r)} \right] \quad (17)$$

For instance, with a helium-radium ratio of 5×10^{-8} using equation 5 we find an age of 1340 million years. It will be noticed that the term t occurs in the value of r (equation 15). We can, however, employ the value of t from equation 5 to evaluate r . t is then determined for the same He/Ra ratio from equation 17, r redetermined, and a new value of t found. By repeating this process the final value of t which fits equation 17 is found to be 1263 million years, or 5.75 per cent lower than that calculated when the effect of the actinouranium is not taken into account. Moreover, by changing the activity ratio and the disintegration constant considerably, the percentage difference is not greatly altered. This is due to the presence of actinouranium being partly taken into account in equations 5 and 6 by the use of the disintegration constant of the mixture of UI and AcU. As the proportion of thorium increases, the error in neglecting to treat the problem by equation 17 becomes smaller. Having regard to the present accuracy of the analyses, equation 6 may be used especially for the younger rocks and minerals.

THE RESULTS

The age of the meteorites

The first determinations of the age of the meteorites were made by Paneth, Gehlen, and Guenther (31) in 1928. The helium was determined by the method here described, but the measurements were made by the McLeod method. The radium contents are those given by Halledauer (34) except in the case of Toluca, which was determined by Quirke and Finkelstein (40). Table 6 gives the results of the preliminary investigation. The average radium content of the meteoric types is given by Urry (41) as; iron, 2.5×10^{-14} , pallisitic (stone and iron) 7×10^{-14} , stony (Chondritic) 12×10^{-14} , and achondritic 20×10^{-14} gram per gram.

Owing to the possible inhomogeneity previously mentioned it was at once seen necessary to make the complete analysis on one and the same sample. Accordingly the Halledauer method and later the compensated method of measuring these border line radium contents was developed by Paneth and Koeck (30), and the accurate measurement of helium by a modified Pirani-Stern manometer system was worked out by Paneth and Urry (28) in the same laboratory. In table 7 both measurements are made on the same sample. The necessity for the analysis on the same sample is brought out in table 8, where the helium contents of some of the accessory minerals of the iron meteorites and of the iron and stone portions of the pallasites are given. In the case of

TABLE 6
The ages of the meteorites

NAME	He $\times 10^6$	Ra $\times 10^{14}$	AGE IN MILLIONS OF YEARS
Savik.....	cc. per gram < 0.0002	grams per gram —	
Toluca.....	1.2	21	16
Seeläsgen.....	2	—	
São Julião.....	2	—	
Mount Joy.....	9.7	4.7	570
Cocke County.....	14	4.0	930
Nelson County.....	20	1.8	2600

the latter, the higher helium content of the stone portion is at least partly due to the higher radium content, but it has also been suggested that the iron has entered the stone matrix at some later date. This can be determined when the radium contents are known.

The question of the origin of the meteorites, whether from our own planetary system or from interstellar space, has been fully discussed by Paneth in a lecture to the Bunsen Gesellschaft (24) in the light of these results. If we accept the long period for the universe, the age of our solar system is most probably only of the order of one-thousandth of the age of the universe or on the short period estimate about one-third. If only some of the meteorites

TABLE 7*
The age of the meteorites

NAME	He × 10 ⁶	Ra × 10 ¹⁴	AGE IN MILLIONS OF YEARS
Savik (Cape York).....	<i>cc. per gram</i> < 0.0002	<i>grams per gram</i> < 0.2	—
Coahuila.....	0.23	—	—
Uwet.....	0.39	—	—
Bethany, Farm Goamus.....	0.48	—	—
	0.42	1.3	100
Bethany, Farm Gröndorn.....	0.49	—	—
Löwenfluss.....	0.47	—	—
Braunau.....	0.53	—	—
Canon Diablo.....	1.05	—	—
Magura.....	1.19	—	—
San Martin, Chile.....	2.13	1.4	420
Copiapo.....	2.51	—	—
Santa Rosa, Colombia.....	3.14	—	—
Nejed.....	3.7	—	—
Tamarugal.....	4	2.0	550
Seeläsgen.....	4.87	4.9	120
Cranbourne.....	4.96	0.8	1600
Augustinowka.....	5.21	—	—
Toluca.....	5.82	17.0	100
Arispe.....	7.22	1.3	1500
Mooranoppin.....	7.54	—	—
Narraburra Creek.....	11.44	—	—
Wichita County.....	11.50	1.3	2100
San Angelo.....	11.86	4.2	800
N'Goureyma.....	13.91	2.9	1250
Hraschina.....	14.9	2.6	1450
Sacramento Mts.....	15.03	2.5	1550
Seneca Falls.....	15.03	2.0	1900
Charcas.....	15.65	4.4	1000
Silver Crown.....	17.35	—	—
Staunton, Mass. III.....	18.82	2.1	2150
Staunton, Mass. V.....	18.92	2.4	2000
Joe Wright Mt.....	19.28	4.1	1200
Burlington.....	19.31	3.6	1400
Williamstown.....	20.77	2.1	2400
Lenarto.....	22.23	2.3	2300
Carthage.....	23.84	—	—
Thunda.....	28.57	2.3	2800
Mount Ayliff, South Africa.....	35.81	2.8	2800

* In all the determinations the helium and radium were measured in the same sample.

have an interstellar origin, we might expect to find some of an age older than that of the solar system. The ages given in tables 6 and 7 are maxima, but as may be seen from table 5 they would be reduced by only about 15 per cent, taking into account thorium in the ratio $\text{Th}/\text{U} = 1.0$, which according to V. M. Goldschmidt

TABLE 8
The helium contents of various portions of the meteorites

NAME	ACCESSORY PORTION		IRON PORTION
	Description	He $\times 10^6$	He $\times 10^6$
Magura.....	Troilite (Sulfide)	<i>cc. per gram</i> 0.13	<i>cc. per gram</i> 1.19
		0.09	
Seeläsgen.....	Troilite	2.73	4.87
		2	
Cranbourne.....	Troilite	3.13	4.96
		1.40	
Wichita County.....	Troilite	9.07	11.50
Santa Luzia.....	Rind (Oxide)	1.06	—
	Schreibersite (Phosphide)	1.25	—
Brenham (Pallasite).....	Stone (Olivine)	6.36	
		6.87	1.11
Krasnojarsk (Pallasite).....	Stone weathered away	—	1.21
Mincy (Pallasite).....	Stone	21.7	4.81

is the upper limit of the thorium content of such material. However, even neglecting this correction, the oldest found meteorites are not over the possible border line of the time of formation of the solar system. Taking into consideration the thorium, the ages of some meteorites are still greater than the oldest known minerals estimated by the lead method.

The age of the substance of the earth

As has previously been mentioned, following the success of the preliminary investigation of the meteorites, Holmes and Dubey attacked the problem of the estimation of geological age by the helium method. Their results have already been given in table 3. Tables 3, 6, and 7 probably contain all the present available modern determinations, but the results of the prolonged studies of Strutt (Lord Rayleigh) already referred to should not be omitted from consideration in this problem. Space does not permit the inclusion of his results, which have conveniently been tabulated in the two books of previous reference (9). The author, in collaboration with Professors A. C. Lane and F. Paneth, has under completion a study of the ages of a comprehensive series of the Keweenaw rocks and minerals. The helium content of these fine-grained basalts was found to vary between 195×10^{-6} and 14.5×10^{-6} cc. per gram, but the copper minerals were found to contain much less, the lowest being 0.17×10^{-6} . The native copper contained in 32 grams between 10^{-9} and 10^{-10} cc. of helium. This infers from an approximate knowledge of the age that the radium content of the copper would be too small to detect, as was actually the case. The radium contents of the Keweenaw rocks have been published (42), but the ages cannot be given until the thorium contents have been accurately measured.

CONCLUSION

There thus remains open a very wide field of research on the rocks, one of the most prolific materials of the earth's crust, the results of which will be of great interest in the building up of a closely graded geological time scale, but the applications are not limited to the geological field; nature has supplied us a source of cosmic material in the form of meteorites to aid our probe, at least, into interplanetary space.

APPENDIX I

The age of a radioactive mineral is given by a knowledge of the ratio $\frac{\text{Original uranium}}{\text{Present uranium}}$. If the crystal network has remained

unchanged, and there is evidence of such in at least one uraninite, then, as A. C. Lane has suggested, the total oxygen associated with the uranium and lead present in the uraninite today is to the original uranium as the ratio of oxygen to uranium in UO_2 . This oxygen is distributed at present in the forms UO_2 , UO_3 , and PbO . In analysis reports the oxygen of the lead monoxide is usually counted twice, and thus to find the oxygen associated with the original uranium as UO_2 , one calculates the oxygen of the present day $\text{UO}_2 + \text{UO}_3$ found by analysis. Having determined this quantity, the amount of original uranium is calculated from the formula UO_2 . The present uranium is known by analysis and hence the age can be determined. The Wilberforce uraninite referred to above is the only material on which the fivefold check of the age has so far been applied. The results are shortly to be published by A. C. Lane.

REFERENCES

- (1) MEYER, S., AND V. SCHWEIDLER, E.: *Radioaktivitaet*. Teubner, Berlin (1927).
- (2) RUTHERFORD, CHADWICK, AND ELLIS: *Radiations from Radioactive Substances*. Cambridge University Press, England (1930).
- (3) v. HEVESY, G., AND PANETH, F.: *Lehrbuch der Radioaktivitaet*. J. A. Barth Verlag, Leipzig (1931).
- (4) RUTHERFORD AND SODDY: *Phil. Mag.* [5] **441**, 561 (1903).
- (5) RAMSAY AND SODDY: *Proc. Roy. Soc. London* **A72**, 204 (1903); **A73**, 346 (1904).
- (6) ASTON, F. W.: *Nature* **123**, 313 (1929).
- (7) BOLTWOOD, B. B.: *Phil. Mag.* [6] **9**, 599 (1905); *Am. J. Sci.* [4] **23**, 77 (1907).
- (8) RUTHERFORD, E.: *Popular Science Monthly* **67**, 34 (1905).
- (9) *Bull. Natl. Research Council*, No. 80. *The Age of the Earth*. Washington, D.C. (1931); *Abegg's Handbuch der anorganischen Chemie*, IV, 3. Erster Teil. Verlag S. Hirzel, Leipzig (1928).
- (10) ASTON, F. W.: Reference 6, and *Nature* **120**, 224 (1927).
- (11) HEVESY AND PAHL: *Nature* **129**, 846 (1932).
- (12) JEANS, SIR JAMES: *The Universe Around Us*. Macmillan Co., New York (1929).
- (13) MAXWELL, L. R.: *Nature* **122**, 997 (1928).
- (14) COCKCROFT AND WALTON: *Proc. Roy. Soc. London* **A137**, 229 (1932).
- (15) URRY, WM. D.: *Nature* **130**, 777 (1932).
- (16) HOLMES, A.: *Bulletin No. 80*, see Reference 9. *Radioactivity and Geological Time*, Chap. II, p. 159.
- (17) KOVARIK, A. F.: *Bull. Natl. Research Council*, No. 80, Part III, p. 73.

- (18) See, however, KIRSCH, G., AND LANE, A. C.: Proc. Am. Acad. Arts Sci., **66**, No. 10 (1931), and FENNER, C. N., AND PIGGOT, C. S.: Nature **123**, 793 (1929).
- (19) WOOD, O. D.: Proc. Roy. Soc. London **A84**, 70-8 (1911).
- (20) PANETH, F., AND PETERS, K.: Z. physik. Chem. **B1**, 3/4, 253 (1928).
- (21) PIUTTI, A.: Z. Elektrochem. **28**, 452 (1922).
PIUTTI, A., AND BOGGIO-LERA, E.: Atti accad. Lincei [5] **14**, (1923).
- (22) PANETH, F., AND PETERS, E.: Z. physik. Chem. **134**, 5/6, 353 (1928); **B1**, 1/2, 170 (1928); and reference 20.
- (23) URRY, WM. D.: J. Am. Chem. Soc. **54**, 3887 (1932).
- (24) PANETH, F.: Naturwissenschaften **19**, 7, 164 (1931).
PANETH, F., AND URRY, WM. D.: Z. physik. Chem. **A152**, 1/2, 127 (1931);
Z. Elektrochem. **36**, 727 (1930).
- (25) DUBEY, V. S., AND HOLMES, A.: Nature **123**, 794 (1929).
- (26) DUBEY, V. S.: Nature **126**, 807 (1930).
- (27) HOLMES, A.: Bull. Natl. Research Council, No. 80, see reference 9, p. 411.
- (28) PANETH, F., AND URRY, WM. D.: Z. physik. Chem. **A152**, 1/2, 110 (1931).
- (29) NODDACK, I. AND W.: Naturwissenschaften **18**, 757 (1930).
- (30) PANETH, F., AND KOECK, W.: Z. Physik. Chem., Bodenst.-Festband, p. 145 (1931).
- (31) PANETH, F., GEHLEN, H., AND GUENTHER, P. L.: Z. Elektrochem. **34**, 645 (1928).
- (32) SODDY, F.: Phil. Mag. [6] **16**, 513 (1908).
- (33) STRUTT, R. J.: Proc. Roy. Soc. London **A89**, 499 (1914).
- (34) HALLEDAUER, G.: Ber. Wien. Akad. **134**, 39 (1925).
- (35) HOLMES, A.: Bull. Natl. Research Council, No. 80, see reference 9, p. 423.
- (36) RUTHERFORD, E., AND GEIGER, H.: Phil. Mag. [6] **20**, 691 (1910).
- (37) KIRSCH, G.: Ber. Wien. Akad. **131**, IIa, 551 (1922).
- (38) RUTHERFORD, E.: Nature **123**, 313 (1929).
- (39) v. GROSSE, A.: Phys. Rev. **42**, 4, 565 (1932).
- (40) QUIRKE, T. T., AND FINKELSTEIN, L.: Am. J. Sci. [5] **44**, 237 (1917).
- (41) URRY, WM. D.: Proc. Am. Acad. Arts Sci., Part II, **68**, 4, 137 (1933).
- (42) URRY, WM. D.: Proc. Am. Acad. Arts Sci., Part I, **68**, 4, 125 (1933).