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Final Technical Report

Contract N6 onr 271 Task Order 18

The Ionium Method of Age Determination

January 1955

Lamont Geological Observatory

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Task Order 18

Final Technical Report

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Abstract

The Ionium Method of age determination, applicable to deep sea sediments over the past 400, 000 years, has been studied in an attempt to define its limitations and conditions. The mathematical theory on which the method is based is given in detail as are the various techniques and measurements used in obtaining the data. These measurements include total radium and gas phase radon by low-level ionization chamber techniques, total alpha emission by scintillation counting, and absolute surface area determination by gas adsorption. These techniques were employed on a number of deep ocean cores from the Atlantic and Pacific Oceans and the Caribbean Sea.

The geological theory on which the Ionium Method is based was discussed in some detail. In order for the method to apply a chronologically undisturbed sediment column must be present and the sediment must be homogeneous with regard to chemisorption potential.

A complete age analysis was carried out on two cases, one a red clay core from the Pacific and the other a globigerina ooze core from the Caribbean. This analysis emphasizes the source of error. For those cores that meet the geological requirements, the accuracy of the dates is largely dependent on the accuracy of the radium determination and the frequency with which the samples are taken along the core.

From these two cores rates of sedimentation can be calculated with fair precision. From 200, 000-300, 000 years ago until 30, 000-40, 000

the rates of sedimentation were apparently constant for the red clay at 0.15±.05 cm./1000 years and for the globigerina ooze at 0.60±0.20 cm./1000 years. During the last 30,000 years the rates of sedimentation for both sediment types have increased by at least factors of 2-4. This is ascribed to the increased erosion rate and world-wide temperature rise since the peak (~40,000 years ago) of the Wisconsin glaciation. The lack of evidence for a similar increase in rate in earlier glacial periods is probably due to the sparse experimental data and the relative insensitivity of the method to changes in the rate of sedimentation over relatively short time intervals.

Preliminary experiments in which ionium and C^{14} dating were done on the same cores confirm the validity of the Ionium Method and indicate that the integrated cosmic ray flux has not changed by more than 20% any time during the past 30,000 years.

The Ionium Method holds considerable promise as a dating technique but it is limited to restricted areas of the deep ocean floor. Future applications should aid greatly in establishing average sedimentation rates on the ocean floor as well as permitting world-wide correlation of climatic change during the Pleistocene.

I. Introduction

In the last decade a number of laboratories have been investigating the absolute dating of geological materials. This research has already produced or extended several reliable age methods which will add greatly to knowledge of the origin and development of the earth's crust. These methods, such as those based on the radioactive decay of U^{238}, U^{235}, Th^{232}, or C^{14}, are applicable to more than 99 per cent of geologic history, spanning more than three billion years. The remainder, less than one-tenth of one per cent of the lifetime of the planet, comprises the span from 30,000 to about 10,000,000 years ago. Although this undated portion is but a small fraction of all geologic time, its importance is great for two reasons: (a) this most recent increment of geologic history provides more details of earth processes than any other, and, (b) it covers the major climatic changes of the Pleistocene period which accompanied repeated continental glaciation. If the rate of these processes and changes can be determined, it may be extrapolated to all earlier periods of earth history.

In theory, the Ionium Method of Age Determination based on the inequilibrium relationships of radioelements of the uranium-238 series is applicable to a portion of this time span, i.e., from the present to about 500,000 years ago. Unlike some of the other available dating methods which measure the ratio of final products to the long-lived parent in equilibrium decay, this method depends upon the decay of ionium to equilibrium with its parent and daughter. The inequilibrium, brought about by the preferential adsorption of ionium ions by the particles of sediment depositing on the ocean floor, is expressed by changing concentrations of the radioelements with depth in the sedimentary column. Thus the samples used in this method are cores of sediment obtained from the ocean floor.

A quantitative dating method specifically applicable to oceanic sediments of the last one-half million years could do a great deal to clarify several important geological problems such as the exact time for the subdivisions of the Pleistocene period, the time for a continental glacier to grow and decay, and the rate of sediment accumulation in the ocean basins. This study was initiated to examine some of the assumptions of the Ionium Method and to define its area of application.

It is concluded that the method is valid for deep sea sediments which are homogeneous and which have been produced through normal sedimentation processes. The kinds of measurements required to obtain reliable dates are also defined. No actual core has yet been measured which satisfies these conditions with enough rigor to yield highly precise dates. Nevertheless, several measurements on cores prove the validity of the Ionium Method.

Historical Development

Since early in this century it has been known that certain deep sea sediments near the surface of the ocean floor contain abnormally high concentrations of radium. The mechanism of concentration of this radium has been the subject of much study and speculation.

(1) Joly (1908) suggested direct precipitation of radium or a radium compound from ocean water unsupported by any of its long-lived parent radioelements. This seemed unlikely because of the relatively short half-life of radium. Since the half-life of radium is only about 1600 years, and the excess radium only 2-20 times that for equilibrium with the uranium, the unsupported radium would be negligible in about 10,000 years. Considering both observed and calculated rates of sedimentation, this 10,000 years would encompass a maximum of only the top 10 to 20 centimeters of the deep ocean floor. It has, however, been observed that the excessively high radium contents persist to depths of usually 50 to 100 centimeters and in some cases even to 200 centimeters.

(2) In later studies the high radium concentrations were explained as being uranium supported; that is, that the uranium series are in radioactive equilibrium (Joly, 1908a; Piggot, 1933). For this explanation to be valid, however, uranium concentrations in deep sea sediments would have to be higher than those observed by approximately a factor of 100. Further, on this hypothesis, it would be expected that the radium content would remain essentially constant at the high value through much greater depths than the 50 to 200 centimeters observed, since the uranium half-life is so large (about 5×10^9 years).

(3) H. Pettersson (1930, 1938, 1953) studied the radium content of ocean water and compared the observed values with uranium concentrations of similar deep sea water samples. He found that the relative concentrations of the two elements in sea water are far from being in radioactive equilibrium. The values indicate that either uranium is concentrated or radium is depleted in ocean water by approximately a factor of six. Pettersson concluded from this study that apparently 84% of the radium produced from the dissolved uranium is withdrawn from oceanic circulation. Next Pettersson compared the relative concentrations of thorium in continental rocks and sea water. The thorium was found to be greatly depleted in the ocean. In continental rocks thorium is higher in concentration than uranium by a ratio of generally about 3:1. In the sea, however, this ratio was found to be approximately 0.01 : 1(Koczy, 1949). On the basis of these data, Pettersson suggested that an ocean wide precipitation of the mother isotope of radium (Th 230), was the significant cause of radium enrichment in the deep sea sediments. This isotope of thorium decays by alpha emission to radium with a half-life of about 83,000 years, and is called ionium.

(4) C.S. Piggot and W.D. Urry studied the radium concentration of deep ocean sediment from several cores and observed a characteristic behavior with depth (Piggot and Urry, 1939, 1941, 1942; Urry and Piggot, 1942). If radium concentration is plotted against depth, the curve ideally showed a peak in radium content a short distance below the top of the

core which smoothly diminished with depth. On the basis of these data they proposed an age determination method based on the relative concentrations of uranium, ionium and radium in deep ocean cores. (Piggot and Urry, 1942a; Urry, 1942, 1948, 1948a, 1949). The increasing radium content in the upper portion of the core was attributed to the approach to radioactive equilibrium between radium and ionium. This was followed by decreasing radium content which was attributed to the approach to equilibrium of ionium and uranium. Since the half-life of ionium is about 83,000 years, it should be possible to follow the changing radium content in the core back in time about 500,000 years.

(5) Holland and Kulp (1954) studied the mechanism of removal of ionium and radium from ocean water. Using short-lived radioisotopes of thorium and radium they concluded that base exchange phenomena play the important role in the removal of ionium and radium from ocean waters on the surface of deep ocean sediments. They further suggested that the Ionium Method of Age Determination is applicable only to core samples having equivalent base exchange properties with respect to ionium and radium.

Outline of the Problem

As may be inferred from the foregoing account of the historical background of the Ionium Method of Age Determination, a fairly large number of radium determinations on deep sea cores have been made, but aside from the mechanism study by Holland and Kulp the fundamental conditions and assumptions upon which the method is based have not been experimentally investigated. The work of Holland and Kulp showed that thorium is chemisorbed with a much greater affinity than radium in the concentration range of these elements in sea water. Radium in turn was adsorbed preferentially to uranium. Therefore, with the reconnaissance experimental work completed and the basic chemical mechanism established, the next step is to study the area of application, the potential accuracy and the limitations of the Ionium Method. This is the purpose of the present investigation.

Measurements were carried out on selected ocean bottom cores from the large collection at the Lamont Geological Observatory, along with several other cores obtained through the cooperation of Dr. J. L. Hough and Dr. W. D. Urry. The purpose of these additional measurements was two-fold. (1) It was desirable to examine a wider variety of cores than had been selected previously. (2) A number of scientists both here and abroad have been skeptical of the results obtained by Urry and Piggot on the more ideal cores. The measurements reported here, made with quite different experimental techniques, generally confirm the work of Urry and Piggot.

The sediment samples were studied by several different methods in order to test various aspects of the theory. The measurements used were: (a) scintillation counting, to determine the total alpha emission: (b) fusion, to determine the radium content within sediment particles; (c) radon leakage, to determine the radon content in the gas phase; and,

(d) surface area measurements, to determine the absolute surface available to ions in solution.

An analysis of these measurements along with the data of other investigators makes it possible to resolve the conflicting opinions regarding the validity of the Ionium Method of Age Determination and define its area of application.

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Several of the critical core samples were supplied by Dr. W. D. Urry and J. L. Hough. Dr. Urry and Dr. P. M. Hurley contributed helpful discussions of many phases of this study and Dr. Hurley permitted the author to spend some time in his laboratory studying the techniques employed there. Dr. H. D. Holland aided considerably in the early phases of the project. Dr. M. Ewing, Director of the Lamont Geological Observatory of Columbia University, made available the Lamont core collection and consistently encouraged the project. Mr. D. B. Ericson, micropaleontologist at the Lamont Observatory, contributed very helpful discussions of the lithologic and stratigraphic details of the cores.

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II. Theory

General Statement:

The Ionium Method of Age Determination was proposed by Piggot and Urry (1939, 1941, 1942, 1942a) and Urry and Piggot (1942) on the basis of data obtained by measuring the radium content of a core taken from the ocean floor as a function of depth. An idealized average of their experimental curves is illustrated by Figure 1.

Ions of the radioelements of the Uranium 238 series dissolved in sea water are adsorbed on the surfaces of ocean floor sediments. These muds are made up of particles of rock flour, clay minerals and microscopic shells . The ratios of the concentrations of these ions on the surfaces at the time of deposition differ greatly from the fixed ratios at radioactive equilibrium, due to the different base exchange capacities of the ions. Ionium (Th^{230}) is found on the surface in great excess of that necessary for equilibrium with the radium, while much less uranium is present than is required for equilibrium with either the radium or ionium. The build-up and decrease of radium content through the length of the core, is a function of time as established by the laws of radioactive disintegration, and is dependent upon the initial amounts of uranium, ionium and radium present on the surface of the particles. Therefore, the linear measure of depth in the core is a function of time in some complicated way. Figure 2 illustrates the theoretical plot of radium content versus time rather than depth, and indicates the various regions of the curve.

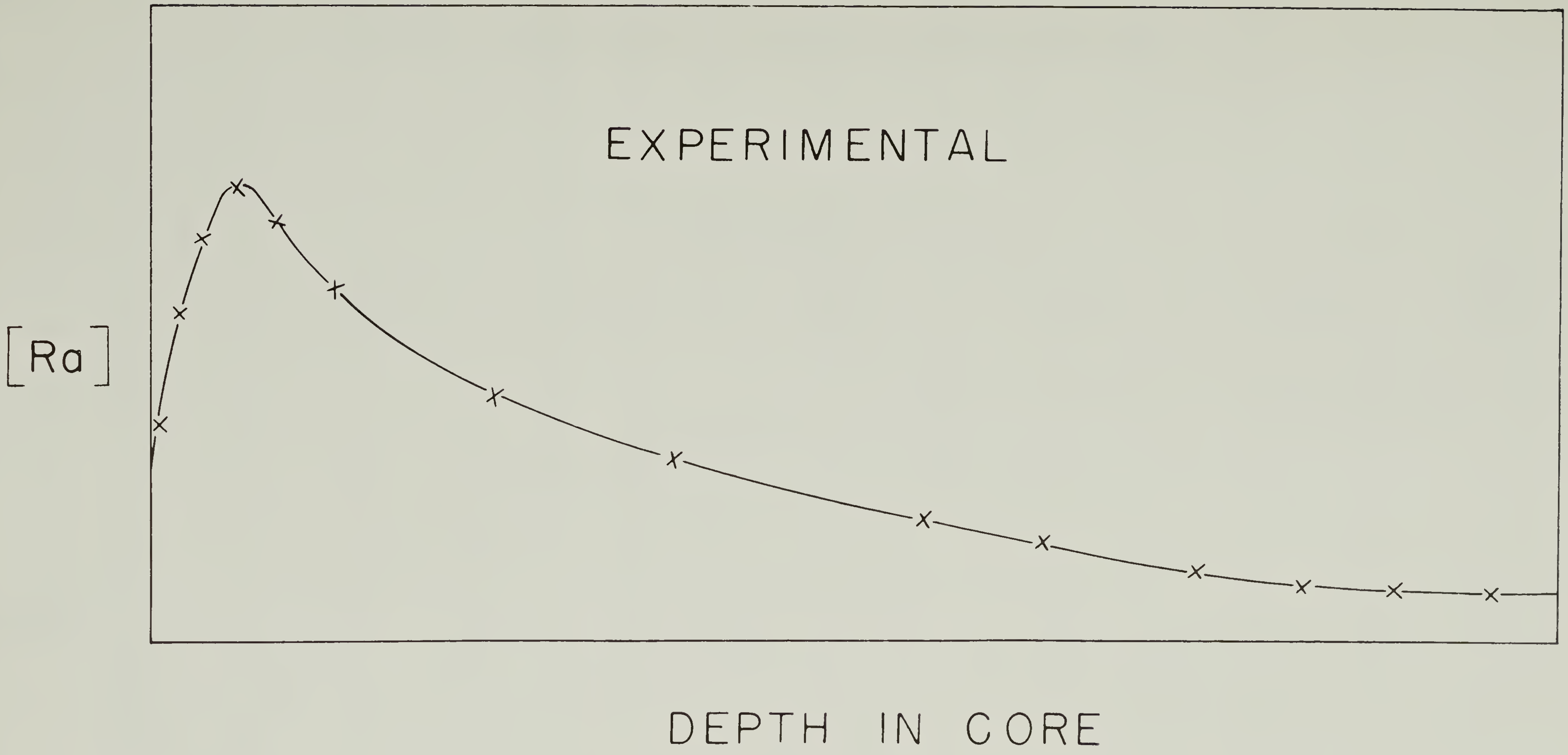

Figure 1. Radium content as a function of depth

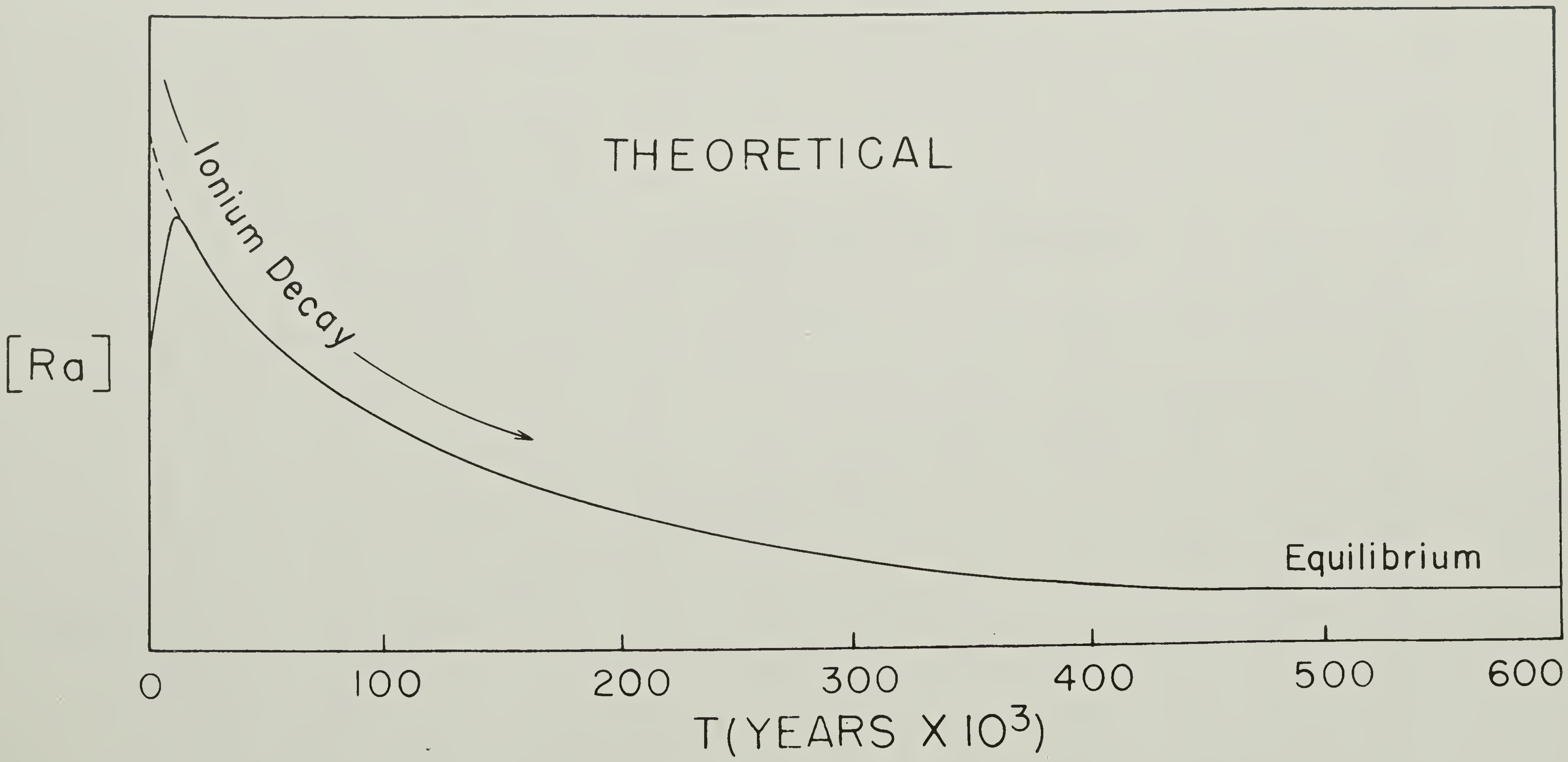

Figure 2. Radium content as a function of depth (theoretical).

The experimental curves obtained by Piggot and Urry (Figure 1) are thus explained in the following way. The initial increase in radium content is due to the production of radium by ionium at a rate in excess of the rate at which radium is decaying. Once equilibrium between ionium and radium has been achieved, the radium concentration is controlled by the decay of the ionium. The decreasing ionium concentration with depth in the core occurs because of insufficient uranium to support it. Finally radioactive equilibrium between all three elements is established when the uranium present is producing the same number of atoms of ionium as are disintegrating.

The theoretical treatment of the experimental data primarily aims at converting units of depth in the core to time intervals. The mathematical treatment of accomplishing this conversion has been given by Urry (1942) in what appears a most useful and efficient form, and the derivations included here are essentially identical.

Development of the General Equation

In the system under consideration, the problem is to express the approach to radioactive equilibrium of several members of the uranium 238 series . From Table 1 it is apparent that only three elements, U-238, Th-230, and Ra-226 are important, since U-234 is an isotope of uranium and Th-234 and Ra-226 have comparatively short half-lives. Thus the following relationships have been derived for the specific case of the three long-lived elements in the U-238 series, although they are applicable to any system of three successive radio elements.

Table 1

Uranium	U-238 (UI)	4.51×10^9	Years
Thorium	Th-234 (UX_1)	24.10	Days
Protactinium	Pa-234 (UX_2)	1.14	Min.
Uranium	U-234 (UII)	2.50×10^5	Years
Ionium	Th-230 (Io)	8×10^4	Years
Radium	Ra-226	1620	Years

Since the final product is radium, and this element can be determined quite rapidly and quantitatively in concentrations as low as 10^{-14} g radium per gram of sediment, (Bate, Volchok and Kulp, 1954), the problem is defined in terms of radium content as a function of time.

Symbols:

t_o = time of deposition of the sediment material

t = time elapsed since t_o

U_o = Number of atoms of uranium present at t_o

I_o = Number of atoms of ionium present at t_o

Ra_o = Number of atoms of radium present at t_o

Ra_t = Number of atoms of radium present at time, t

λU = Decay constant of uranium

λI = Decay constant of ionium

λR_a = Decay constant of radium

It is required to express the amount of radium present after any time t, when initially at $t=o$ there was present a complex mixture of radium and its ancestral elements.

The total number of radium atoms present after some time t, has originated from three sources: (1) radium atoms produced due to disintegration of original atoms of U-238, (2) radium atoms due to disintegration of original atoms of ionium, and (3) radium atoms remaining from original radium present. The equations for these three sources of radium have been solved, (Bateman, 1910), and may be written in the forms given below.

The number of atoms of radium Ra'_t, produced due to the disintegration of original U-238 atoms:

$$Ra'_t = U_0 \lambda_u \lambda_I \left[\frac{e^{-\lambda_u t}}{(\lambda_I - \lambda_u)(\lambda_{Ra} - \lambda_u)} + \frac{e^{-\lambda_I t}}{(\lambda_u - \lambda_I)(\lambda_{Ra} - \lambda_I)} + \frac{e^{-\lambda_{Ra} t}}{(\lambda_u - \lambda_{Ra})(\lambda_I - \lambda_{Ra})} \right] \quad (1)$$

Considering their relative values λ_U may be neglected compared with λ_I and λ_{Ra}. Equation (1) may then be re-written:

$$Ra'_t = U_0 \lambda_u \lambda_I \left[\frac{e^{-\lambda_u t}}{(\lambda_I \lambda_{Ra})} - \frac{e^{-\lambda_I t}}{\lambda_I(\lambda_{Ra} - \lambda_I)} + \frac{e^{-\lambda_{Ra} t}}{\lambda_{Ra}(\lambda_{Ra} - \lambda_I)} \right] \quad (2)$$

The number of atoms of radium Ra''_t, produced due to disintegration of original ionium atoms:

$$Ra''_t = \frac{I_0 \lambda_I}{(\lambda_{Ra} - \lambda_I)} \left(e^{-\lambda_I t} - e^{-\lambda_{Ra} t} \right) \quad (3)$$

The number of atoms of radium Ra'''_t, remaining from the original radium: $Ra'''_t = Ra_0 e^{-\lambda_{Ra} t}$ (4)

Thus the total number of radium atoms Ra_t present after time t is:

$$Ra_t = Ra'_t + Ra''_t + Ra'''_t \quad (5)$$

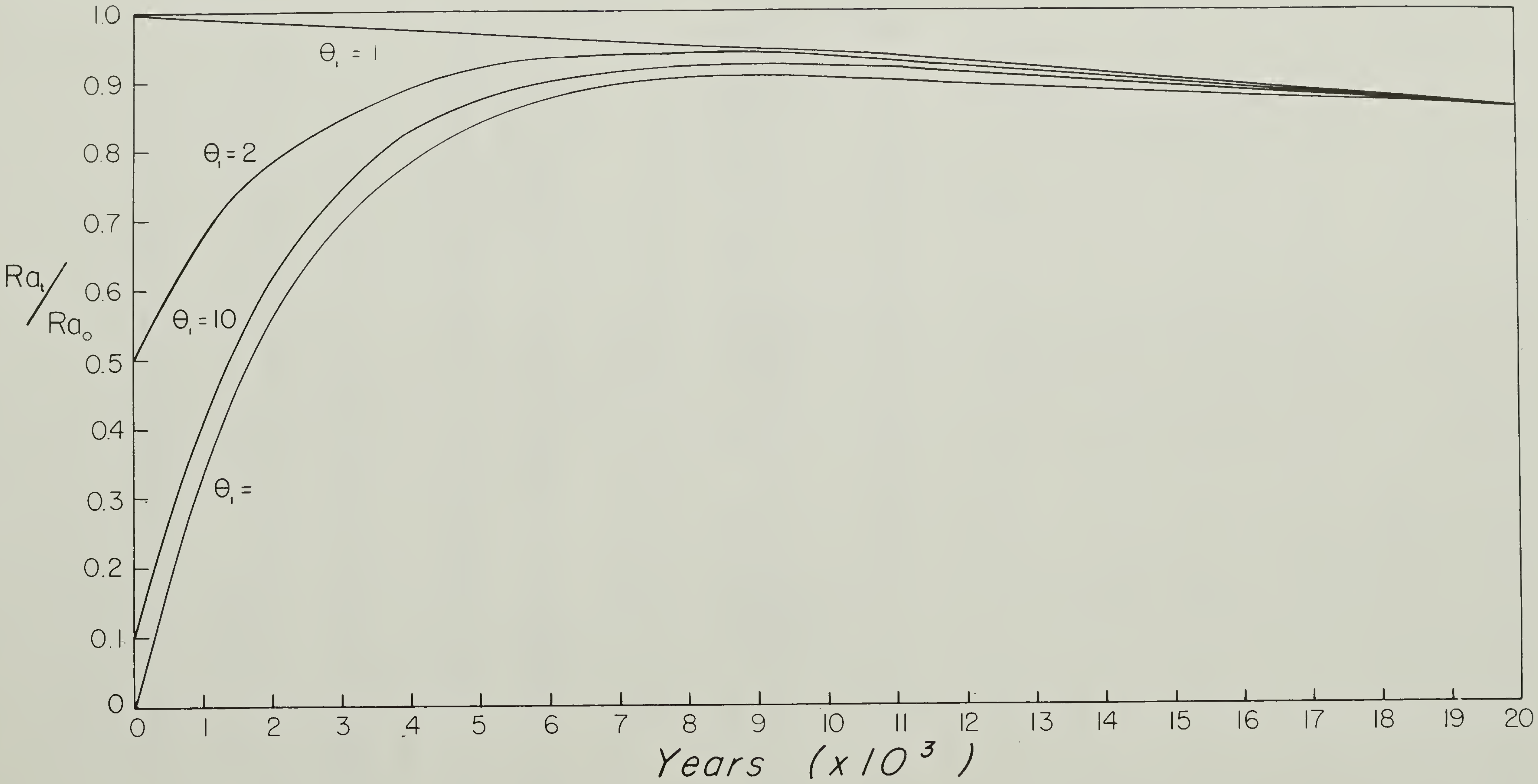

Figure 3. Variation of radium concentration as a function of time. $\Theta_2 = 0$ and various values of Θ_1

To perform the summation of equation (5) and obtain the solution in terms of radium only, the original amounts of uranium and ionium are expressed as ratios of the amounts which would be in equilibrium with the initial amount of radium. Thus two parameters θ_1 and θ_2 are defined such that:

$$\theta_1 = (I_0 \lambda_I)/(Ra_0 \lambda_{Ra}) \tag{6}$$

$$\theta_2 = (U_0 \lambda_U)/(Ra_0 \lambda_{Ra}) \tag{7}$$

substituting equations (6) and (7) into equations (2) and (3) and summing according to equation (5), the general relationship is obtained:

$$\frac{Ra_t}{Ra_0} = \theta_2 e^{-\lambda_U t} + \frac{\lambda_{Ra}(\theta_1 - \theta_2)}{(\lambda_{Ra} - \lambda_I)} e^{-\lambda_I t} + \frac{\lambda_{Ra}(1-\theta_1) - \lambda_I(1-\theta_2)}{(\lambda_{Ra} - \lambda_I)} e^{-\lambda_{Ra} t} \tag{8}$$

The values of Ra_t in equation (8), as a function of time t, may attain either a maximum or minimum value, or decrease or increase continuously, depending upon the values of θ_1 and θ_2. For radioactive equilibrium through the entire history, $\theta_1 = 1$ and $\theta_2 = 1$, and Ra_t, because of the long half-life of uranium is essentially constant through the length of the core. The concentrations of actual deep ocean cores studied, however, indicate $\theta_1 > 1$, and $\theta_2 < 1$. That is, ionium is in excess of that amount which would be in equilibrium concentration. This condition results in a general curve of Ra_t/Ra_0 vs. t showing a maximum. Figure 3 shows several curves of this function with various values of θ_1 and θ_2. For simplicity the curves were constructed with $Ra_0 = \theta_1$. These curves are typical of several experimental curves of

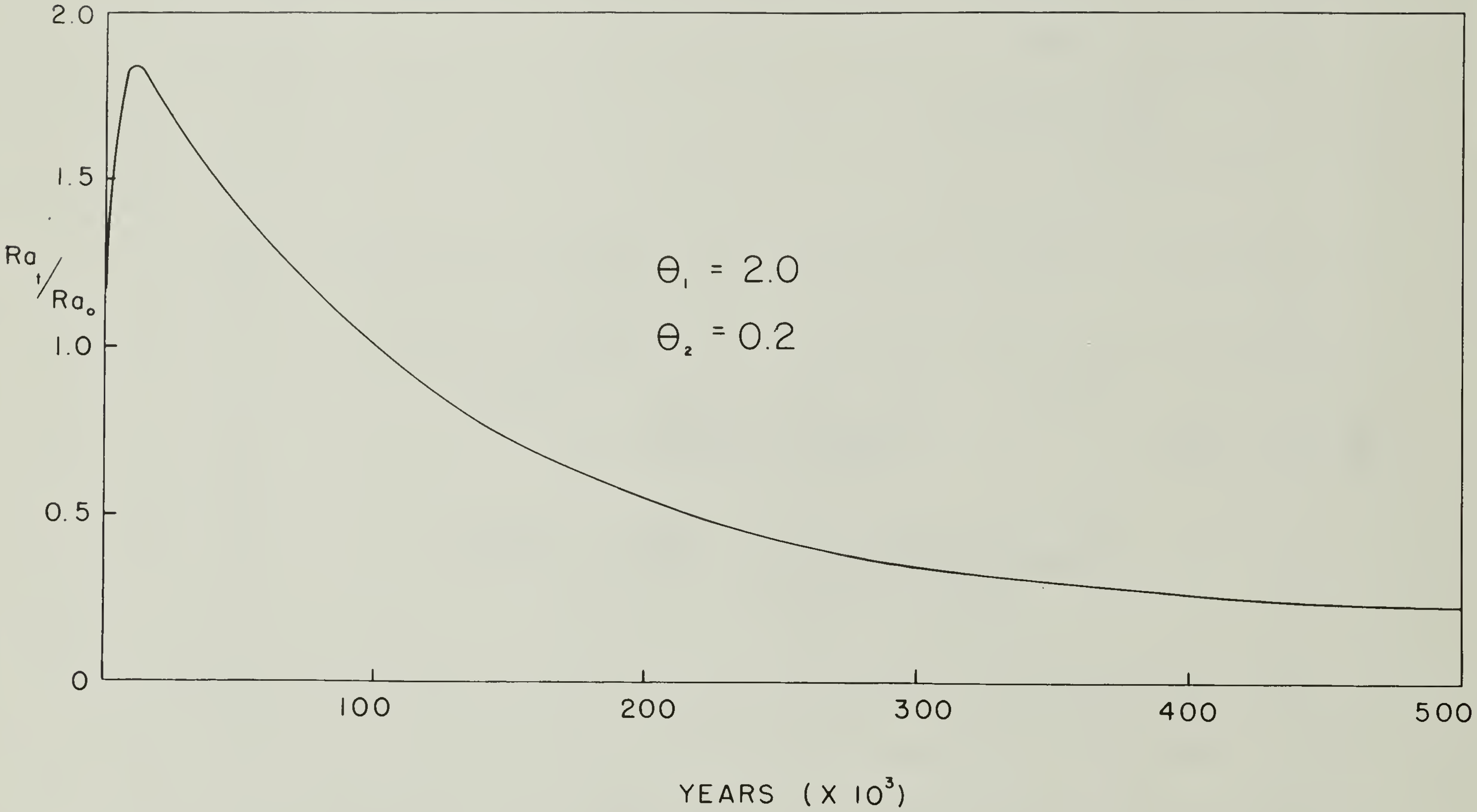

Figure 4. Variation of radium concentration as a function of time.

Urry and Piggot and also of those obtained in this laboratory. In the cores studied, values of Θ_1 ranged from about 1.2 to 2.7 while those of Θ_2 were from 0.06 to 0.62.

In Figure 4 one theoretical case ($\Theta_1 = 2.0$, $\Theta_2 = 0.2$) has been followed out to the attainment of equilibrium with the uranium present. This indicates that the practical limit of usefulness of this method of age determination is about 400,000 years.

Practical Solution of the General Equation

Some simplification of equation (8) is feasible because of the magnitude of certain of the constants and the practical limit on the time of 400,000 years.

In the first term of equation (8) the constant λ_u has a value of about 1.5×10^{-10}. Thus no value of time t up to 400,000 will make the exponential larger than unity. The first term of equation (8) therefore reduces to simply Θ_2.

In a similar manner, the last term of equation (8) has the constant λ_{Ra} which has a value of about 4.3×10^{-4}. In this case any value of time greater than about ,15,000 years will reduce the exponential term to essentially zero, so except for the cases younger than 15,000 years, the entire third term of equation (8) is negligible and may be omitted.

On this basis we may write for a general equation:

$$\frac{Ra_t}{Ra_o} = \Theta_2 + \frac{\lambda_{Ra}(\Theta_1 - \Theta_2)\, e^{-\lambda_I t}}{\lambda_{Ra} - \lambda_I} + \frac{\lambda_{Ra}(1 - \Theta_1) - \lambda_I(1 - \Theta_2)}{\lambda_{Ra} - \lambda_I}\, e^{-\lambda_{Ra} t} \qquad (9)$$

and as a special equation, where t is greater than 15,000 years:

$$\frac{Ra_t}{Ra_o} = \Theta_2 + \frac{\lambda_{Ra}(\Theta_1 - \Theta_2)}{\lambda_{Ra} - \lambda_I} e^{-\lambda_I t} \tag{10}$$

Evaluation of the Constants

Ra_o: This is the radium content at the top of the sediment column, that is at 0 centimeters depth. By graphically extrapolating the curve of radium content versus depth to zero depth. Ra_o can in most cases be determined fairly accurately. The accuracy of the value of Ra_o obtained in this manner is dependent upon how well the curve is defined at the very top of the core. Thus closely spaced determinations for the uppermost few centimeters are essential for defining Ra_o with the least possible error. In most of the cores studied, one sample was always taken from 0-1 cm. from the top and another at about 2 cm. Ra_o could therefore be determined with an accuracy of about plus or minus 10% in the worst cases considered.

Θ_2: Having determined Ra_o, Θ_2 may be known if the uranium content of the core is known. Where a core is representative of at least $4x10^5$ years, the radium curve should exhibit a tail of constant radium content in the deepest part. This radium is the amount in equilibrium with the uranium present in the core, which over the time span, considered here will not have measurably decayed. (See Fig. 2). In those cores which exhibited a constant radium content at depth, the tail was extremely flat. This enabled determination of the uranium content to an accuracy of about plus or minus 15%. Many of the cores, however, did not exhibit the flat tail, indicating they do not encompass the time necessary to establish equilibrium between ionium and radium. The uranium content must then be determined by direct measurement. This must be done at several points in the core to establish its constancy. This measurement was only carried out by Urry in one of the cores studied (Urry 1941) and the value obtained had an accuracy of about plus or minus 25%.

$\underline{\Theta_1}$: Analogously, Θ_1 may be determined by estimating the initial ionium content. By extrapolating the radium curve beyond the maximum to give the intercept with the ordinate, the amount of radium in equilibrium with this initial ionium is obtained. Dividing this value by Ra_o gives Θ_1 . For example in Figure 4, the extrapolated curve would cut the ordinate at 2, and since $Ra_o = 1$, Θ_1 is equal to 2. As will be shown later with the experimental data, this method of obtaining Θ_1 is subject to very large errors.

Θ_1 may be determined in another way, if the maximum in the experimental curve is well-defined. By differentiating equation (8) with respect to t, and equating $d\,Ra_t/dt = o$, an expression for the position of the maximum in years is obtained.

$$e^{(\lambda_{Ra}-\lambda_I)T_m} = \frac{\lambda_{Ra}-\lambda_I}{\lambda_I}\left[\frac{\lambda_{Ra}}{\lambda_{Ra}-\lambda_I} - \frac{1}{\Theta_1-\Theta_2}\left\{1-\Theta_2\left(1-\frac{\lambda_U}{\lambda_{Ra}}\,e^{(\lambda_{Ra}-\lambda_U)T_m}\right)\right\}\right] \qquad (11)$$

The term - $1 - \frac{\lambda_u}{\lambda_{Ra}} e^{(\lambda_{Ra} - \lambda_u) Tm}$ is always very close to unity in equation (11). Thus a much simpler working form of equation (11) is possible.

$$e^{(\lambda_{Ra}-\lambda_I)T_m} = \frac{\lambda_{Ra}}{\lambda_I} - \frac{\lambda_{Ra}-\lambda_I(1-\Theta_2)}{\lambda_I(\Theta_1-\Theta_2)} \tag{12}$$

Values of T_m from equation (12) for various values of Θ_1, and the known Θ_2 are substituted into equation (9), which is then solved for Ra_{Tm}/Ra_o. Then by a plot of both $1/\Theta$ and Ra_o/Ra_{Tm} versus T_m, and having experimentally determined $\frac{Ra_o}{Ra_{Tm}}$, T_m may be read off the graph and $1/\Theta_1$ picked off in turn.

Figure 5 is an example of how this method of obtaining Θ_1 is carried out. Using the data of Figure 4, (assuming Θ_1 is not known), equation (12) is solved. That is, the known $\Theta_2 = 0.2$ is substituted into equation (12) with various values of Θ_1 and solved for T_m. Curve I of Figure 5 is the plot of resulting values of $1/\Theta_1$, versus T_m obtained.

Then substituting the corresponding Θ_1 and T_m values into equation (9), (still using $\Theta_2 = 0.2$), values of Ra_{Tm}/Ra_o are obtained. Curve II of Figure 5 is the plot of these Ra_o/Ra_{Tm} values versus the T_m values used.

Now by referring to Figure 4, we find that the value of Ra_{Tm}/Ra_o for this data is 1.89, and the inverse Ra_o/Ra_{Tm} equals 0.53. Finding the value 0.53 on the Ra_o/Ra_{Tm} ordinate of Figure 5, and reading off the corresponding T_m in years on curve II, it is seen that $1/\Theta_1$ on curve I corresponding to this value is 0.50, thus $\Theta_1 = 2.0$ which checks with the original value used in constructing Figure 4.

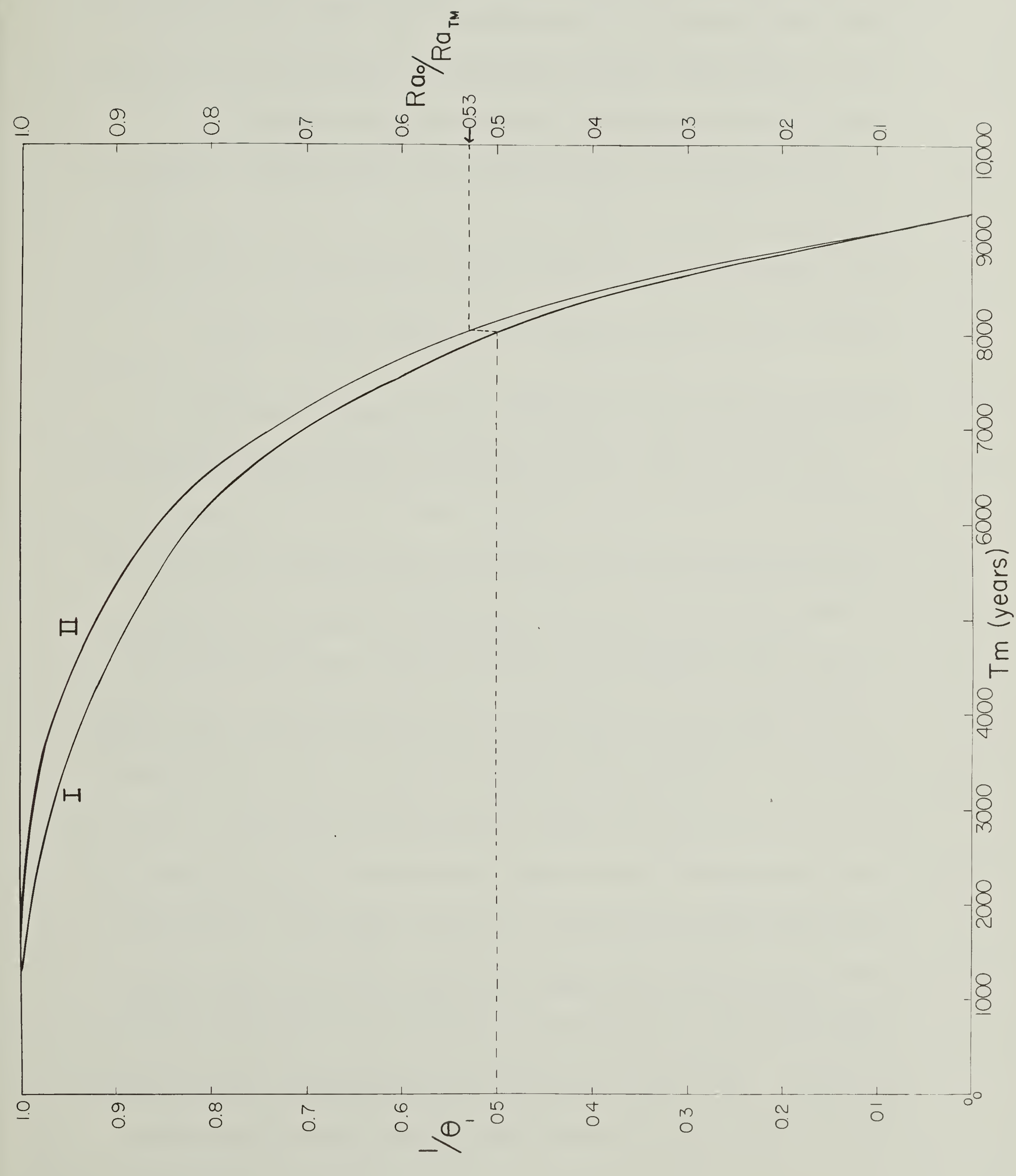

Figure 5. The time required to establish a maximum number of radium atoms versus the amount of ionium ($1/\Theta_1$) and the ratio of Ra_o/Ra_{Tm}.

Referring to even the very ideal curve of Figure 4, it may be seen that obtaining Θ_1 by extrapolation of the curve to the ordinate is quite difficult. The method outlined above, using the maximum radium value, is far more accurate, although more time consuming.

Once Θ_1 and Θ_2 have been determined, equation (9) is then plotted as Ra_t/Ra_o versus t, letting Ra_0 be equal to 1. Thus samples along the length of a core may be dated, if the radium content of the specimen relative to the radium content at the top of the core is known.

Emission of Radon to the Gas Phase from Deep Sea Sediments

A fraction of the radium of deep sea sediments originates from the ionium adsorbed on the particle surfaces during sedimentation. This fraction may be close to 100% in the upper layers of certain types of sediments, but for those older than 500,000 years it is negligible. If in the decay sequence from ionium through radium to radon it is assumed that none of the atoms are driven into the grains, and further if no radon originating within the grain leaks out, then all of the radon derived from the surface ionium would be in the gas phase. In this case measurement of the gas phase radon would be a direct indication of the adsorbed ionium content. If, on the other hand, all the radon atoms end up within the grains, as a result of the recoil due to the ionium and radium alpha emission, no radon would be present in the gas phase. The actual situation does not correspond to either of these simple cases. Some of the gas phase radon is derived from ionium originally within the grains. Radium and radon from ionium originally adsorbed on the surface of a grain may be driven into that grain or any adjacent grains by recoil, or may end up in the gas phase. The problem is to estimate the significance of each of these possibilities in an effort to define the source of radon in the gas phase.

The leakage of radon from samples of deep sea sediments is high compared to leakage from ordinary rocks and minerals. Cryptocrystalline pitchblende shows 1 - 10% leakage at room temperature. Other minerals of high uranium content show much lower leakage, but the deep sea sediments seem to leak some 30-60% of their radon.

A calculation of the expected leakage of radon from radium within these sedimentary materials may be made. Using the theoretical development of Flügge and Zimens (1939), the fraction of radon atoms emitted from a spherical grain due to recoil may be expressed:

$$Fr = (3/4)R/r_o - \frac{1}{16}(R/r_o)^3 \qquad \text{for } 2\,r_o \geq R \quad \ldots\ldots\ldots\ldots \quad (13)$$

where:

R = recoil range

r_o = radius of the grain

Using a typical surface area for these sedimentary materials of about 20 m^2/g (Kulp and Carr, 1950) and an average density of 3 g/cm^3, the grain radius r_o may be found by:

r_o = 3/density x surface area

and is found to be 5×10^{-6} cm.

The range of the recoiling radon atom, R, may be calculated by the use of some approximations. Using the available data (Behairel 1949) on alpha recoil distances, it is found that the ratio Ra_{α}/Ra = Range of alpha particle in air/Range of recoil atoms in air is rather constant for atoms of similar alpha energies . This ratio indicates that the recoil atom will travel about 3×10^{-3} as far as the alpha particle associated with it. Thus the range of the radium alpha particle in sediment must be determined. Using the Bragg Kleeman rule a value of 1.7×10^{-3} cm. is found for the range of the radium alpha particle in sediment. Thus the recoiling radon atom is seen to have a range, R, of 5×10^{-6} cm. in the same material. Using these values of R and r_o in equation (13), the fraction of radon atoms emitted due to recoil is seen to be about 70%. A similar analysis of the radon ultimately derived from surface ionium shows that about 78% of such radon atoms will escape to the gas phase, if it is assumed that none are driven into grains other than the one on which the parent ionium ion was adsorbed. This value of 78% is in effect the per cent of total radon which leaves the environs of the grain particle which adsorbed its parent ionium. Thus 78% represents the maximum radon in the gas phase of deep sea sediment. It is clear that the actual fraction of radon in the gas phase will not be 78%. The sizes of grain particles, the spaces between these particles, and the relative stopping powers of these media suggest that in the radium decay some fraction of the recoiling radon atoms will be driven into adjacent particles. The effect of reflection of recoiling radon atoms from a particle surface will tend to lessen the fraction trapped in other grains. The magnitude of these effects appears impossible to evaluate by a theoretical calculation because of the many uncertainties of the actual mechanisms involved. However, it is certain that the fraction of radon in the gas phase of these sediments should be considerably less than the theoretical maximum of 78%.

Most important, however, is the observation that for this particle size, the fraction of radon that ends up in the gas phase is similar regardless of whether the ancestral ionium ions were inside the grains, or on the surfaces. This means that the radon content of the gas phase of a given quantity of sediment is proportional to the total radium content. Since measurements of gas phase radon is much simpler than the fusion method of measuring the total radon, and since the sample is preserved in gas phase measurement, this result is of considerable practical importance.

It was originally thought that the gas phase radon measurement might be made up almost entirely of radon from adsorbed ionium, and therefore such a measurement could be used to distinguish adsorbed and total ionium contents. Unfortunately this is not true as the above analysis indicated. If sediments of much larger grain radii are selected differentiation of the two sources of radon is theoretically possible by this method. A simple calculation using equation (13), shows that to decrease the fraction of leakage from within the grains to 1%, the radius of the grains must increase by a factor of about 100. This increase of radius causes a decrease in surface area per gram by a factor of about 100. Thus such a method would fail because the adsorption on particles of such low surface area would not be measurable by present techniques. Further, it should be pointed out that no deep sea sediments measured had surface areas differing by more than about a factor of 3 from the 20 m^2/g used in the calculation.

III. Experimental Techniques

Determination of Radon within Sedimentary Grains

The samples of sedimentary core material were dried at 110°C and powdered to less than 60 mesh. After a 2-4 gram portion of each sample, was removed for determination of gas phase radon, about five grams were placed in a fusion furnace, the sample evacuated and then melted to liberate the radon trapped inside the mineral grains. This radon is henceforth called internal radon. This procedure differs from that described by Urry and Piggot (1941) who measured the internal radon and radon in the gas phase in a single measurement. The major reasons for introducing the two completely separate measurements, have been discussed in detail in chapter II.

Fusion Apparatus

The sample is completely melted in a direct-fusion high vacuum furnace diagrammed in Figures 6, 7, and 8, modified after similar units described by other workers, (Evans, 1935; Urry and Piggot, 1941). The furnace contains a graphite sample boat mounted horizontally which serves as the high resistance element. The entire furnace jacket and internal components are cooled by continuous cold water flow from four separate water inlet lines. The furnace face, seen in Figures 7, and 8, has an internal cooling coil, water entering at H_1 and discharging at H_2. The furnace jacket, pictured in Figure 6, is hollow, cooling water entering at R and leaving at S. The electrodes across which the graphite crucible is clamped, are made of 1/2 inch

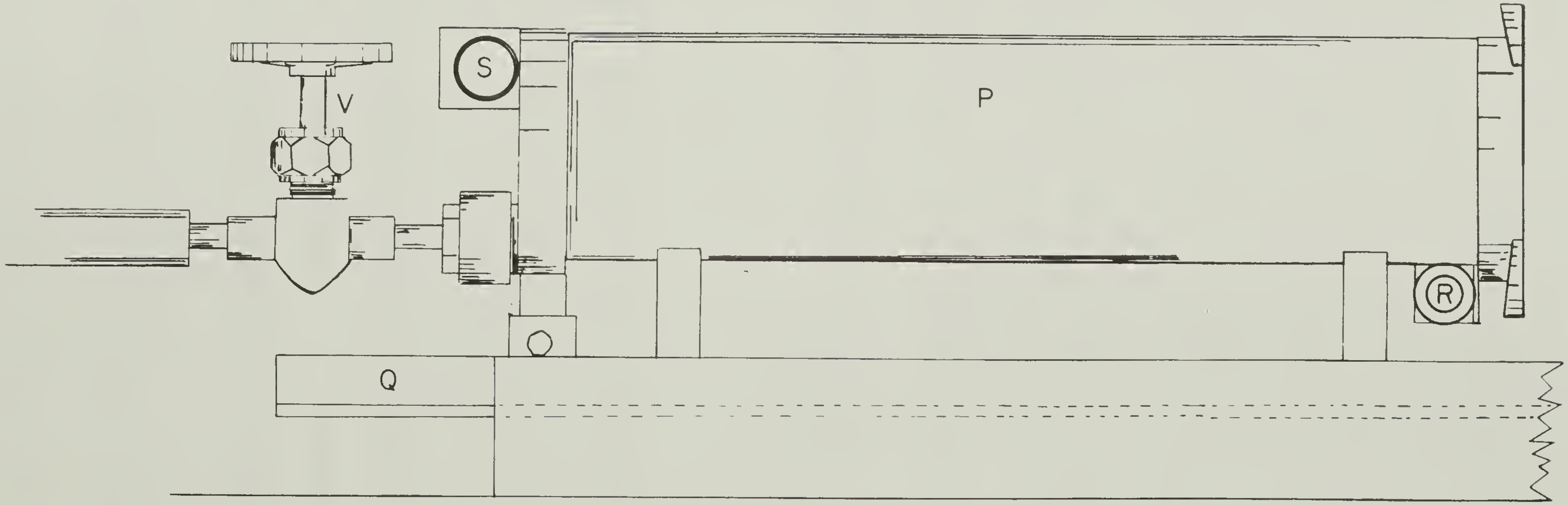

Figure 6. Fusion furnace jacket.

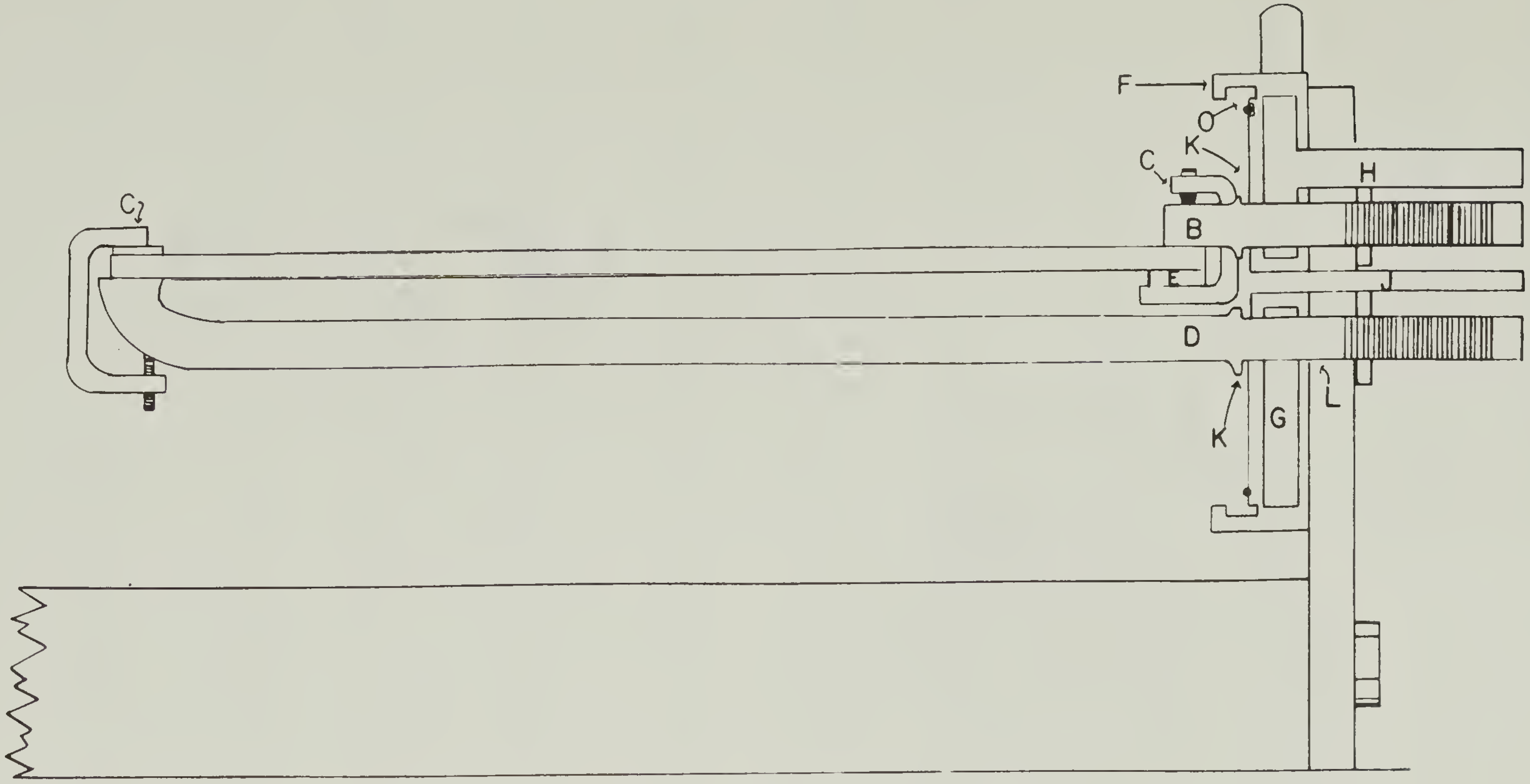

Figure 7. Fusion furnace, side of interior.

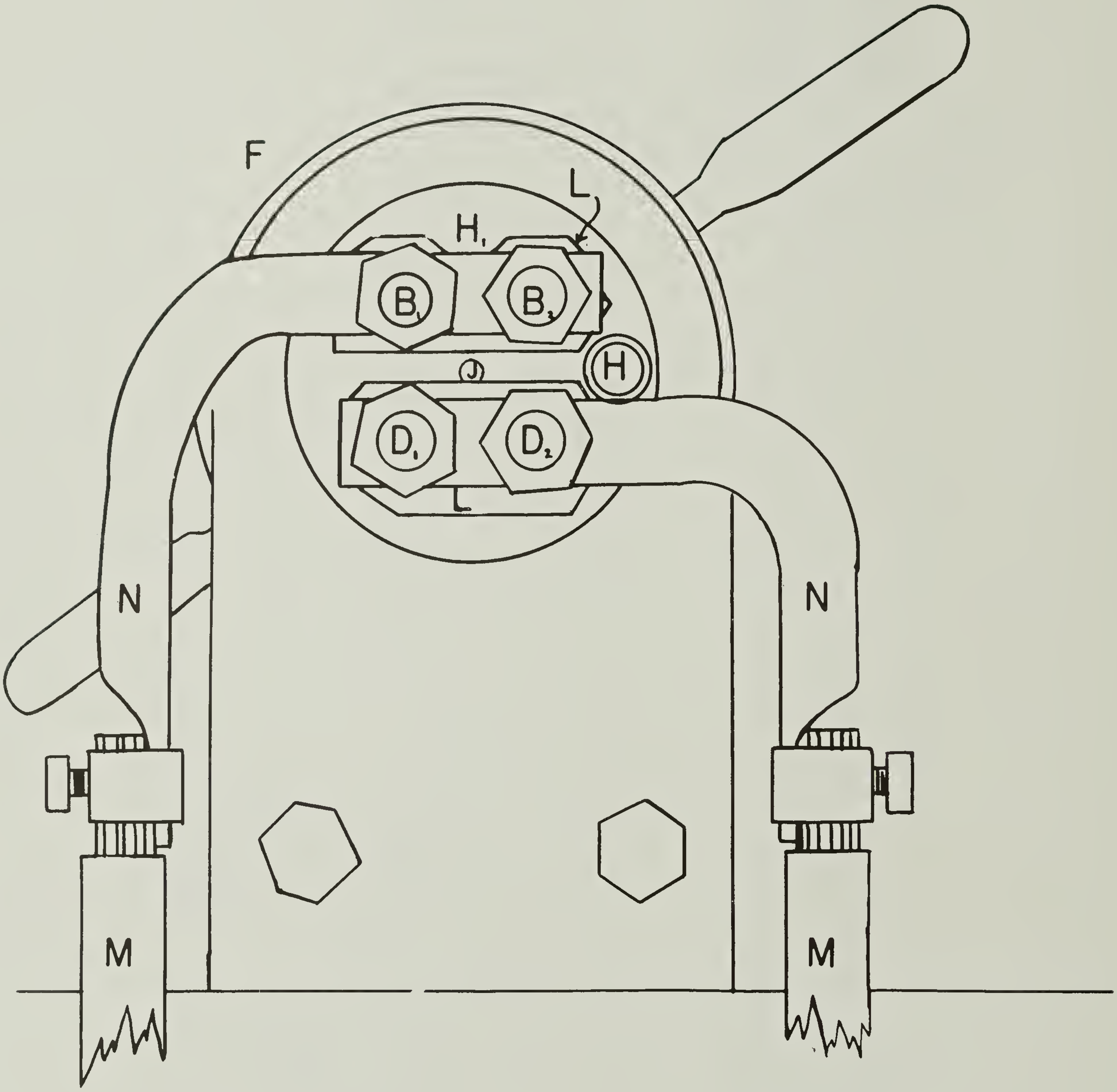

Figure 8. Fusion furnace, face.

copper tubing, with a flat contact surface built up by brazing (B and D of Figure 7). When operating these electrodes also have a steady flow of cold water streaming through them, in at B_1 and D_1 and discharging at B_2 and D_2 respectively.

The graphite boat is clamped to the electrodes by thin "C" clamps which are insulated both thermally and electrically from the boat by thin plates of alundum, (E, Figure 7).

The water cooled jacket (P, Figure 6) is mounted on a sliding carriage (Q) in such a manner as to allow efficient changing of the sample and graphite crucible, The jacket may be tipped up for inspection and cleaning.

The furnace face (see Figures 7 and 8) is provided with a sliding collar lock (F), which, when coupled to the furnace casing (P), may be pulled up tightly, compressing the "o" ring in a machined groove in the inner face, thus providing a vacuum seal at that point.

Passing through the furnace face completely, are four copper tubes which constitute the electrodes, (B and D of Figure 8). These are vacuum sealed to the furnace face by "o" ring-collar arrangements, as shown by (K), of Figure 7. The cooling leads H_1 and H_2 for the face, are soldered to the external side of the face. The smaller copper tube (J) which is the exit tube for gases evolved during the fusion also passes completely through the face . This tube leads to the gas purification system.

The heavy electrical leads from the transformer are coupled to the water cooled electrodes by short copper sleeves, (N of Figure 8).

Insulation between the furnace and the electrode tubing is maintained by sleeves of shellacked fiber around the copper tubes and strips of fiber between the face and the tightening nuts, on the pipes, (L of Figures 7 and 8).

Proper care in mounting the sample boat and "0" rings, allows for quite rapid evacuation to about 10^{-4} centimeters, the leakage over a period of one hour has been found to be negligible.

Power is supplied from the "Amesweld", transformer, model A.S.H.C.25, made by the Ames Spot Welder Company, Inc. Two hundred and twenty a.c. primary volts is applied to any of the five stages of the transformer. Automatic adjustable timers on each of the stages enables a desired heating sequence to be set and easily reproduced. At the usual running conditions, 2000° centigrade is obtained in the center of the sample boat, at the fourth stage of heating, using about 15 a.c. volts and 900 amperes.

Gas Purification System

The vacuum system for transferring and purifying of the gases from the furnace, is shown in Figure 9. Except for thorough drying of the gases, no other chemical pre-treatment is necessary if a low voltage ionization chamber is used for the radon assay. The small manometer M_1 is used during evacuation of the furnace as a coarse leak indicator. During the heating of the furnace, the evolved gases which enter the system go down through stopcock S_1 and are largely

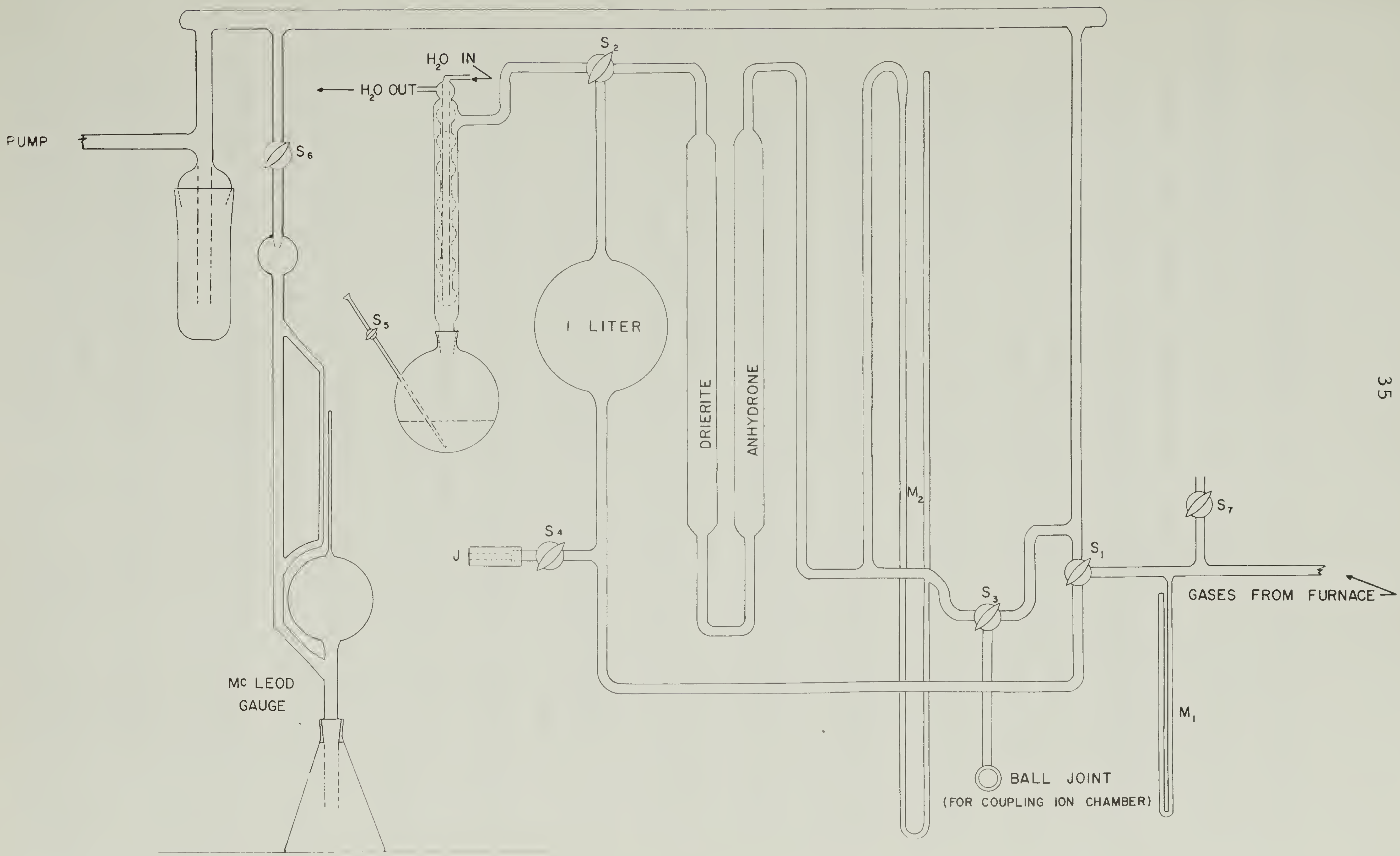

Figure 9. Radon gas purification system.

collected in the one liter bulb. During the fusion stopcock S_2 is open between the liter bulb and the drying tubes. Thus the pressure developed during the heating may be read on the large manometer M_2. Stopcock S_3 is turned so that the ionization chamber coupled to the ball joint is constantly pumped while the fusion is taking place. This precaution eliminates the small errors due to air leakage into the ionization chamber, for most of the time of the run. At the completion of the fusion, dry radon-free nitrogen is admitted to the far end of the furnace, and stopcock S_3 is turned bringing the ionization chamber into the vacuum system. The flowing nitrogen flushes the gases through the furnace, liter bulb and drying tubes, into the ionization chamber. Pressure in the entire system is brought to one atmosphere with the nitrogen, reading this on M_2, and the ionization chamber is then closed and uncoupled from the vacuum system, ready for counting.

The relatively high efficiency of Drierite and Anhydrone in drying the evolved gases, allows for rather rapid filling of the ionization chamber in the last step, generally requiring from about two to four minutes.

Stopcock S_4, of Figure 9, is kept closed during a fusion run. The side arm with short piece of rubber vacuum tubing (J), coming from S_4, is used for measurement of the surface radium content, to be described in a later section.

The flask shown in Figure 9, provided with a side arm and water cooled condenser, contains a radium solution of known concentration, provided by the National Bureau of Standards. These are used for absolute calibration of the system.

Counting System[1]

Many experimental arrangements have been proposed for counting radon gas. The earliest method (Rutherford, 1905) involved integration of ion current produced by radon and its solid decay products by means of an electrometer. This method was satisfactory for high radon concentrations but for low level work it does not have the required electronic stability and displays large fluctuations in background. This latter effect was reduced by using two ion chambers back to back to compensate for such fluctuations (Evans, 1935; Urry, 1930). For the long time periods required for measuring low level samples the apparatus provided for automatic voltage calibrations and photographic recording of the trace. This integration method is cumbersome and is not as sensitive or as stable as some of the later techniques.

At this stage in the history of radon measurement, two different methods were followed. One involved the use of the ion chamber as a proportional counter at high voltage ($\sim$ 2000 volts), thus requiring a high gain, fast amplifier. This system permits high level as well as low level counting. It was proposed first by Curtiss (Curtiss and Davis, 1943) and most recently improved by Hudgens, et al, (1951) so that the 10^{-14} grams Ra range could be reached. The other method was to employ the ion chamber as a low voltage ion-collection device and with large amplification to detect pulses rather than to integrate

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[1] The section on counting system comprises, with only minor modifications, the paper published by the author and colleagues, (Bate, Volchok and Kulp, 1954).

the ion current. Two detecting systems have been employed: (a) earlier the output from an FP-54 electrometer tube was recorded photographically from a Leeds and Northrup Type R galvanometer in a balanced bridge circuit (Finney and Evans, 1935); (b) more recently, a vibrating reed electrometer has been utilized with a Brown pen recorder, (Hurley, 1951).

Both high voltage and low voltage chambers have given satisfactory performance in low level radon counting. The high voltage method required rather elaborate chemical clean-up of the gases to be used. This type of counter is particularly sensitive to water and acid vapors, carbon dioxide and oxygen. The long-range stability required in the high voltage method places severe restrictions on the electronic design and construction of the high voltage supply and the accompanying high gain, fast amplifier. The main advantage of this system appears to be the range of activity which it can handle. It was designed by Hudgens, et al (1951) for use with radon concentrations ranging from those of radioactive ores down to ordinary rocks. For this purpose it is admirably suited. For the lowest levels of radon concentration in naturally occurring substances the inherent difficulties in this system appear greater than in the low voltage method.

The low voltage method as described above has one serious handicap. The thousands of alpha pulses per run (if the counting error is to approach 1%) must be counted visually. This is a demanding task if many determinations of high precision are to be made. On the other hand, for special studies where the size or shape of peak can be used to differentiate various isotopes or to determine the location of radiation (Hurley, 1950), the pen record is valuable.

The system described below is based on the low voltage ionization chamber - vibrating reed electrometer arrangement. It not only combines the features of electronic stability and simplicity of chemical pre-treatment but, most important, includes an electronic circuit for totalizing the slow pulses which are passed by the electrometer. The system has given satisfactory performance for over a year with an efficiency of about 80%, and a very low background.

Ionization Chamber

A detailed drawing of the ionization chamber is shown in Figure 10. The 4 liter chamber is constructed of carefully selected stainless steel to obtain the lowest possible background. The dimensions are not critical. The use of multiplace "0" ring seals and metal stopcock and ball joint makes the chamber rugged and easily disassembled for cleaning. The size of the insulators prevents appreciable surface leakage under the normal operating conditions.

General Circuitry

The basic components of the detecting and counting system are shown in the block diagram of Figure 11. The detecting arrangement is quite conventional, consisting of a large grid resistor R in series with the ionization chamber and supply voltage V. The ionization current I gives rise to a pulse of magnitude IR, which is then amplified for recording purposes. When the center probe is connected to the negative side of V, the reed delivers a negative-going pulse.

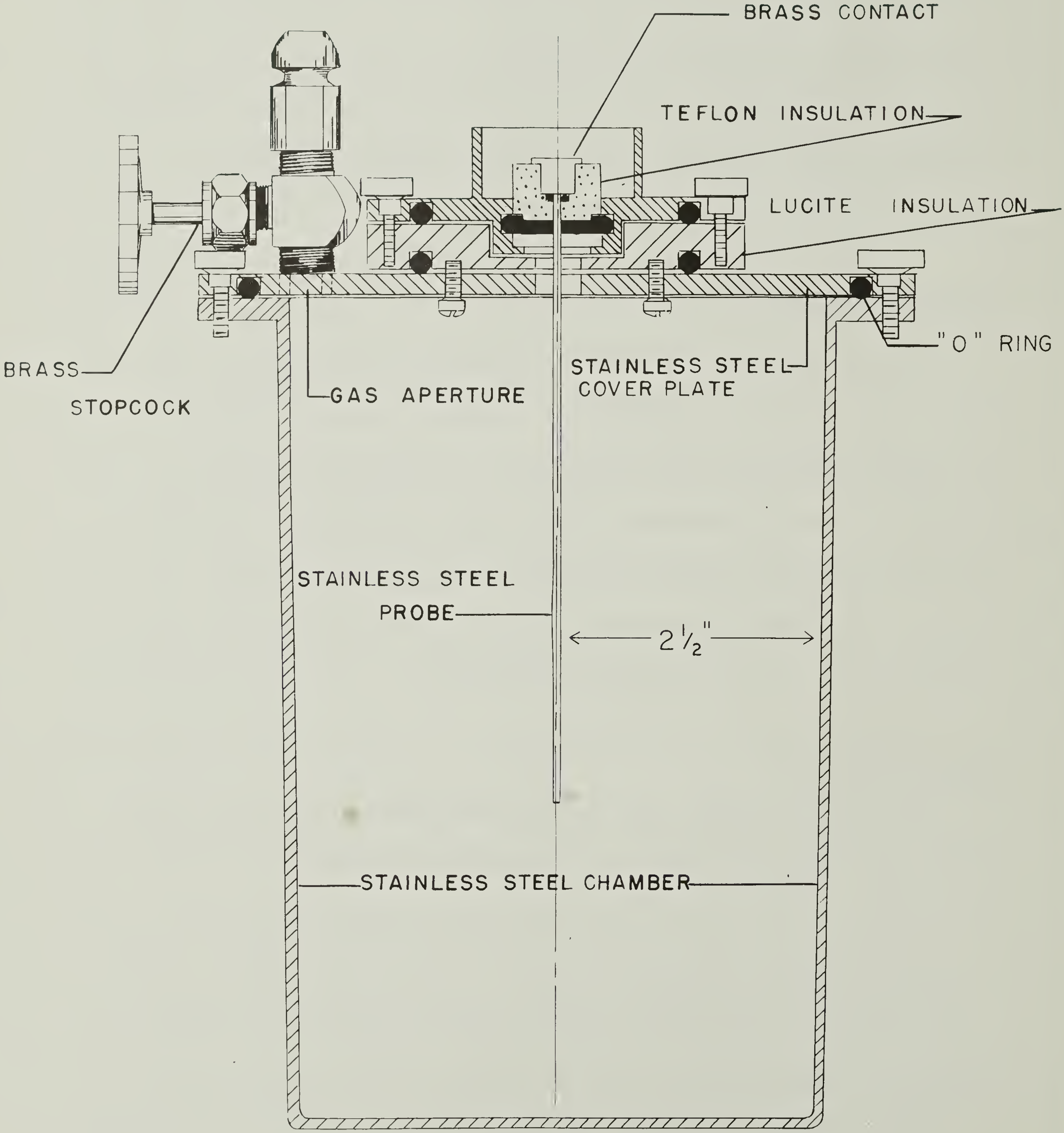


Figure 10. Radon ionization chamber.

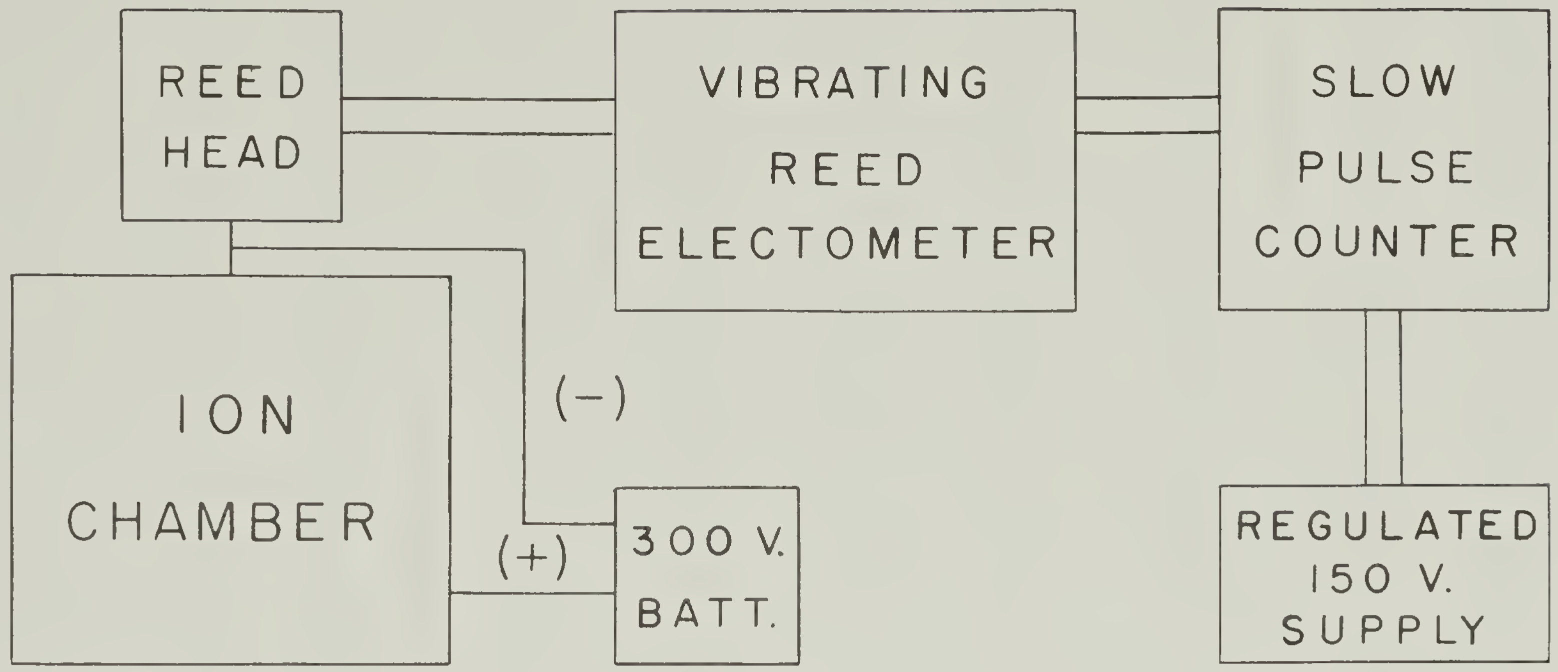


Figure 11. Block diagram of radon measurement system.

The choice of R is determined primarily by the time constant R'C, where R' (composed primarily of R) is the effective resistance to ground, and C consists of the distributed capacitance of the input grid and collecting-electrode system. R'C should be small enough so that with the maximum average rate of arrival of pulses there is small probability of one following another within the time R'C; on the other hand, R'C should be large enough to permit the full voltage pulse to be developed. C is fixed by the geometry of the detecting circuit, and with the system described, the optimum value of R was found to be 2×10^{10} to 3×10^{10} ohms. However, over an even wider range R was not found to be critical, and values ranging from $R=10^{10}$ to 4×10^{10} ohms were found usable. Resistors manufactured by the Victoreen Instrument Company of Cleveland, Ohio, were employed. These can be conveniently mounted directly in the input sleeve of the electrometer-head, or in a special adapter provided specifically for the Victoreen-type resistor.

The supply voltage V was not found to be critical, and was somewhat arbitrarily taken at 300 volts. Voltages as low as 90 volts were found to give comparable results. New commercial B-batteries gave good service for periods as long as twelve months and although the system is very sensitive to small operational variations in the battery voltage, it was not found necessary to attempt improvement of the stability of the B-battery supply. With aging, erratic fluctuations of battery voltage eventually set in, quite spontaneously, and the necessary battery change is indicated by the appearance of large amplitude "noise" in the electrometer output.

The model 30 vibrating reed electrometer manufactured by the Applied Physics Corp. of Pasadena, California, is suitable for amplification of pulses of this kind and gives dependable operation. The chief advantages of the instrument are its high sensitivity and freedom from zero-drift over long periods of time. The reed head is placed on top of the ionization chamber which is suspended in a wood frame set on a foam rubber mat. The mat effectively damps out mechanical vibration to which the reed is sensitive, but no other measures are necessary to provide quiet, stable operation. With the parameters of the detecting system as described above, the pulses (as seen by the reed) range in amplitude up to 2 mv, which permits consistent operation of the reed on the 10 mv scale. The output of the reed may be used to drive a recording milliameter, or a voltage signal may be taken off the output resistance loop and introduced into an electronic counting system. For reasons already mentioned, the latter alternative is much to be preferred and the development of a satisfactory electronic counter constituted one of the major problems.

Counter Circuit

The overall function of the counter amplifier is to activate a register drive circuit for each pulse delivered from the reed. Therefore, the amplifier must (1) respond to all pulses over their characteristic range of rise time, (2) resolve all pulses delivered by the detector-reed system, and (3) by incorporation of an electronic

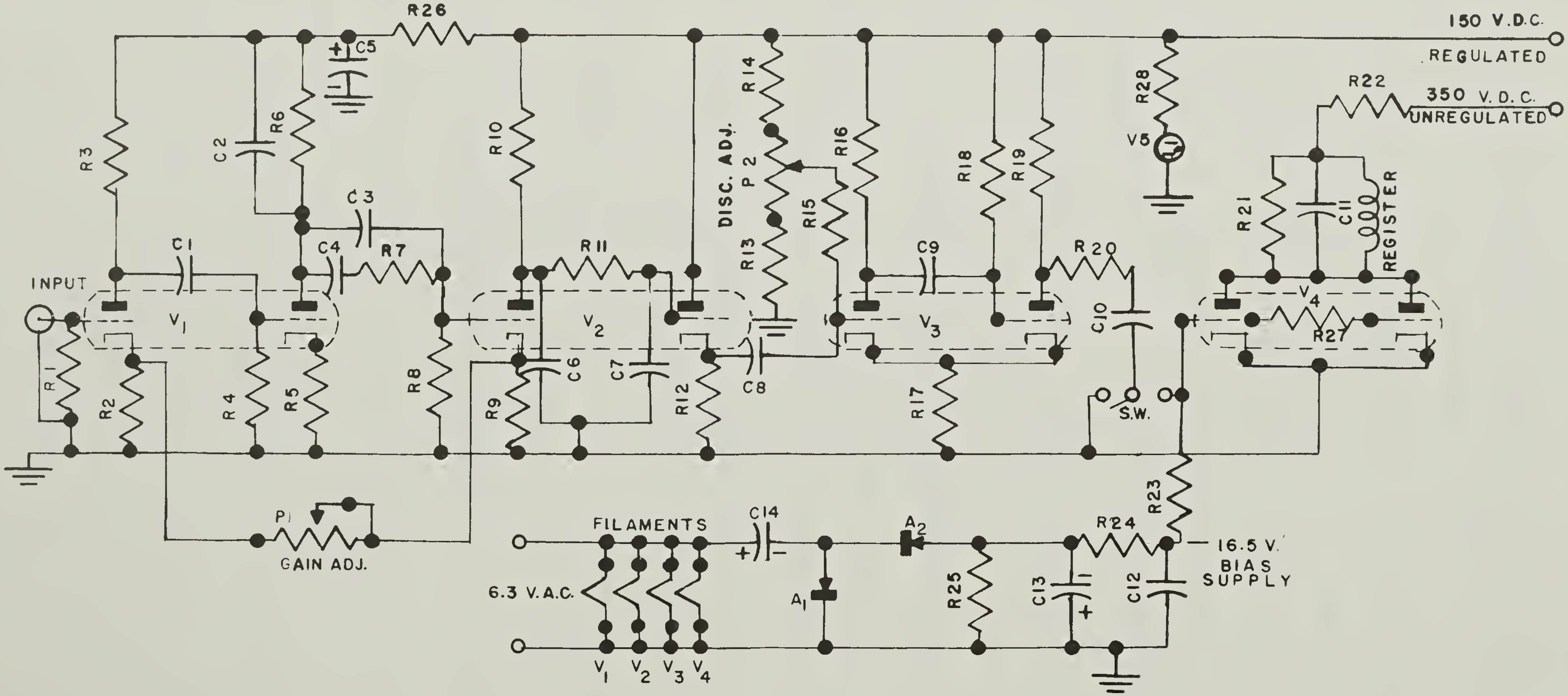


Figure 12. Schematic of slow pulse counter.

discrimination level reject pulses whose amplitude is less than a specified minimum. This level of discrimination should, moreover, be maintained at a constant value within narrow limits, for many weeks.

The basic amplifier-discriminator circuit in operation at present is shown in Figure 12. Tubes V_1 and V_2 constitute a feedback amplifier of high stability and low noise level. The output of this amplifier is then used to trip V_3, a mono-stable, cathode-coupled multivibrator, which in turn fires the register-drive tube V_4, and consequently the register (Veeder-Root series 1248). Filament and d.c. supply voltages are obtained from a commercial regulated power supply (a modified model 28-111, Lambda Elec. Corp. is readily adaptable for this purpose). In earlier models a scaling circuit was incorporated prior to the register drive stage, but this feature was subsequently dispensed with, inasmuch as the resolution time of the Veeder-Root register was demonstrated to be adequate for count rates up to 1000 cph.

The pulses delivered by the reed to the counting system range in magnitude up to .34 volts, with an average close to .15 volts. The rise time of these pulses, as measured on a cathode ray oscilloscope, ranges from about .01 to .5 sec. For low-level counting, a resolution time of .1 sec. is adequate. The amplifier itself has sufficient band width to respond to all pulses, so that the pulse response of the system is determined by the characteristics of the multivibrator. The input noise level is more than 2- db below the noise of the reed.

Although more gain was incorporated in the amplifier, a gain of 200 was found to give optimum performance. The coupling between the two sections of V_2 acts as a low pass filter, designed primarily to remove a small 450 cycle signal coming from the reed.

The output of the amplifier is capacitatively coupled to the input grid of the mono-stable, cathode-coupled multivibrator. The level of activation of the multivibrator is determined by the bias of the input grid (the input side is non-conducting when the tube is in the quiescent condition). The discriminator potentiometer permits a maximum grid bias of about 10 volts below cathode. The discriminator rejects noise from the reed output which ranges in amplitude up to about 30 millivolts maximum, when the reed is operated on the 10 mv scale. It will be noted that some real pulses will also be rejected inasmuch as the pulse height (dependent upon the path-length of the α -particle in the ionization chamber) ranges over a continuum of values from zero to the maximum value. However, the distribution is concentrated toward the higher amplitude portion of the spectrum, and pulses giving rise to signals less than 30 mv on the reed output are a small fraction of the total.

A battery supplied discrimination potential level is open to some objection because this does not insure constant potential difference between grid and cathode, due to the possibility of cathode drift. Although cathode drift was assumed negligible, attempts to incorporate dry cells were not successful, inasmuch as the decrease of terminal voltage of the cells changed the discrimination level within a short time, in spite of the use of large bleeder resistors. The use of wet cells was not explored because of other objectionable features.

The stability of discriminator potential obtained by electronic means is limited by the regulation of the d.c. source. An alternative to rigid regulation of the d.c. source consists of selecting that set of operating conditions which will minimize the effect of small variations in the potential level of discrimination. The latter course was followed with the result that as currently operated, the system will tolerate a variation of about 1.3% in the 150 volt supply of the circuit. After initial aging of all electronic components, the minimum period of stable operation (i.e., in which no measurable change in counting efficiency was detected) for three counters is about one week, and occasionally a unit may run as long as one month (continuous operation) before a change in counting efficiency necessitates adjustment of the discriminator potentiometer setting. This change is thought to be primarily due to drift in the discriminator grid bias. To further the long period stability of the counter, long-life tubes and high-stability resistors were employed as indicated in the schematic (Figure 12). The 110 volt a.c. operating potential for both the reed and power supply was supplied from a constant voltage (Sola) transformer.

The parameter controlling the pulse response of the counter is the RC time constant of the multivibrator (R18 and C9 in Figure 12).

The optimum value was found to be .75 sec., which permits resolution of all pulses delivered by the reed. With this value, the counter does not respond to pulses of rise time longer than .5 sec. which, however, are of infrequent occurrence.

The register drive circuit is similar to those used in standard electronic counters. The necessary grid bias is obtained from a voltage doubler circuit operated off the filament supply.

Calibration

Calibration of the radon counting system was accomplished by the use of standard radium solutions supplied by the National Bureau of Standards. Two calibration flasks were prepared, each containing 1×10^{-12} grams of radium. Prior to use, the flasks and distilled water to be used were checked for radium contamination. The flasks were sealed and stored for at least thirty days to allow equilibrium between radium and radon to be established. The radon was then transferred into the ionization chamber by flushing with nitrogen, and the pressure of the chamber was brought to one atmosphere. An interval of 3 to 4 hours must be allowed before counting to permit the daughter products of radon to achieve equilibrium, thereby simplifying the calculation (Hudgens et al, 1951).

Although there are actually two daughter α emitters which are in equilibrium with the radon, both of these are solids and have been found to condense on the inner wall of the ionization chamber

(Graveson, 1952). Under these circumstances each of the daughters has a counting efficiency of 50% and the total activity after equilibrium has been achieved is two times the activity of the radon. The efficiency as used here is defined as the percentage of the expected activity from the standard radium solution which is recorded by the detection device. This factor was measured at the time the apparatus was built and then was checked occasionally in the succeeding months. The reproducibility of this constant between the two flasks used, in several different ionization chambers and through a period of almost 3 years, has remained constant (within statistics) as seen in Table 2 below.

Table 2

Absolute Efficiency of Radon System

Flask	Ion Chamber	Date	Efficiency
C	7	Aug. 1951	77.0±2.5%
A	1	Aug. 1951	80.0±2.0%
A	5	Sept. 1951	77.0±2.0%
C	1	Oct. 1951	77.8±1.8%
A	3	Oct. 1951	76.3±1.8%
C	5	Apr. 1952	79.3±1.4%
C	3	July 1952	80.5±1.2%
C	1	Sept. 1954	79.7±1.4%
		Average -	78.5±1.2%

By the use of this efficiency factor several rock specimens of known radium content, supplied by the Bureau of Standards, were then measured as a further check of the absolute accuracy of the system. These rocks were melted in the graphite resistance fusion furnace, the resulting gas was dried and counted in the ionization chambers. Results are tabulated in Table 3.

Tabe 3 Accuracy of Radon System

Sample	Bureau of Standards Value $\frac{g\ Ra \times 10^{-12}}{g}$		Measured Value $\frac{g\ Ra \times 10^{-12}}{g}$
Graniteville Granite	3.3±0.1		3.27±0.10
			3.36±0.09
			3.35±0.09
			3.10±0.09
			3.22±0.07
		Average	3.26±.05
Carthage L.S.	0.15±0.03		0.145±0.03

From Tables 2 and 3 it can be seen that both the accuracy and precision of the present radon measurement technique as a means of determining radium content of solids or liquids is satisfactory to about 3%.

Although necessary to establish the absolute counting efficiency of the radon system, the method outlined above is rather time-consuming and cumbersome. Each flask must be allowed to accumulate radon for at least thirty days. Special precautions must be taken in making the run to insure that all radon is removed from the solution and that no contaminating material is included. Because it is desirable to make daily checks on the operating level of the counting apparatus, a secondary calibration of the relative efficiency of the counters was devised, utilizing standards prepared at this laboratory. The secondary standard is prepared by mounting a very small piece of uranium-containing mineral (in this case zircon) inside an ionization chamber in such a way so as to shield the detector from all particles emitted by the mineral, yet allowing the radon released to diffuse freely into the volume. This was accomplished by use of a small stainless steel cup ($\sim$ 1 cm radius) mounted open-end down on the base of the chamber. Several small holes were drilled in the top of the inverted cup and the zircon speck mounted on the under side. With this arrangement all of the alpha particles from the solid were prevented from causing ionization in the chamber proper, while the escaping radon was quite free to fill it. After having mounted the radon source, the ionization chamber was sealed, evacuated and filled to 1 atm. pressure with dry, radon-free nitrogen. This ionization chamber was then put on a counting unit and the activity was measured daily and plotted as a function of time. The resulting curve indicated that the activity was due entirely to radon build-up and after approximately a month leveled off to a constant value of steady state equilibrium. This standard chamber was then counted several times before and after efficiency determinations made with the Bureau of Standards radium solutions. In this way the secondary standard of known activity was prepared. This secondary standard has proven extremely useful as a day-to-day check of the sensitivity level of the counters, which, when having drifted from the level of 78% counting efficiency, can be brought easily to this level by adjustment of the discriminator level. At the present time two such secondary standards are in operation, one with an activity of about 900 cph and the other about 500 cph.

Background

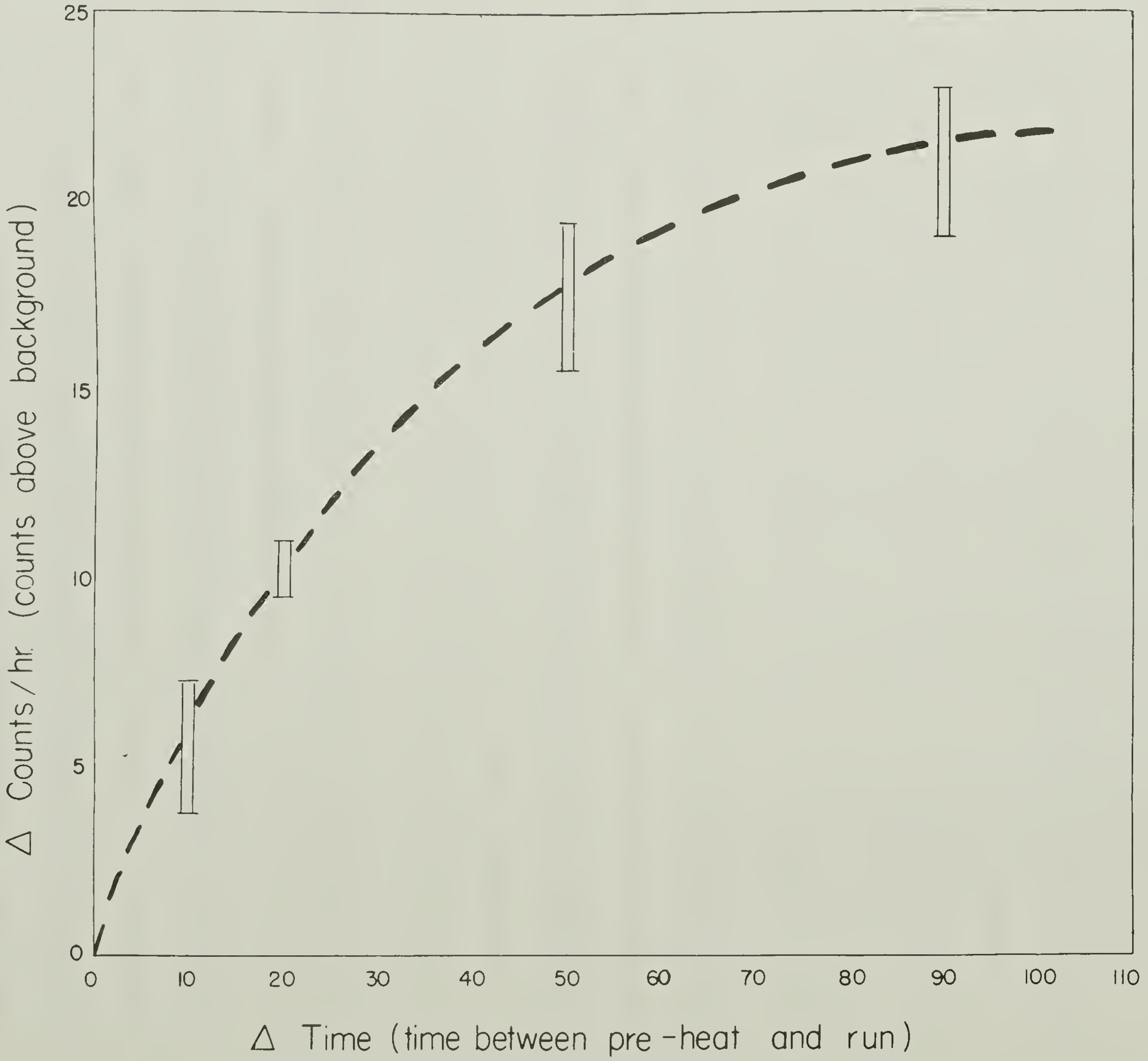
The background of the six ionization chambers now in operation varies between 14 and 30 counts per hour and has remained constant in most cases for long periods of time. The origin of this residual activity has been found to be almost entirely from the internal metal parts of the chamber. The nitrogen used as filling gas is stored for at least 30 days to allow any appreciable radon to decay. Runs made with evacuated chambers have shown that spurious counting of electronic origin contributes less than 0.1 cph.

Optimum background is obtainable only by careful selection of the stainless steel used to construct the ionization chambers. This is accomplished by pre-counting the steel "pots" before any machining is done. After the parts are constructed, a washing in aqua regia, thorough rinsing in triple-distilled water followed by careful drying, has been found to aid materially in lowering the background due to surface contamination. Once assembled and vacuum sealed, the background rate of a chamber has been found to remain entirely constant.

Procedure

Before beginning each radium determination run, the furnace is thoroughly cleaned, the copper electrode contacts polished and new alundum insulators cut. A clean graphite crucible is then clamped in place across the electrodes, the furnace sealed, and evacuated. After evacuation, a five minute check is made under static conditions to detect any leakage of air into the furnace. If necessary, grease is applied to the large, "0", ring on the furnace face to correct the leak. When the furnace is vacuum tight, the cooling water is turned on, and the furnace is pre-heated. Pre-heating consists of going through an identical heating sequence as that used during the run, for the purpose of driving out any radon from the furnace components. As a check on the cleanliness of the equipment blank runs were made on empty crucibles, after the completion of the pre-heating. It was noticed at this time that the blanks were not constant and not equal to the normal background of the ionization chamber. This proved that additional background was coming from the heated furnace, but the inconsistency of this was not clear until a series of runs were made in measured time intervals. The results plotted in Figure 13, indicate clearly, that enough radium is present in some components of the assembled furnace to release

Figure 13. Pre-heat correction curve.



measurable amounts of radon when heated and build up radon when cold. Because of this, the procedure in a radium determination had to be standardized with respect to time, in order to operate with a known background. For convenience twenty minutes were chosen as the time between the end of the pre-heat and the beginning of the fusion. This allowed sufficient time to cool the furnace, mount the sample, evacuate and check the vacuum before beginning the fusion run. However, with the curve of Figure 13, it is possible to correct the background if the time interval is known.

After pre-heating, several minutes must be allowed for the furnace to cool before the boat can be handled for mounting the sample. In this interval the dried sample is weighed and then carefully poured into the graphite boat as evenly as possible leaving about two centimeters of bare boat at either end. The sample is then completely covered with a mat of asbestos fiber. This practice was introduced to counteract the popping action of sediment particles when heated. Blank runs made with the same quantity of asbestos in the crucible showed negligible radium concentration.

With the sample and asbestos properly mounted, the furnace is again closed, evacuated, and checked for vacuum tightness. Once pumped down and tight, stopcocks (S_1) and(S_2) of Figure 9 are turned so that the furnace and glass system are continuous and static while the ionization chamber continues to be pumped. At the expiration of the chosen time interval the heating sequence is started. The emerging gases are collected largely in the one liter bulb of Figure 9 because of its large volume The pressure build-up during the run may be observed on the manometer (M_2). At the conclusion of the heating program the valve on the rear of the furnace is opened allowing dry radon free nitrogen to flush through the interior which is still hot. Before the pressure in the system reaches one atmosphere, stopcock (S_3) is turned bringing the ion-chamber into the system and all the gases are flushed into it until the entire train reaches one atmosphere. Closing the valve on the ionization chamber and detaching it from the ball joint completes the run and the chamber is ready for counting. It is necessary to note the time of filling of the chamber, as this must be used in the calculation of the radium content.

The can is now allowed to stand for at least three hours, before counting is begun. During this interval the daughter products achieve equilibrium with radon, and calculation is simplified a great deal. The length of the waiting interval must also be accurately timed, as it also enters into the equations used in the calculation.

When at least three hours have elapsed, the ionization chamber is coupled to the head of the vibrating reed electrometer and the actual counting started. All that is necessary to record during the run are the times of starting and ending the count and the total number of counts recorded.

Method of Calculation

In the theory of the Ionium Method of Age Determination the equations were written in terms of the radium contents of the core material. It is necessary, therefore, to convert the measured activity of the daughter radioelement, radon, into concentration of radium.

Since at the moment of release of the radon from the specimen by fusion it is in radioactive equilibrium with the radium present, by the law of secular equilibrium their activities are equal. That is:

Where A = activity

N = no. of atoms

λ_{rn} = decay constant of radon

λ_{ra} = decay constant of radium

$$\lambda_{ra}N_{ra} = \lambda_{rn}N_{rn} \quad (14)$$

and since:

$$A = \lambda N \quad (15)$$

merely by knowing the activity of the radon and the decay constant of radium, the number of atoms of radium may be known. The important calculation, therefore, is determining the activity of the radon at the time it was released from the rock.

Letting: t_1 = time from release of the radon to the start of the counting,

t_2 = time from release of the radon to the end of the counting,

N_1 = number of disintegrations occurring during t_1.

N_2 = number of disintegrations occurring during t_2.

$$N_1 = N_o\, e^{-\lambda_{Rn} t_1} \qquad (16)$$

$$N_2 = N_o\, e^{-\lambda_{Rn} t_2} \qquad (17)$$

where N_o = the number of atoms of the kind, N, initially present.

In the counting period we record the number of disintegrations (after the correction for counting efficiency) which have occurred between the times, t_1 and t_2. Thus we experimentally obtain $N_2 - N_1$. From equations 16 and 17 we obtain:

$$N_2 - N_1 = N_o(e^{-\lambda_{Rn} t_2} - e^{-\lambda_{Rn} t_1}) \qquad (18)$$

or,

$$N_o = \frac{N_2 - N_1}{(e^{-\lambda_{Rn} t_2} - e^{-\lambda_{Rn} t_1})} \qquad (19)$$

since,

$$\frac{dN_o}{dt_o} = -\lambda_{Ra} N_o \qquad (20)$$

substituting equation(20)into(19)

$$\frac{dN_o}{dt_o} = -\frac{\lambda_{Rn}(N_2 - N_1)}{e^{-\lambda_{Rn} t_2} - e^{-\lambda_{Rn} t_1}} \qquad (21)$$

which, by equation (15) is equal to the initial activity of the radon, A_{Rn}

Equation(21) is the one finally used for the calculation of the radon activity. It directly tells the initial activity if only the decay constant λ_{Rn}, of radon is known the number of counts recorded in the time interval $N_2 - N_1$, and the beginning and end of the counting time. Once this initial activity, A, is known it may be substituted back into equation(15) with the decay constant, λ_{ra}, of radium and the number of atoms of radium calculated. A useful constant is the decay constant of radium divided by the number of grams per atom of radium. This number, equal to 1.33 x 10^{14}, may be divided into the initial radon activity, to directly obtain grams of radium. Thus:

$$\text{Radium Content (grams)} = \frac{A_{rn}}{1.33 \times 10^{14}} \quad \ldots\ldots\ldots\ldots \quad (22)$$

Equation (22) gives the total grams of radium of the measured sample. Dividing this value by the number of grams of sample used in the determination results in:

Grams of radium/gram of sediment

which is the common unit in reporting radium concentrations of sediments.

Determination of Radon in the Gas Phase

Studies of radon leakage carried out at the Lamont Observatory (Giletti and Kulp, 1954) have revealed that the escape of radon from minerals is generally slight. Pitchblende samples were found to leak only about 1 - 10% of their radon at room temperature. Other minerals, such as samarskite, leaked less by about a factor of ten. It thus appeared that for most minerals under normal conditions leakage of radon was negligible.

As outlined in Chapter II, however, the degree of radon leakage is controlled very directly by the size and surface area of the particle grains containing the radioelements. The calculation carried out in Chapter II indicated that in deep sea sediments these grains are of such dimensions tnat a large fraction of the radon may escape and further that the radon of the gas phase is proportional to the total radium content. This calculation suggested a much simpler and economical method of measuring the radium content of core samples than had been previously employed. This method is very similar to that used by Urry and Piggot (1941) to measure what they called the "escaped radon". It is simpler in that the procedure involving the fusion furnace is completely avoided, and it preserves the sample in unaltered form. In measurement of total radium content as was done by Piggot and Urry, the samples are destroyed in fusion. By the present method repeat determinations may be made at will and subsequent studies of the lithology or paleontology of the samples are possible.

For the foregoing reasons a study of the radon in the gas phase was carried out. If the radon in the gas phase is truly an appreciable fraction of the total radon, and if this fraction is constant throughout the core, the measurement of radon in the gas phase should yield as accurate a measure of the ionium content as a "total radon" method.

Sample Preparation

No special preparation of the samples is necessary other than drying the samples at 110° Centigrade. The particle size has no appreciable effect on the determination.

The samples are stored in glass tubes, about eight inches long and one quarter inch diameter. Closed on one end, these tubes are pulled out to a long thin point on the other end, after a weighed amount of sample has been inserted. The sealed tubes are then dated and stored for at least thirty days, the time necessary for the radon to achieve equilibrium with radium. No special precautions as to filling gases are necessary as the thirty day accumulation time is sufficient to decrease the concentration of any radon of the air in which the sample was sealed to a negligible amount.

Procedure

When the accumulation period of at least thirty days is completed the sample is ready for analysis. The vacuum system used in the internal radium determinations, pictured in Figure 9, is employed. The pointed end of the sealed sample tube is firmly inserted into the length of rubber vacuum tubing near stopcock S_4, at (J) in Figure 9. The entire system up to stopcock S_4 is at this time evacuated. Now by turning the stopcock, the air filled space between S_4 and the sample tube is also evacuated, and leaks around the rubber-glass seal may be seen on the manometer and corrected. When the train is satisfactorily vacuum tight stopcock S_3 is turned so only the ionization chamber is being pumped, S_1 closed, and the glass system up to the end of the sample tube is now statically evacuated. Stopcock S_4 is now closed and the rubber tubing near the end of the sample tube pinched with pliers, thereby breaking off the thin glass tip. At this point S_4 is carefully reopened to the rest of the vacuum system. The reason for breaking the sample tube with S_4 closed and then reopening it later, is to try to eliminate a sudden surge of gas leaving the sample tube which may carry particles of the sample into the vacuum system. The very large volume of the system relative to the sample tube is sufficient to bring essentially all of the accumulated radon out of the tube. The pressure rise in the system is observed on the manometer M_2 and when this pressure becomes constant S_4 may be again closed. Stopcock S_1 is now opened letting a flow of nitrogen build up the pressure in the system and S_3 opened bringing the ionization chamber into the system. When the pressure reaches one atmosphere the chamber is closed, time recorded, and the run is completed.

The counting procedure and the method of calculation of radium content is the same as that described under radon within sedementary grains.

Determination of Total Alpha Emission

If the excess adsorbed ionium and its decay products contribute a significant fraction of the total alpha activity, and if the concentration of the uranium and thorium series is reasonably constant in the bulk sediment, a curve of total alpha activity versus depth should exhibit the same characteristic shape as the radium concentration - depth curve. Such a curve would permit age estimates to be made in much the same way as the radium curve is analyzed. This procedure would have several advantages: (1) the samples need not be destroyed, (2) the measurement is rapid, and (3) the measurement is simple.

Use of thin sources of the sediment samples would be a more desirable method of counting the core, since absolute analyses in terms of alpha particles emitted per unit weight and time can be obtained.

However, the total activity in such sources is prohibitively small so that thick sources must be used.

For thick sources absolute activities may be determined only if the distribution of the radioactivity, chemical composition and particle sizes are well known. For materials of similar mineral composition relative activities can be measured with moderate precision .

Theory

The theory of solid alpha counting has been developed by Finney and Evans (1935), Nogami and Hurley (1948) and Beharrel (1949).

Where:

N = alphas/cm^3 emitted from the source
R = mean range of alphas in air (generally at 15°C and 760mm)
u = range in substance/range in air
p = residual range required to activate the counter (in air cm.)
a = total thickness of absorber (in air cm.)
t = thickness of the source (in air cm.)

If $t \geq R - p - a$ . . . . (23)

the source is thick.

If a homogeneous source contains a single alpha emitter surmounted by absorbers, the counting rate in alphas/cm^2/min. is:

For a thick source

$n = (Nu/4)\ (R - p - a)^2/(R - p)$ . . . . (24)

For a thin source

$n' = (Nu\ t/4)\ (2(R - p - a) - t)/(R - p)$ . . . . (25)

If by internal standardization, with similar material containing the same alpha emitters with the same average range, it is possible to state the disintegration rate in terms of alphas/cm^2/min. *leaving the surface of the source*, then the terms a and p can be dropped so that (24) and (25) become,

$$n = (Nu/4)\ R = (N''ud/4)R \tag{26}$$

$$n' = (Nu\ t/4)\ (2-t/R) = (N''udt/4)\ (2-t/R) \tag{27}$$

where d = density in gm/cc

N'' = alphas/gm/min.

$$\text{Since}\quad t = m/udA \tag{28}$$

where m = mass

A = area

equation (27) becomes

$$n' = (N''m/2A\ \ (1-m/2udAR) \tag{29}$$

For sources on the order of one mg/cm^2 or smaller, $m/2ud/AR$ will be less than 0.1; thus any uncertainty in ud will be only of second order importance. It is mainly for this reason, that thin source counting is to be preferred. In the thick source equation (26) however it is seen that the ud term is of first order importance, and it is this factor which makes any absolute counting with thick sources a difficult problem. Only if the distribution of most of the activity can be well defined in the rock sample, can estimates of the ud be made with any degree of accuracy; and specific activities be calculated.

Sample Preparation

For thick sources, the sample is crushed to pass a 60-mesh screen and dried at 110°C. It is then poured into the sample tray, which is 2.7mm deep, (considerably greater than the critical value for a "thick" source), and the surface smoothed to the level of the top of the tray. This procedure was found to be entirely satisfactory to reproduce the counting conditions.

For thin sources a new rapid technique has been developed which is superior in results to the alcohol slurry method described by Evans and Goodman (1944). Stainless steel sample plates were made, precisely machined to fit the tray receptacle in the slide of the scintillation counter. A thin film of silicone grease is applied to the upper face of the plate, and the sample, which has been reduced to greater than 300 mesh is dusted on and excess shaken off. Sources ranging from 0.5 mg/cm^2 to 2.5 mg/cm^2 may be readily obtained in this way. The preparation is very uniform even when viewed with a binocular microscope and provides activity measurement reproducible within the statistical error to one or two per cent.

Counting System

The total alpha emission rates of the selected core samples were measured with an alpha scintillation counter developed in this laboratory, (Kulp, Holland and Volchok, 1952).

Housing

Figure 14 shows the housing of the low level scintillation counter used in measurement of the core samples. The sample tray is placed in the closely machined depression in the sliding plate under the phosphor at a distance of about 0.7 millimeters. Light is excluded during sample changing by the hinged external cover. Light is prevented from entering from the top of the housing by lightight seals at the cap, and by the clamping ring which holds the photomultiplier tube. Once the desired distance between the phosphored end of the photomultiplier tube and the sample is achieved, the photomultiplier tube is clamped firmly in place. The size of the sample tray (42 square centimeters) is chosen to offer "infinite area" geometry, that is, alpha particles emitted from the outermost radius are not detectable to the photomultiplier tube which itself has a sensitive area of about 12 to 13 square centimeters.

Phosphor

In the present work two commercially available silver-activated, zinc sulfide phosphors, the Patterson type D, manufactured by a DuPont subsidiary, and the RCA No. 33-Z-20A phosphor, have been used. Both have proved to be satisfactory, the Patterson type D having superior mechanical properties. ZnS-Ag phosphor has been found to have an efficiency of 28 pct. in converting the energy of alpha particles into light energy , this exceeds the efficiency of other commercially available phosphors for alpha detection. The light

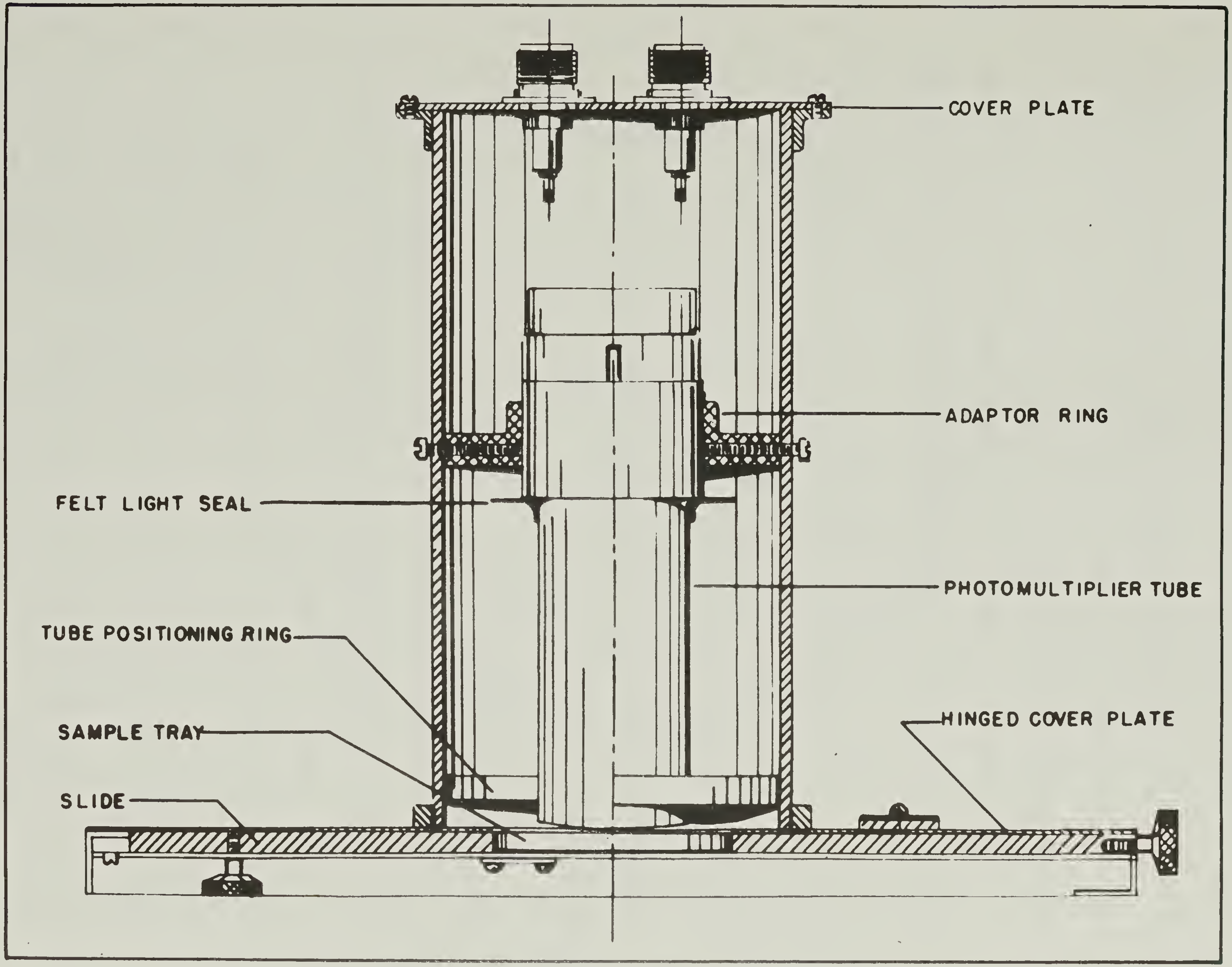


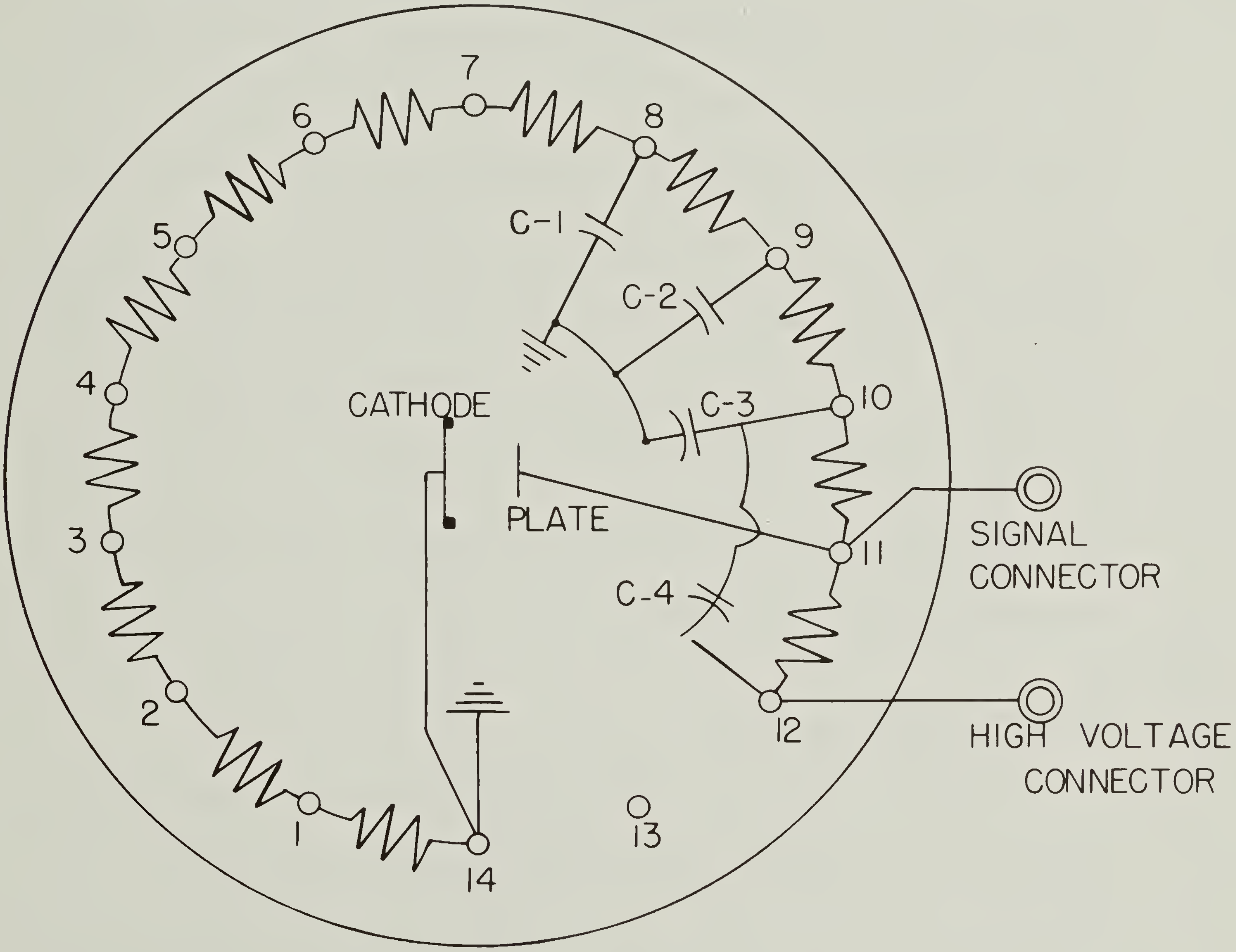
Figure 14. –Low-level scintillation alpha counter

emitted by ZnS-Ag phosphor has an intensity maximum at a wave length of 4500A, not far from the peak response wave length of 4750A of the RCA no. 5819 photomultiplier tube. The phosphor is readily available in the form of small crystals which show relatively little self absorbtion of green light.

The phosphor is applied to the top of the photomultiplier tube by placing phosphor crystals on the surface which is freshly coated with a thin layer of silicone high vacuum grease. The excess phosphor is shaken off, leaving a thin, even, nearly monocrystalline layer. Each time a new coat of phosphor is applied the unit must be recalibrated. It was found however that the procedure is extremely reproducible and that variations between phosphored tubes are negligible.

Photomultiplier Tube

Combining the desirable features of a large photosensitive area, with an end window, the RCA no. 5819 photomultiplier tube was found suitable in this work. The voltages for the individual dynodes of the photo tube are obtained by means of the voltage divider circuit shown in Figure 15. A recent improvement in the RCA photo-tube has been to provide an optically flat end window, in place of the slightly convex shape in the 5819. This development occurred after most of these measurements were completed, but one core was run with the new tube and slightly better results appear to be obtainable.



C − 1 = .003 uf, 1200 DCWV

C − 2 = .003 uf, 1200 DCWV

C − 3 = .01 uf, 1600 DCWV

C − 4 = .001 uf, 600 DCWV

ALL RESISTORS ARE 1 MEGOHM

Figure 15. Photomultiplier tube, voltage divider circuit.

Electronic Components

Satisfactory electronic components are available commercially. A Nuclear Instrument Corp. Model 162 scaler contains sufficient amplification, adequate discrimination and high-voltage-supply regulation, but requires an external register. This instrument was used directly in this work. The Atomic Instrument Co. Model 1040X contains the register and combines a few other features to give more accurate discrimination and high voltage regulation and was also widely used. Graveson and others (1950) describe circuits utilizing a cathode follower stage mounted directly on the counter housing; resulting in operation at lower voltages. One unit at this laboratory was provided with this modification, but no particular advantages could be ascribed to it.

Counting Characteristics

Figure 16 shows the relation of count rate to voltage for a thick source of uranium metal and the background at various discriminator levels. (Zero discrimination means that all pulses and noise pass). The plateaus increase in length and decrease in slope with greater selectivity of the pulses. The plateau at discriminator setting of 30 is at least 100 volts long, while that at 80 is 200 volts long. It is clear that it is advantageous to operate at as low voltages as possible to keep the background to a minimum. Thus normal operating voltage under these conditions is about 870 volts. The length and slope of the plateau is affected

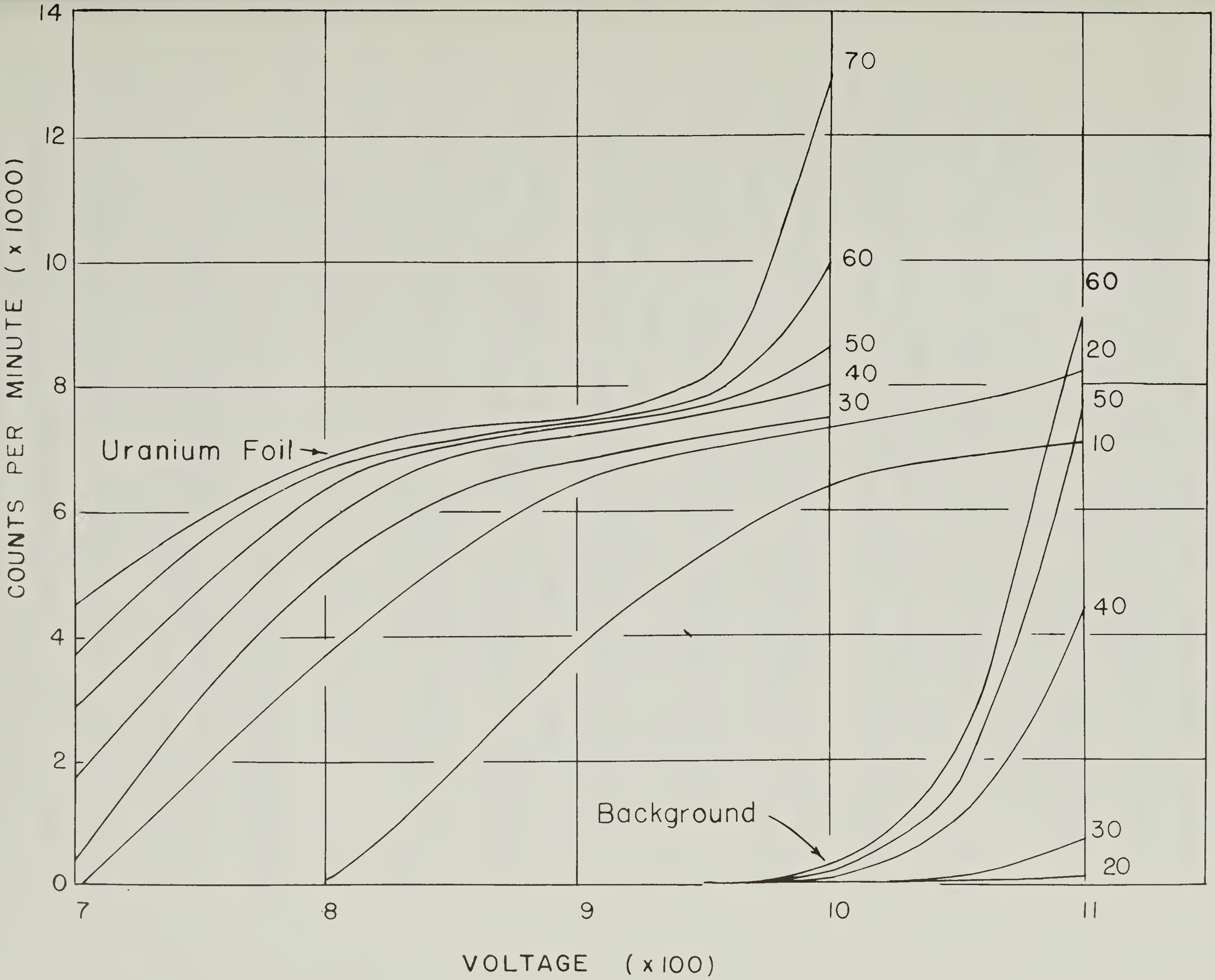


Figure 16. Counting characteristics of alpha scintillation counter.

by the characteristics of the photo-tube, the electronic circuits and the nature of the source. For instance a thin source of one alpha emitter gives a better plateau than a thick source containing several different alpha activities.

The geometry used in these counters is that of the, "infinite area" source as described earlier. The distance from the bottom of the phosphored tube to the top of the sample is made as small as possible (generally about 0.7 mm). Since the faces of the photomultiplier tubes used were slightly convex in an irregular manner. It is not feasible to calculate the number of alphas reaching the phosphor, by correcting for geometry and absorption. Therefore, calibration is done empirically with known sources where necessary. Because only relative activities were required in this study, and because of the difficulty in duplicating natural materials, the counters were not calibrated on an absolute basis for thick source counting. The reproducibility of results, using this method, is about two percent. Thus the results are reported in alphas/cm^2/hr. causing a detectable scintillation on the phosphored end of the photo-tube.

Determination of Surface Area

If the main mechanism responsible for the concentration of radium in the deep ocean sediments is adsorption of ionium (Holland and Kulp, 1954), it seems reasonable to assume that the quantity adsorbed is directly related to the absolute surface area. It was for this reason that the surface area measurements of deep sea sediments were first begun at this laboratory, (Kulp and Carr, 1952), and have been continued by the author.

Sample Preparation

The samples used for surface area determination, were in most cases portions of the same specimens previously prepared for alpha counting. Extensive tests however, showed no measurable difference in surface area, in a sample that was lightly broken up to just fit into the adsorption bulb, and the same sample after it was ground to fine powder with a mortar and pestle. It was further shown that a lightly broken up sample would repeat the same surface area within about 5% over the course of many runs and continued handling, while a finely ground sample tends to become lower in surface area under the same treatment. The reason for this appears to be simply that in the course of repeated runs, the very fine fraction of the ground sample, which of course is highest in surface area, is lost due to being pulled up in the evacuation, or just by pouring the sample from its bottle. Thus wherever possible, fresh samples, lightly broken up to just fit the adsorption bulb, are used.

Vacuum System

The vacuum system for measuring surface areas, shown in Figure 17, consists of an oil pump and mercury diffusion vacuum pump (2), in series, followed by a dry ice trap (3), a McLeod gauge (7), an argon manometer (5), adsorption bulb (4), and gas burette (6). Purified tank helium and spectroscopically pure argon are stored in the bulbs above the manifold.

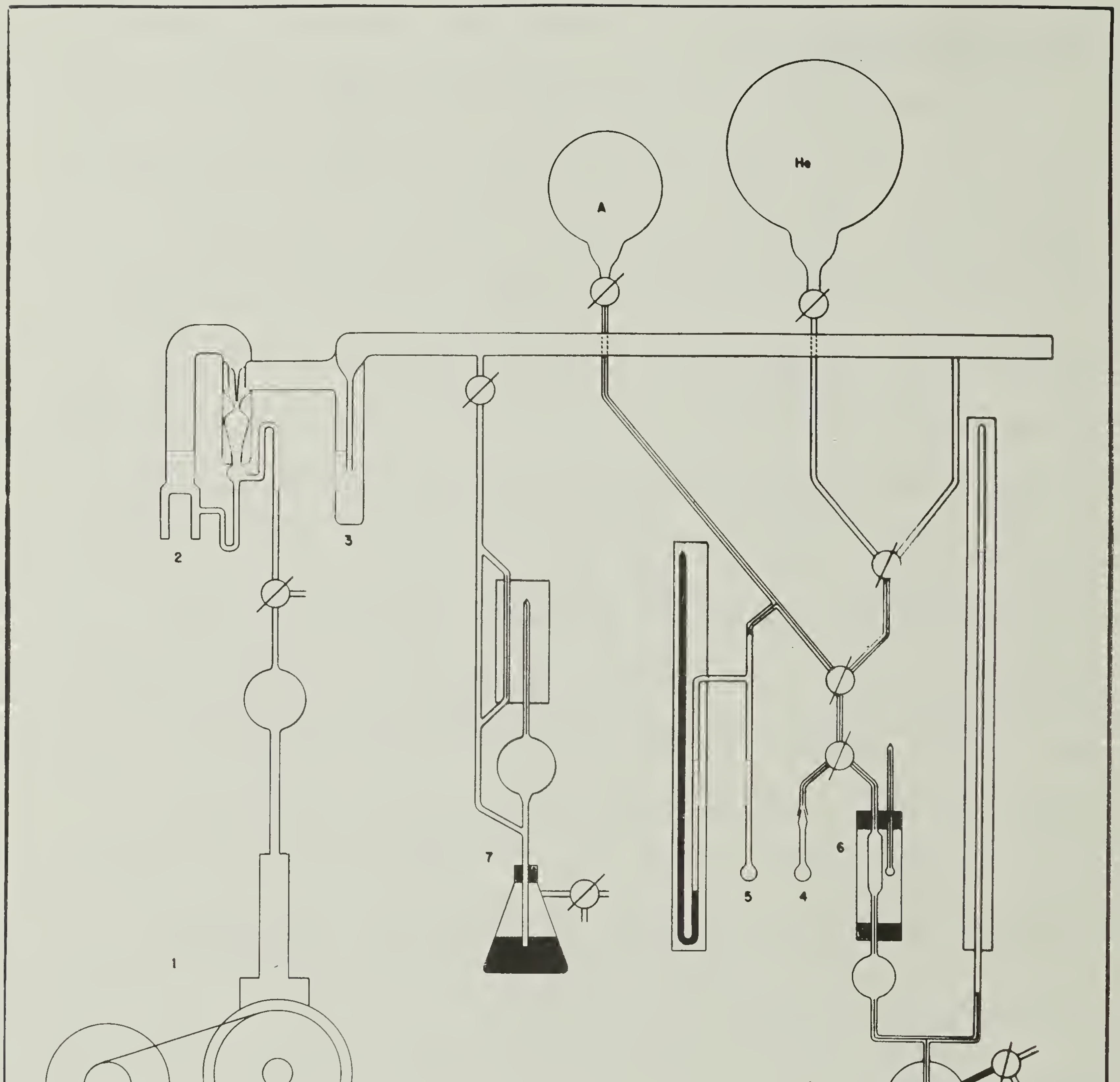


Figure 17. Vacuum system for surface area measurement.

Procedure in a Determination

The sample, generally weighing about one gram, is placed in the adsorption bulb (4) and heated for two hours at 150° C, under vacuum. It was found that the two hour heating, was sufficient to dry the sample completely. Heating at 280° C for 12 hours resulted in no change in surface area, thus the two hour heating at the lower temperature was adopted as the standard procedure. The ground glass joint at the top of the adsorption bulb is cooled by a stream of air during the heating, to prevent melting the vacuum grease. At the end of the heating time the sample is cooled to room temperature, and the entire system pumped to better than 10^{-5} mm. The "dead space" of the sample is then determined, by expanding a known amount of helium from the gas burette (6) into the adsorption bulb (4) after the bulb has been cooled to liquid air temperature. Once the dead space is known the helium is pumped out of the system, and enough argon admitted to the manometer (5), to produce a liquid phase at liquid nitrogen temperature. The liquid nitrogen receptacle used, is wide enough to fit over both the manometer bulb (5) and the adsorption bulb simultaneousely. The vapor pressure of the argon at this temperature is read on the manometer. The adsorption isotherm of argon on the sediment sample is then determined by expanding successive quantities of argon from the gas burette (6), into the sample bulb (4). This process is continued, obtaining a number of final pressures for volumes in the burette.

From these data, the adsorbed volume for each final pressure is calculated and converted to standard temperature and pressure.

With these volumes and pressures a plot of the data based on the Brunauer, Emmet, and Teller (1938) theory of multimolecular adsorption is made. From the slope of this plot, the volume of gas required for a monomolecular layer, may be determined. Then knowing the cross-sectional area of the argon atom and the mass of sample used, the surface area per unit mass may be calculated.

Absolute surface areas are probably correct to 20% while relative values and reproducibility are about 1 to 5%.

IV Results

In the course of this study a total of eight ocean cores were analyzed by some or all of the experimental techniques described in the previous section. These particular cores were chosen as a representative suite to illustrate the limiting conditions of the Ionium Method of Age Determination.

The results are presented in the following pages, one core at a time, giving all of the data obtained for a particular core. The general interpretation and discussion of these results is presented in Chapter V and VI.

Pacific Ocean Core N-2

Through the kind cooperation of Dr. J. L. Hough, of the University of Illinois, essentially half of core N-2 was made available for this study. The core was obtained by Dr. Hough on board the U.S.C.G.C. Northwind, as part of the U.S. Navy Antarctic Expedition of 1946-1947. The core was secured from 1980 fathoms of water, at Latitude 32°21', Longitude 105°55'.

This core is composed of a red clay of very uniform color and texture. It was analyzed by Dr. W. D. Urry, (1949), for total radium content, and the data is plotted in Figure 18. The curve drawn through the points is the interpretation of Urry and illustrates the characteristics predicted by the theory. The relative radium concentrations, apparently smooth variation of radium content, time span involved, and availability of sufficient core material, all

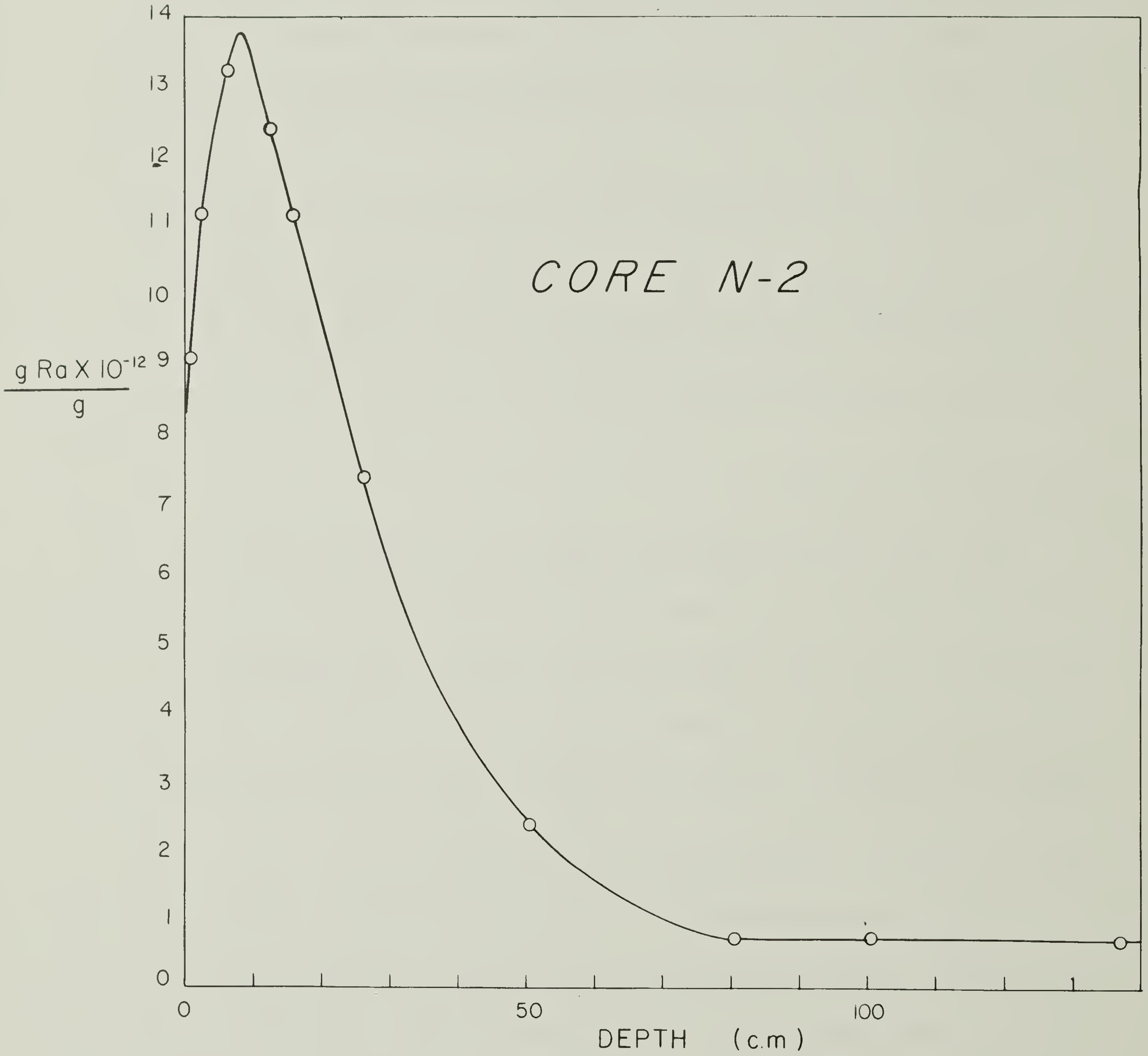


Figure 18. Total radium content, core N-2.

make this core exceedingly valuable for testing the procedures and hypotheses, involved in the ionium method.

Surface area measurements made on this core are listed in Table 4, along with the radium concentrations obtained by Urry. The surface area is essentially constant except for two points. The largest spread of radium concentration between the points at 6 centimeters and 100 centimeters is a factor of about 17. No corresponding spread in the surface areas of these two points can be seen, in fact they differ by only about 0.1%, well within the limit of experimental error. The two surface area values which are higher than the other eight by about a factor of 2 probably can be correlated with a minor difference in chemical or physical composition of the material at those points. If it is assumed that the radium concentration is directly proportional to the surface area, the radium versus depth curve may be corrected for differences in surface area. The curve of Figure 19 illustrates this data so corrected. It can be seen that although the surface areas of two of the points differed from the mean by almost a factor of two, the resulting curve of radium versus depth is still smooth. The apparent age at these depths will of course, be affected.

Thick sources of samples of this core were alpha counted. Because this procedure requires the use of relatively large amounts of sample and since it was desired to conserve the material of this core, only eight samples were run. The results are listed in Table 5. The activities are expressed in alphas counted per hour for the entire

Table 4

Surface Area and Radium Content of Core N-2

Depth (cm.)	Ra(g Rax10^{-12}/g)	Surface Area (M^2/g)
0-0.5	9.08	30.6
2-2.5	11.09	31.4
6-6.5	13.19	32.9
11.8-12.5	12.33	32.1
16-16.5	11.16	31.0
25-26	7.30	51.5
50-51	2.35	57.4
80-81	0.72	32.5
100-101	0.76	32.9
137-end	0.69	26.7

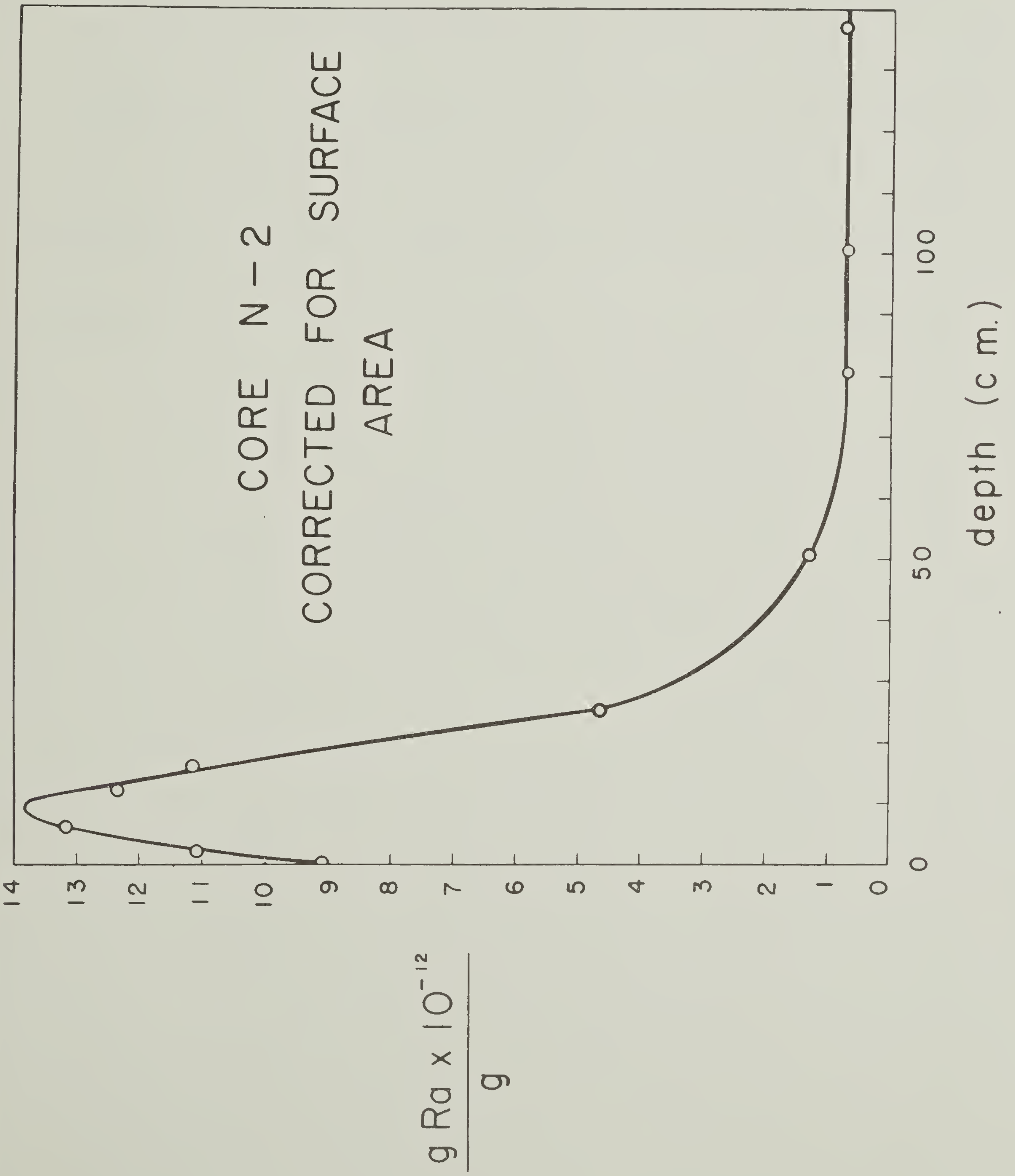

CORE N - 2
CORRECTED FOR SURFACE AREA
$\frac{g\,Ra \times 10^{-12}}{g}$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
0
50
100
depth (c m.)

Figure 19.

Table 5

Total Thick Source Alpha Emission of Core N-2

Sample Depth (cm.)	Alphas/Hour
0.5-2.0	195±2
2.0-3.5	222±2
6.5-8.5	197±2
11-12.5	164±2
20-21.5	110±3
40-42	48.1±1.2
80-81	16.8±1.0
137-139	17.2±1.1

source. A graph of these data as a function of depth is reproduced in Figure 20. Again the same general curve is obtained although the relative values differ somewhat. From these data it seems clear that by the method of total alpha counting at least a qualitative picture of the radium concentration may be obtained. This measurement is so much simpler than any of the others that it should be used first to determine whether or not a given core is suitable for the Ionium Method.

An attempt to measure the gas phase radon was also made on this core. Seven samples were chosen and sealed in the glass tubes for this measurement. The results are plotted as a function of depth in Figure 21. Once again the essential shape of the curve is the same.

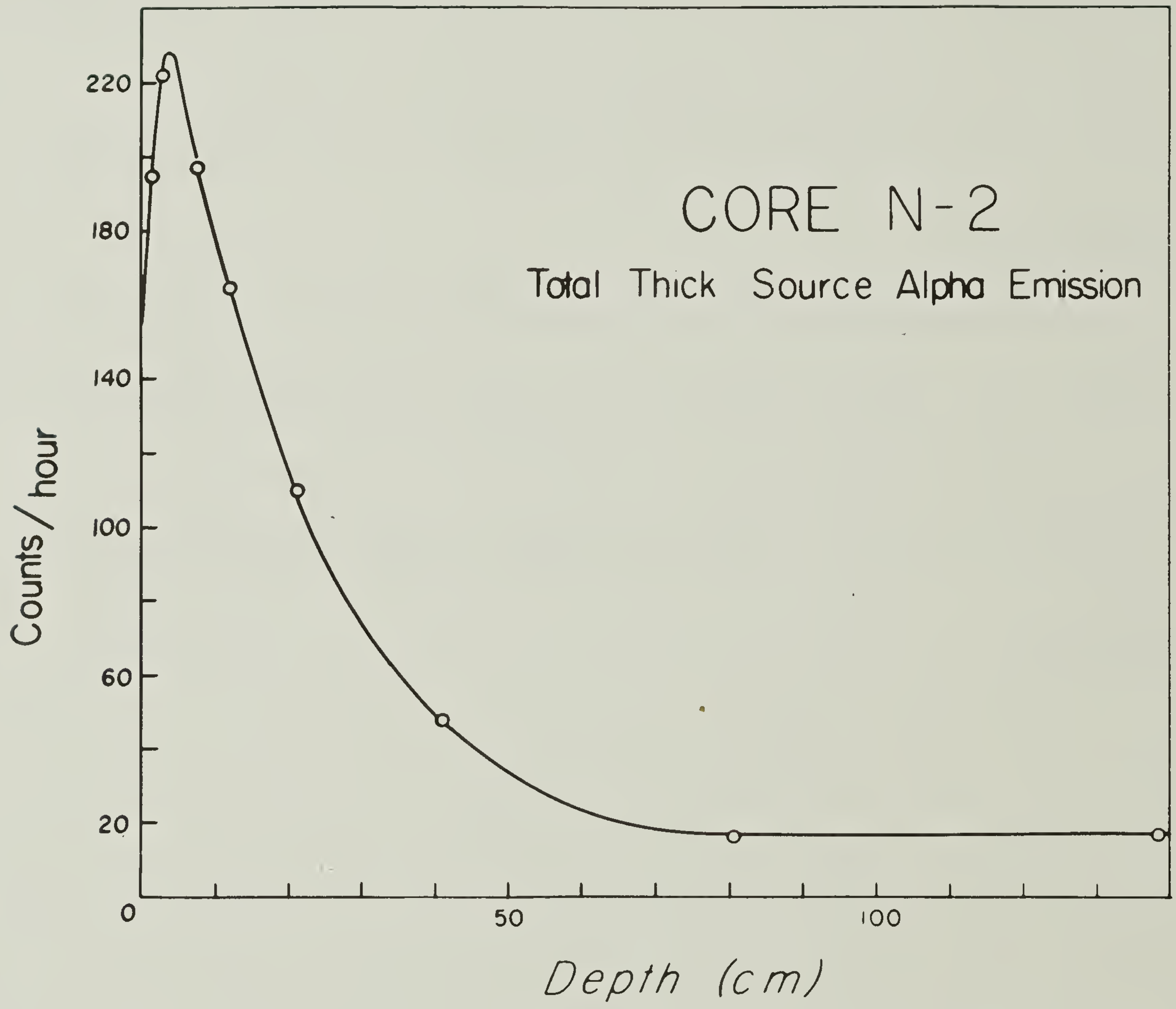

CORE N-2
Total Thick Source Alpha Emission
Counts / hour
220
180
140
100
60
20
0
50
100
Depth (cm)

Figure 20.

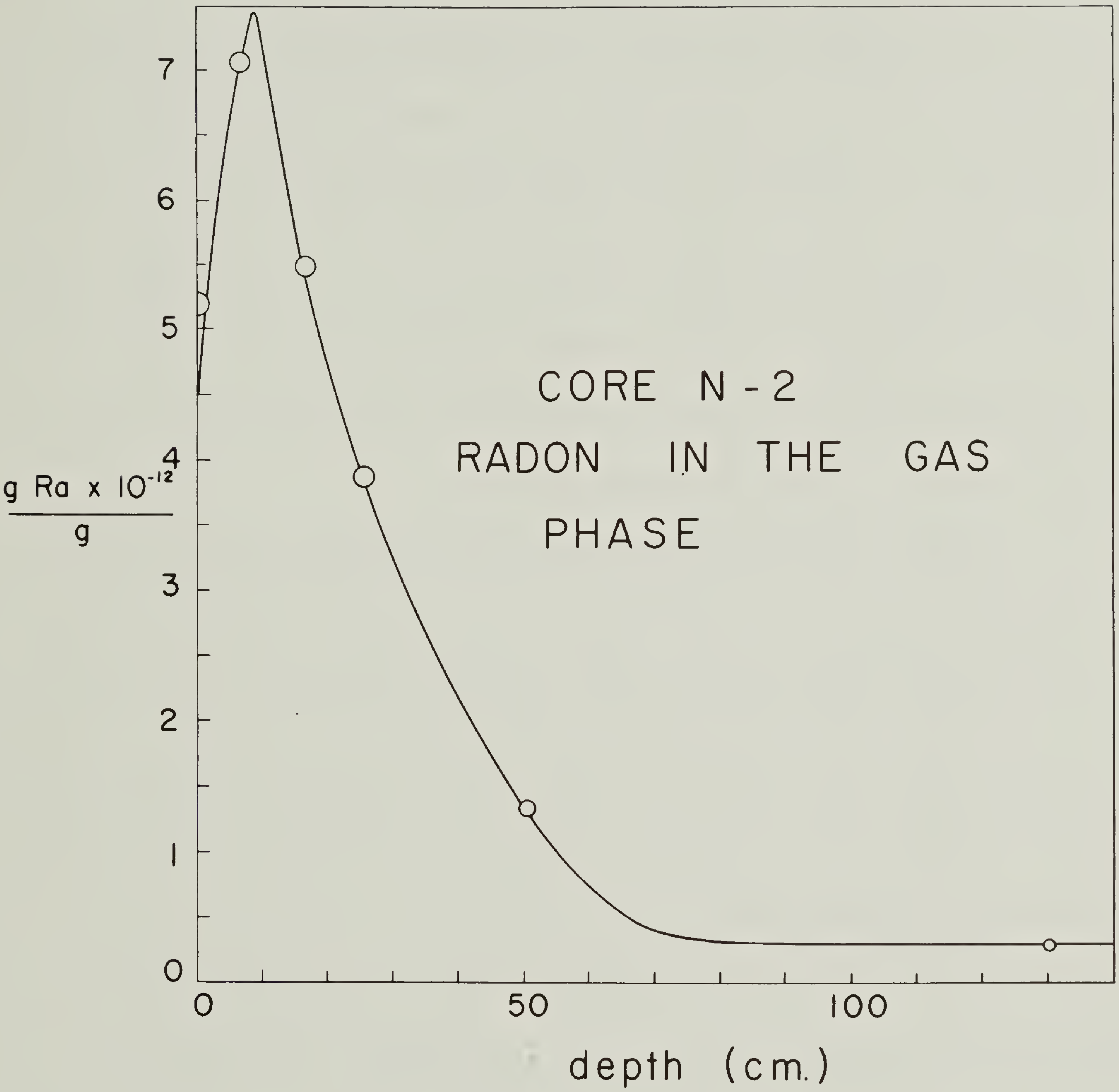

CORE N-2
RADON IN THE GAS PHASE
$\frac{g\ Ra \times 10^{-12}}{g}$
0
1
2
3
4
5
6
7
0
50
100
depth (cm.)

Figure 21.

Caribbean Sea Core P-137

Core P-137 was taken by C.S. Piggot in 1937 aboard the research ketch Atlantis of the Woods Hole Oceanographic Institution, from a point well down on the north slope of the Bartlett Deep in the Caribbean Sea. This core composed of a rather homogeneous globigerina ooze was one of the earliest used by Piggot and Urry in their studies leading to their formulation of the age method, (Piggot and Urry, 1942). The remaining samples of the core were kindly provided by Dr. Urry, as a means of interchecking between laboratories.

Piggot and Urry measured the total radium content of about ten depths in this core. The results are plotted in Figure 22. The curve shown is the interpretation of Piggot and Urry. This curve, like the one for N-2 illustrates the radium variation with depth in the core, predicted by the theory, except that insufficient time has elapsed for complete equilibrium.

At this laboratory samples of this core obtained from Dr. Urry were measured for internal radon content. The results of these measurements are plotted as a function of depth in Figure 23.

Atlantic Ocean Cores

Six cores from the north Atlantic Ocean were chosen from the extensive core collection at Lamont Geological Observatory. Figure 24 shows the location of these six cores. Also on the map is core, Kelvin 5, analyzed by the ionium method by Piggot and Urry, (1942a). Table 6 summarizes the geographical and depth data of the six cores.

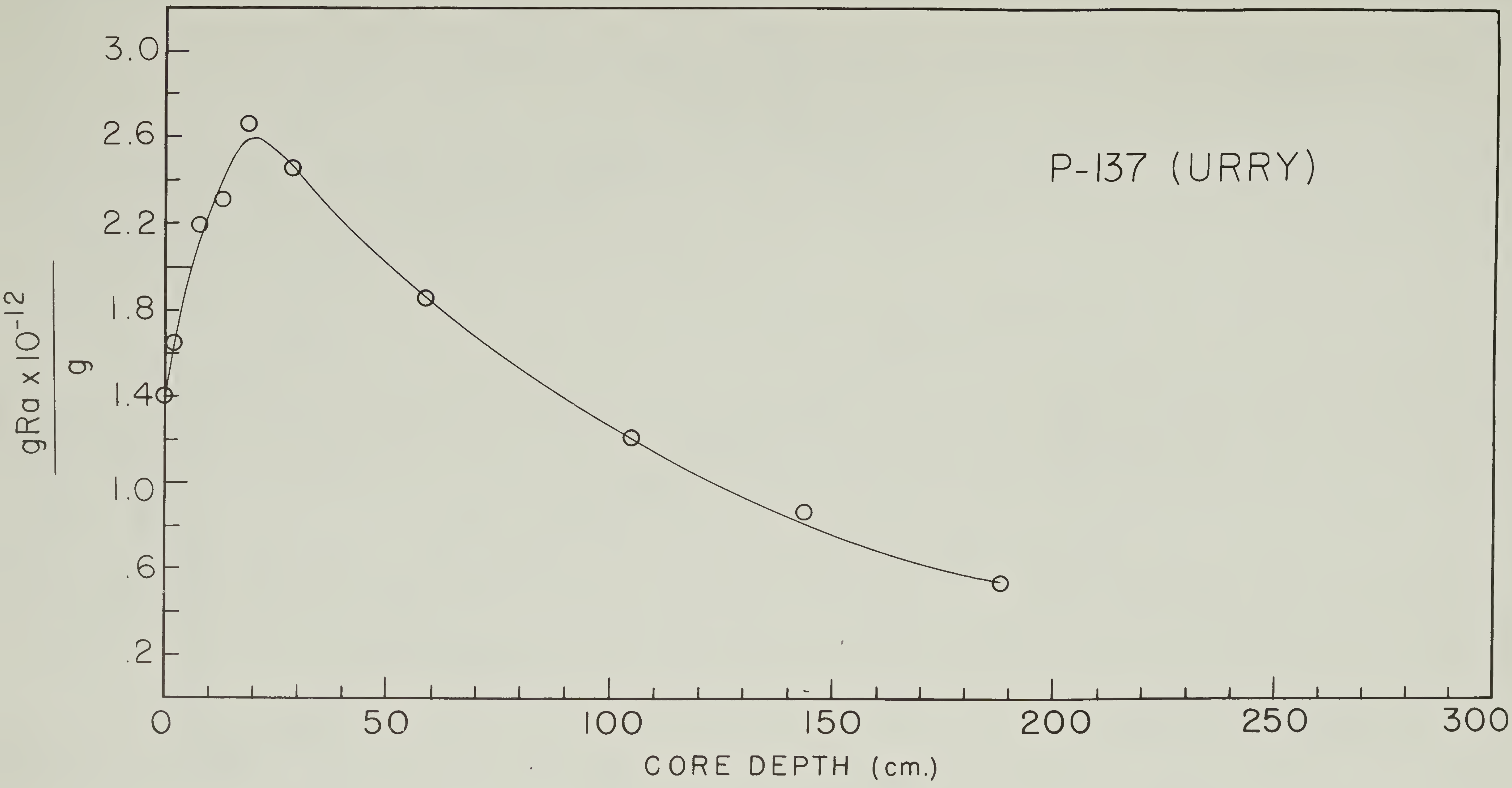


Figure 22. Total radium content core P-137.

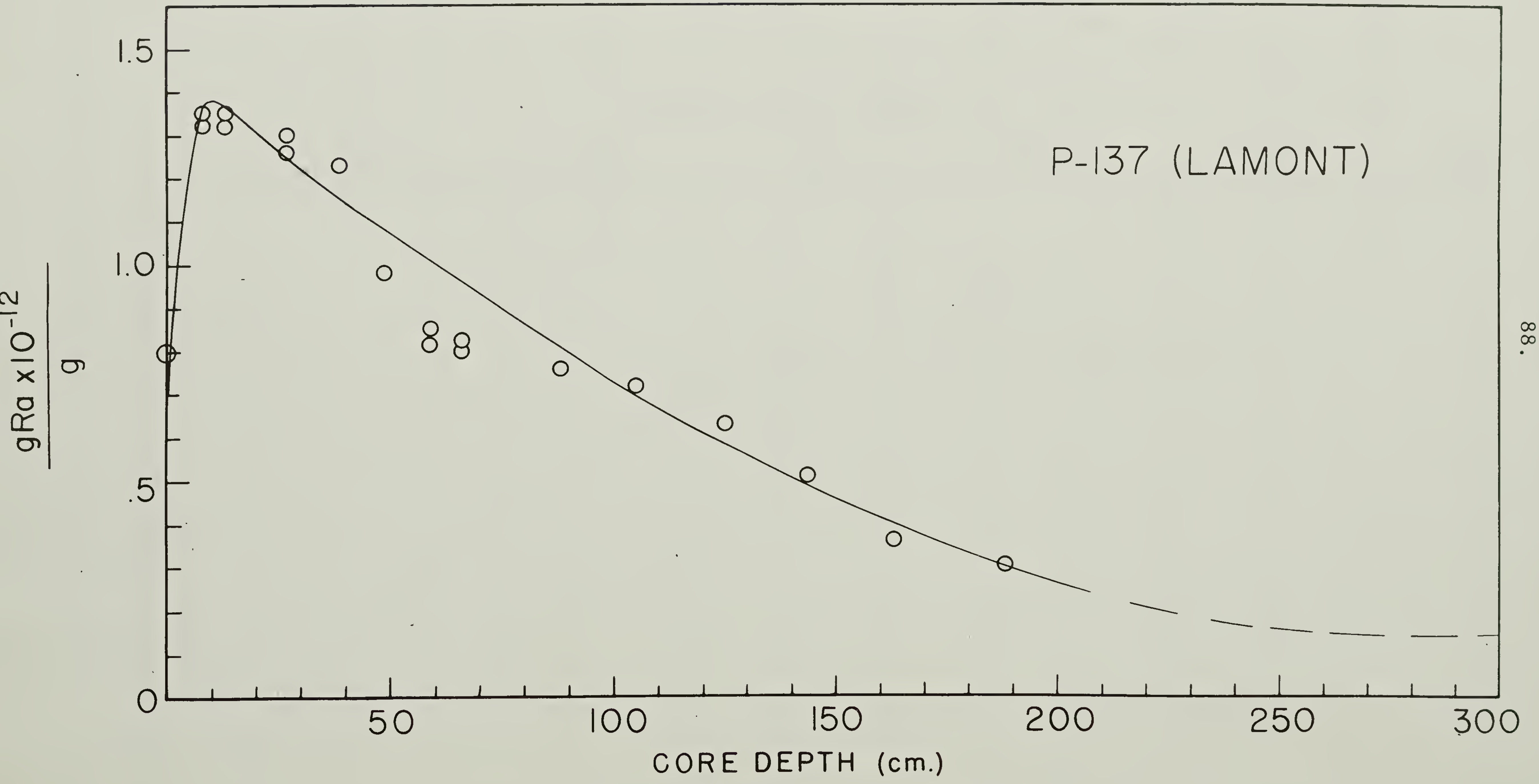


Figure 23. Internal radon content, core P-137.

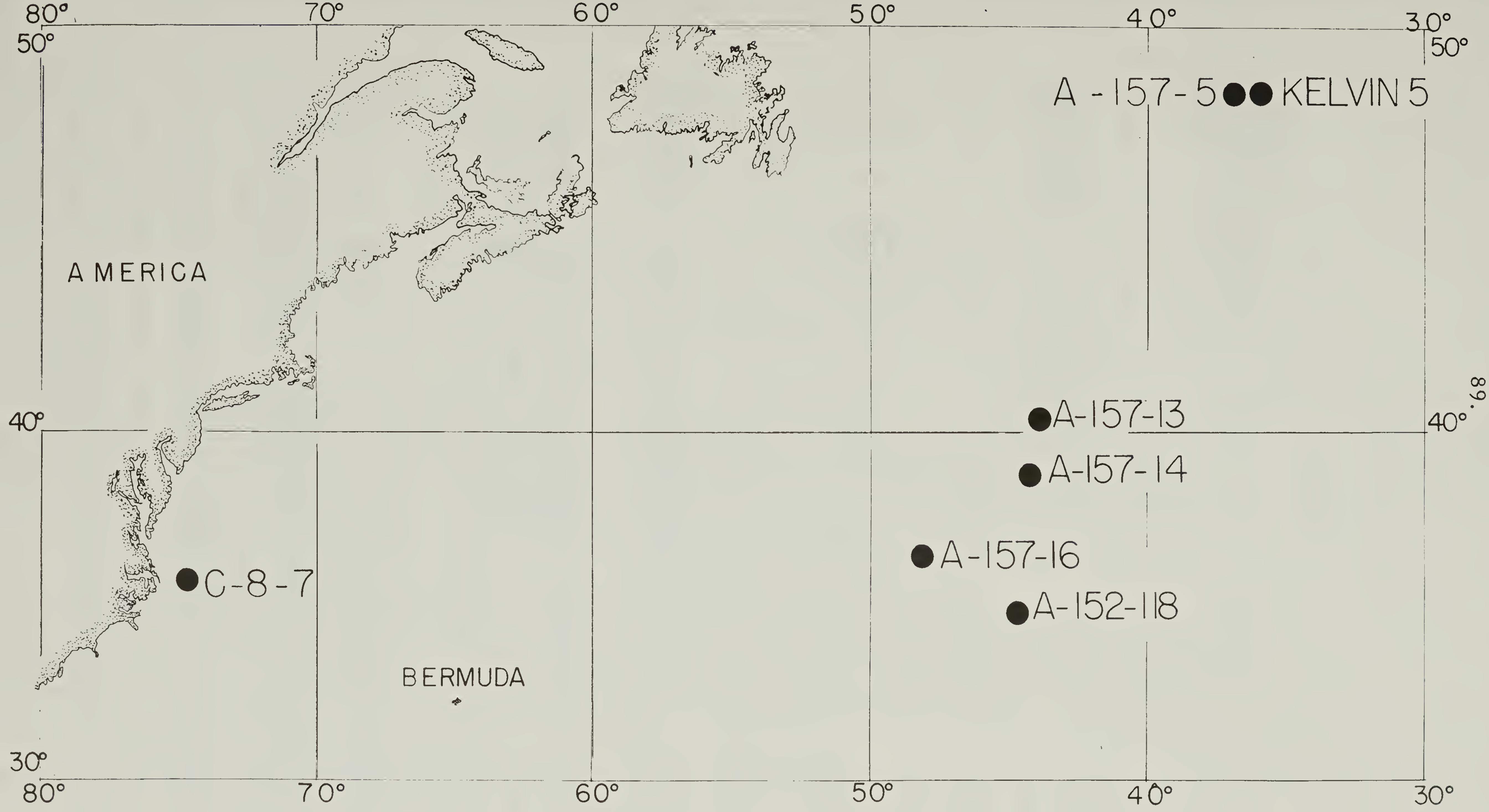


Figure 24. Locations of North Atlantic Ocean cores.

Table 6

Core No.	Lat. (N)	Long. (W)	Depth (M)	Length (cm)
C-8-7	35°56'	74°41'	1370	495
A-157#5	48°35'	36°51'	4500	320
A-157#13	40°30'	43°50'	4680	720
A-157#14	39°00'	44°15'	4775	490
A-157#16	36°45'	48°05'	5230	317
A-152-118	35°07'	44°40'	4340	645

Core C-8-7

As indicated in Figure 24 and Table 6, this core was secured from 1370 meters of water on the continental shelf of the eastern United States. The core contains typical continental shelf sediments indicative of fairly rapid deposition. The top two-thirds of the core consists of a homogeneous green mud with warm water foraminifera. At a depth of 335 cm., there is a sharp change from green mud to rose-gray clay corresponding to a surface water temperature change, as determined by the assemblage of faunal remains.

The total alpha emission rate is plotted on Figure 25 along with that of the other five Atlantic Cores. It may be seen that compared to all of the other cores measured, the alpha activity of this core is remarkably constant throughout its length, ranging from 5.60 to 8.11 alphas/cm^2/hr. It is observed that the total alpha emission of this core does not suggest the decay curve required for the Ionium Method.

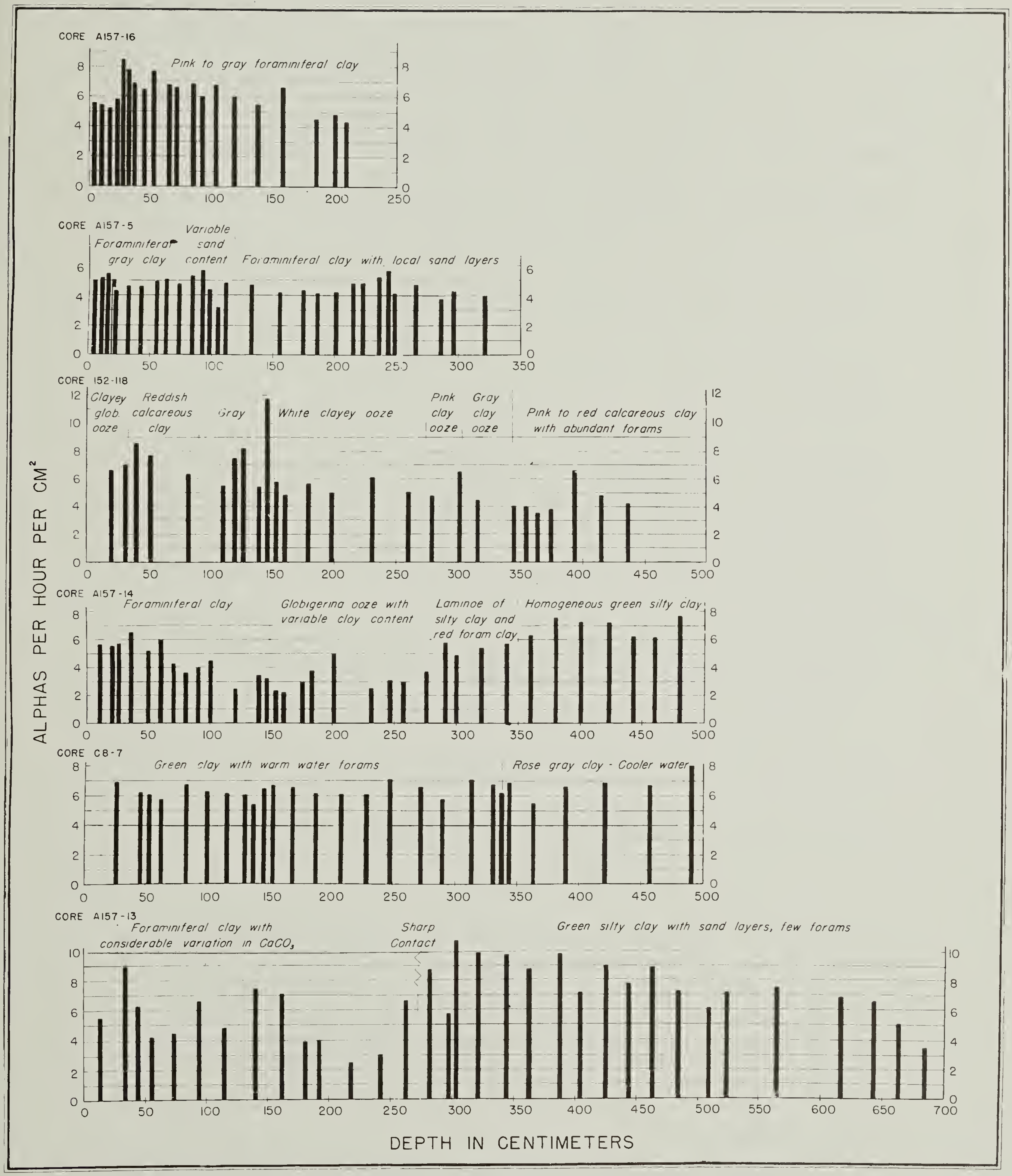


Figure 25. Total alpha emission, North Atlantic cores.

W. D. Urry, (1949), measured the radium content of a core from the shelf of New Zealand and found a smiliar very constant concentration throughout its length. On the basis of this data he concludes that, "the sediments of the continental shelf consist largely of detrital material and that the operation of the mechanism that destroys the state of equilibrium between radium and ionium in deep sea deposition is confined to the deep ocean basins." Actually the fundamental process i.e. chemisorption of the ionium ions on particle surfaces, takes place along continental margins too, but the sedimentation rate is so rapid that the concentration of ionium in the water column through which the particles fall is depleted. Therefore the excess ionium on the particle surfaces becomes a negligible fraction of the total ionium in the sediment.

Surface area measurements on 12 samples of this core likewise were remarkably constant. Table 7 lists these data. Cores with constant surface area throughout their length would most clearly show differences in ionium content due to radioactive decay. Therefore, the constancy of surface area in this core supports the conclusion that the preferential chemisorption of ionium on the surface of freshly deposited particles is masked by other effects.

Core A-152-118

This core was taken from some 4340 meters of water on the northwest flank of the mid-Atlantic ridge. Reference to Figure 25 indicates that the core is composed of varying bands of red to gray

Table 7

Surface Area of Core C - 8 - 7

Depth (cm.)	Surface Area (M^2/gm.)	Description
26	10.5±0.4	Green Clay
53	12.7±0.5	"
99	12.1±0.5	"
130	11.7±0.5	"
145	12.5±0.5	"
188	10.3±0.5	"
227	11.1±0.4	"
330	14.0±0.5	"
340	15.5±0.5	Rose Gray Clay
343	10.7±0.4	"
361	17.3±0.5	"
487	12.6±0.5	"

clay and globigerina ooze.

The total alpha emission of this core is also plotted on Figure 25. Here it will be noticed that the alpha emission is not at all constant, nor does it vary in any regular way. However, it may be seen that the first six points on the graph do exhibit the expected low activity at the top of the core building up to a maximum and then again decreasing. Whether or not this is the reflection of the inequilibrium relations of the Ionium Method curve might be questionable, because of the subsequent points.

Surface area measurements on samples from this core were also made and are tabulated in Table 8, (Kulp and Carr, 1952). The surface areas are likewise not constant, nor do they seem to show any definite trend. From the wide variation in surface area, in several cases having a spread of more than a factor of two, it would be predicted that the radioactivity measurements would be variable.

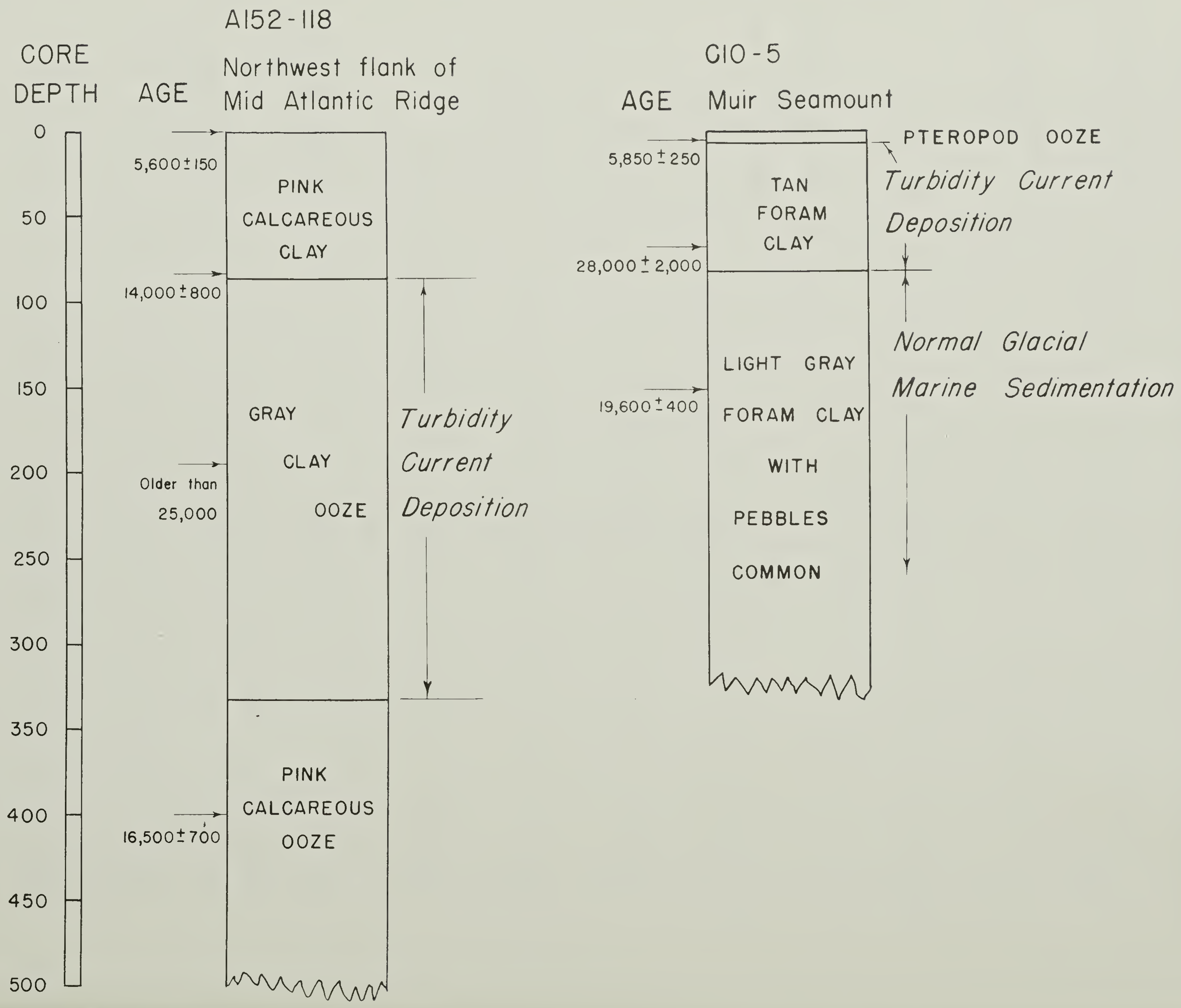
Studies of the lithologic units in this core, by D. B. Ericson, indicated that a large portion of this core was deposited in other than the normal way. Thus at his suggestion, radiocarbon measurements were made on selected samples from this core. The results are shown on Figure 26. With this added information a reasonable explanation of the total alpha activity variations is possible. It may be seen in Figure 26 that approximately 50% of the entire core has been deposited by a turbidity current. This has thoroughly destroyed

Table 8

Surface Area of Core A 152-118

Depth (cm.)	Surface Area (M^2/gm.)	Description
11	13.4	Light Pink Globigerina Ooze
25	17.9	"
30	34.1	Calcareous Red Clay
40	29.7	"
52	27.1	"
75	32.5	"
110	21.9	Grayish White Clayey Globigerina Ooze
128	25.2	
147	23.3	"
150	21.6	"
181	21.7	"
200	23.7	"
210	24.8	"
234	25.0	"
263	25.3	"
285	22.1	Pink to Gray Clayey Ooze
305	18.0	"
360	15.8	Pink to Red Clay with abundant Foraminifera
380	18.8	
400	30.1	"
407	24.2	"
410	24.8	"
420	26.2	"
442	27.6	"
539	24.4	"

Figure 26. Cores illustrating turbidity current deposition.



the chronologic sequence of the core, a rigid requirement for the Ionium Method . Some 250 centimeters of sediment were apparently deposited by turbidity currents between the depths of 80 and 340 cm. Referring back to the graph of total alpha emission for this core on Figure 25 it can be seen that the greatest variations occur within this section of "abnormally" deposited material. Thus the shape of the data for this section of the core is understandable on the basis of the probable origin of the material. It is suggested that this sediment originated partially from a higher portion of the mid-Atlantic ridge and in slumping and transport as a turbidity current was mixed with unknown other material before finally being deposited at the core site.

The five topmost points which all occur within the "normally" deposited sequence seem to vary in the prescribed manner for ionium dating. From this date the peak may be estimated at about 40 cm. in depth. Referring now to Figure 26 it seems that qualitatively the age at this depth of 40 cm. from the Carbon-14 dates would be some 8, 000 to 10, 000 years, which is in substantial agreement with the mathematical peak age of about 10, 000 years as described earlier in the theory of the Ionium Method. On the other hand this may be mere coincidence since even this interval of the core shows variable lithology and surface area. However, this analysis indicates how limited sections of a core might be dated.

The other core pictured in Figure 26 is an additional example of turbidity current deposition disturbing a normal sequence of sedimentation.

Core A-157#14

This core, like the previous one described, was taken from deep water of the North Atlantic Ocean. The core is variable in lithology along its length, as reference to Figure 25 will indicate.

The total alpha emission rates plotted in Figure 25 indicate quite clearly that the simple ionium decay curve does not prevail. Once again some hint of these relationships may be seen in the first 150 centimeters, but the data do not warrant any detailed age interpretation. No measurements of surface area or radium content were made on this core.

Core A-157#16

Core A-157-16 was probably taken south of the glacial zone since it is long enough to be Wisconsin but contains no glacial marine layers. The top 30 centimeters are rather inhomogeneous, but the remainder of the core is pink - gray foraminiferal clay.

The total alpha emission rates (Fig. 25) clearly reflect the lithologic break at 30 centimeters depth, and, less clearly, a break at 53 cm. The very rough downward trend of the activity with depth beyond 30 cm. might suggest ionium decay but is too ambiguous to merit age analysis.

Core A-157*5

The northernmost of the six Atlantic Ocean cores studied, this core was specifically chosen for its proximity to core Kelvin 5, measured by Piggot and Urry, (1942a).

The total alpha count (Fig. 25) does not yield any indication of the theoretical ionium method curve. Table 9 lists all the surface areas obtained on this core and it may be seen that the variation is greater than a factor of two even for these few points.

To further enable comparison with the neighboring core used by Urry, internal radon determinations were made on samples of this core. A detailed lithologic study was made by D. B. Ericson. The results of these investigations, along with similar data from Piggot and Urry, (1942a), are plotted on Figure 27. The actual points from which Piggot and Urry interpreted this curve have not been published. The correlation of lithology between the two cores is apparent. Zone for zone, from top to bottom, the cores match except for differences in thickness. The radium concentrations, however, do not correlate. The rather smooth curve of radium versus depth in the Kelvin 5 (also called P-126) core, was not found in A-157-5. Dating core A-157—5 by use of this radon data is impossible.

Table 9

Surface Area of Core A 157# 5

Depth (cm.)	Surface Area (M^2/gm.)	Description
10	18.8	Foraminiferal Gray Clay
23	27.8	"
43	22.5	"
63	24.5	"
84	28.8	Gray and Tan Glacial Marine Clay with variable sand content
112	32.7	
155	18.3	"
186	14.2	"
222	31.1	"
248	17.8	"

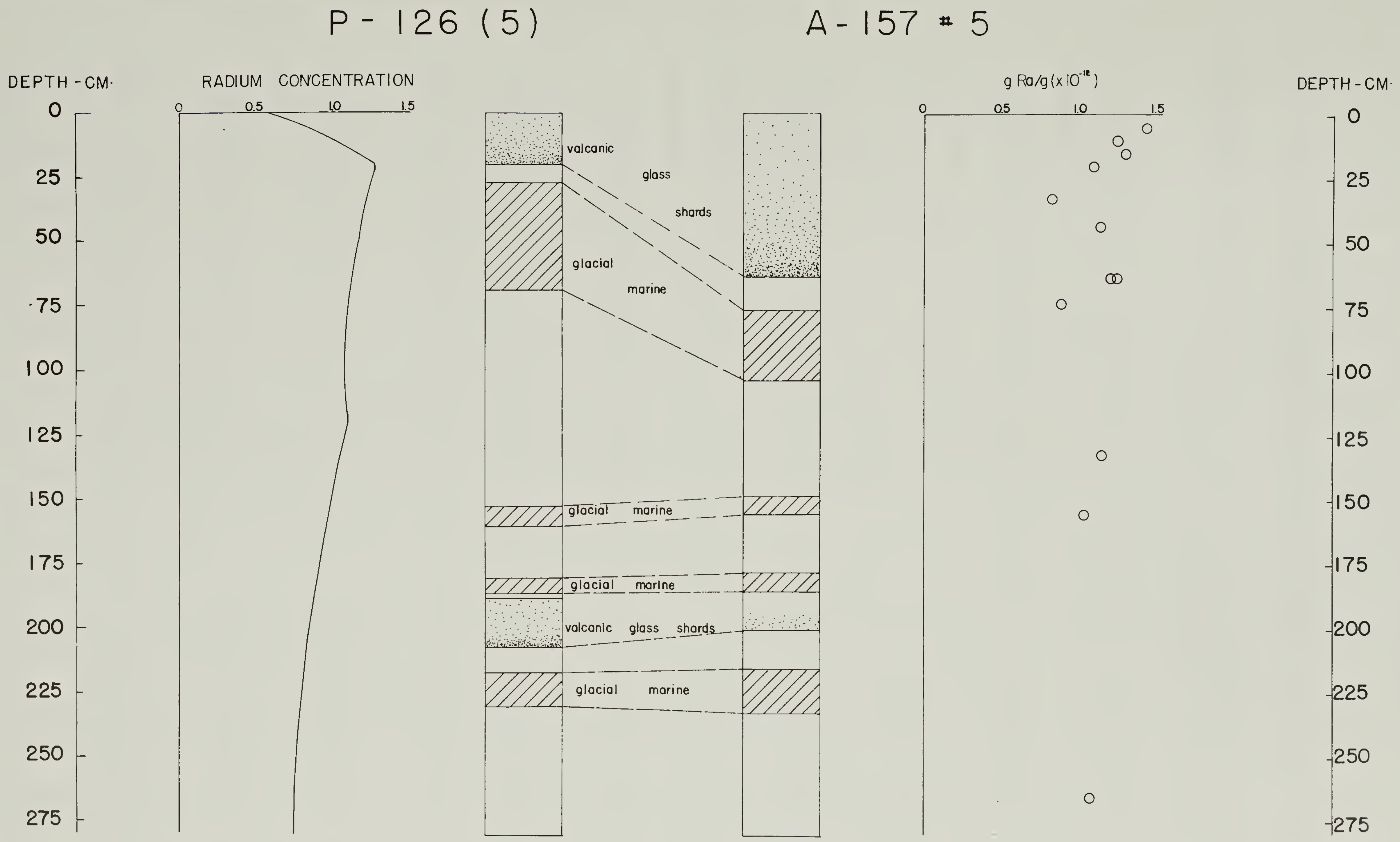


Figure 27. Comparison of radium content and lithology in adjacent cores.

Core A-157# 13

This core is the longest of all the six Atlantic cores (some 720 cm. long) and is of interest because of the very abrupt change in color at a depth of 273 cm., suggesting an uncomformity.

The thick source total alpha rate, shown in the last graph on Figure 25, clearly reflects the contact by a sudden increase in alpha activity. From the top of the core to the contact at 273 centimeters the points seem to vary randomly, and no real hint of an ionium decay curve can be found.

The internal radon content of this core was also measured. The data are listed in Table 10 and plotted as a function of depth in Figure 28. It can be seen from Figure 28 that a well-defined Ionium Method curve is not present. However, the last seven points before the sedimentary break suggest the approach of equilibrium of ionium with uranium. The low radium concentrations in the upper few centimeters of the core, and the very high values at 30 - 50 centimeters, also tend to suggest that in this core the enrichment was not entirely obliterated by other factors.

Surface area measurements were also made on this core in much greater detail than had been done on any of the previous cores. The results are listed in Table 11. These values of surface area again vary considerably. An analysis of these values shows a very direct correlation with radium content point by point along the length of the core. The curves of Figure 29 show the correlation graphically. From the data on core N-2 it may be supposed that the radium curve

Table 10

Radium Content of Core A157#13

Depth (cm)	g Ra x 10^{-12}/g Sed. (in equilibrium with internal radon)
0 - 2	0.91 ± .03
3 - 5	1.14 ± .03
9 - 11	0.84 ± .03
19 - 21	1.40 ± .03
29 - 31	1.73 ± .04
34 - 36	1.95 ± .05
42 - 44	1.17 ± .03
49 - 51	2.46 ± .06
54 - 56	1.04 ± .03
59 - 61	0.89 ± .04
72 - 74	0.78 ± .02
79 - 81	1.31 ± .03
99 - 101	0.96 ± .02
139 - 141	0.42 ± .01
179 - 181	0.22 ± .01
214 - 216	0.16 ± .01
239 - 241	0.15 ± .01
259 - 261	0.15 ± .01
"Sedimentary Break"	
279 - 281	0.58 ± .01
301 - 303	0.71 ± .02
341 - 343	1.28 ± .03
401 - 403	0.68 ± .02
441 - 443	1.08 ± .03

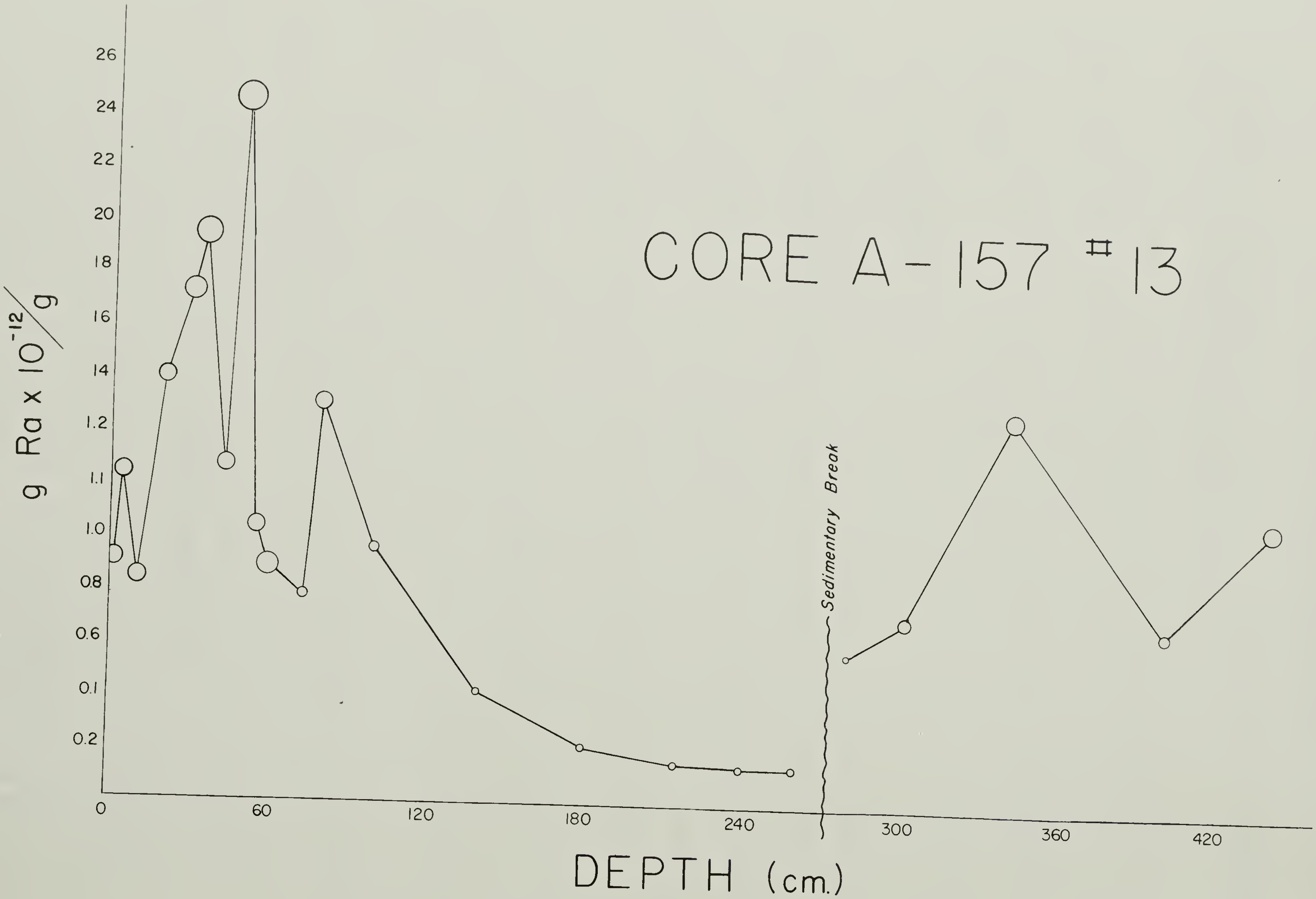


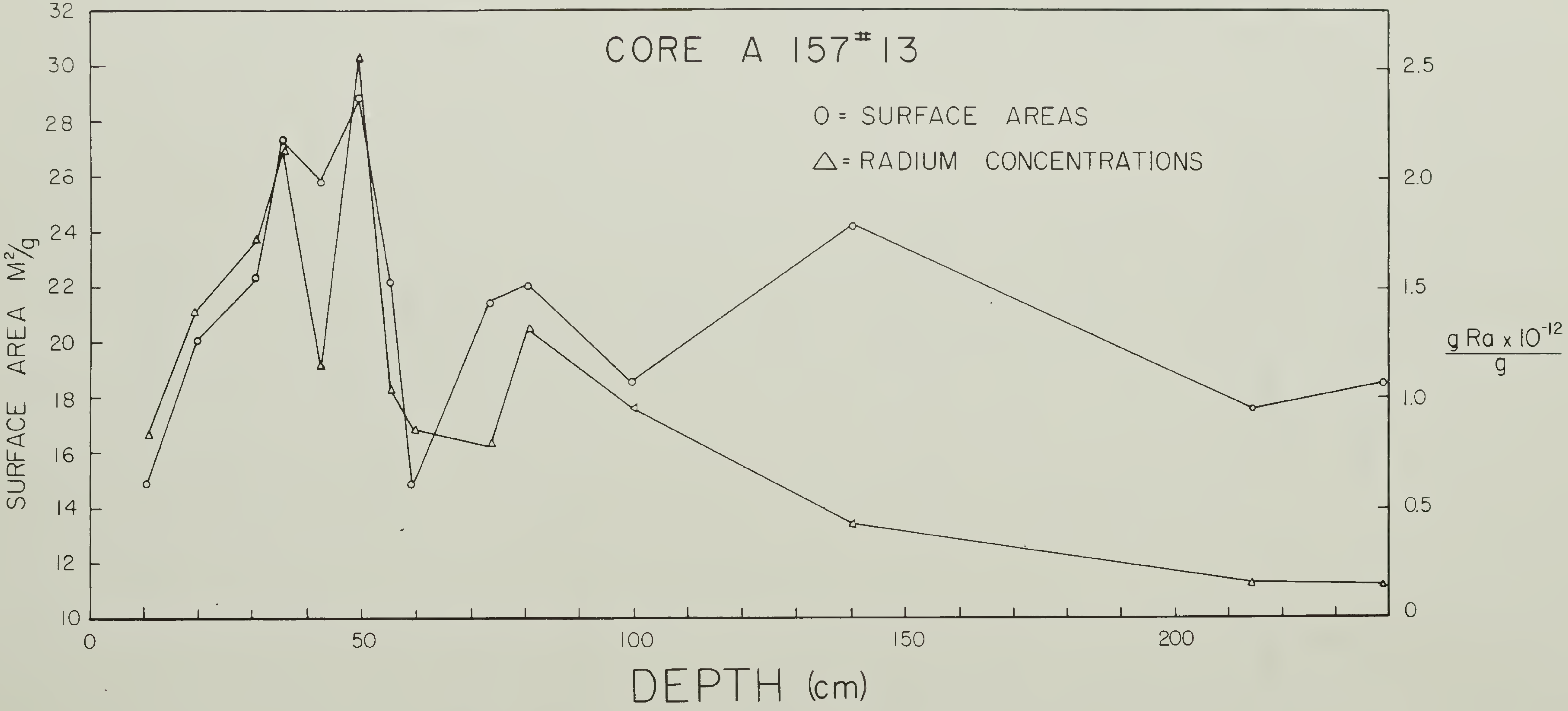
Figure 28. Radium content, core A 157 13.

Table 11

Surface Area of Core A 157 13

Depth (cm.)	Surface Area (M^2/gm.)	Description
10-11	14.97	Inhomogeneous Foraminiferal Clay with considerable variation in $CaCO_3$
19-20	20-07	
30-31	22.34	"
35-36	27.48	"
42-43	25.90	"
49-50	28.78	"
55-56	22.20	"
59-60	14.89	"
73-74	21.50	"
80-81	22.12	"
99-100	18.60	"
140-141	24.33	"
215-216	17.64	"
240-241	18.58	"

Figure 29'. Correlation of radium content and surface area in core A 157 13.



would be correctable by the variations in surface area, resulting in a valid decay curve. However, it was found that this was not the case in this core. Applying corrections for surface area merely modifies the radium curve, decreasing the peak heights somewhat, but does not nearly approximate the theoretical curve. It is quite evident that some sections of the core, e.g. from 80 cm. to about 270 cm., do seem to approximate a decay curve in spite of the surface area differences of the points. This is probably due to the effect of time on these radium contents. Since the surface areas at these points vary only by about a factor of two, original differences in ionium content of a factor of two may be indistinguishable in the time span since deposition.

The variations in the upper younger section between 0 and about 80 cm. in depth are not explainable on this basis. The most probable explanation on the basis of the foregoing data is that this section of core is complicated by factors other than surface area variation. From the location of the core as pictured in Figure 24, there certainly is good probability of turbidity current deposition at that site. Thus the possibility exists that the upper section of the core may be chronologically scrambled in addition to its lithologic inhomogeneity as evidenced by the surface areas. In such a case, since corrections for surface area variations do not correct the radium data to the theoretical values, it is obvious that dating is impossible by the Ionium Method.

V. Geological Theory

The results presented in the previous section show that most cores obtained from the deep Atlantic Ocean floor cannot be dated by the Ionium Method. Apparently to obtain a sedimentary column containing the radioactive relations dictated by the theory a unique set of conditions must be fulfilled during the period of accumulation of the sediment. There are four geological conditions which are necessary for the Ionium Method to be valid.

(1) The ionium concentration of the ocean musthave been constant for at least the last four hundred thousand years.

(2) Apart from the uppermost few centimeters in which the radium content is increasing with depth, radioactive equilibrium between ionium and radium must prevail.

(3) Only "normal" sedimentation processes must have been responsible for the emplacement of the original material of the core, and no subsequent external factors, influenced or disturbed the original sediment column.

(4) The sedimentary material must be homogeneous throughout the length of the core, specifically with regard to its chemsorption properties.

It is believed that all of the anomalies in the measured cores, showing deviations from the "ideal" radium versus depth curve, can be explained on the basis of one or more of the above conditions having been violated. It remains to discuss each condition and to estimate the degree of departure from ideality to be expected.

Condition 1 - The ionium concentration of the ocean must have been constant for at least the last four hundred thousand years.

The validity of this condition may only be estimated through a discussion of the general geochemistry of the oceans. Rubey (1951) after analyzing a great deal of paleontological and and biochemical evidence, concluded that the variations of the compositions of the seas have been within relatively narrow limits, through most of geologic time. Rubey shows that even a relatively small increase of carbon to the atmosphere and ocean would probably exterminate many species of marine organism, and unless addition of CO_2 to the system continues rather steadily, brucite would replace calcite as the common marine sediment. Similarly it is pointed out that because of the osmotic pressures involved many species can tolerate only small variations in the salinity of their environment, and possess very specific requirements for amounts of dissolved calcium, sodium, potassium and other elements. Rubey concludes, "apparently the geologic record shows no such evidence of such simultaneous extinctions of many species nor such deposits of brucite - everything considered, the composition of sea water and atmosphere has varied surprisingly little, at least since early in geologic time ".

On the basis of these evidences it seems reasonable to assume that the concentration of ionium in the sea has likewise remained relatively constant throughout geologic time. Since condition (1) specifies only a minute fraction of this time span the assumption seems even more justified.

Condition 2 - Apart from the uppermost few centimeters in which the radium content is increasing with depth, radioactive equilibrium between ionium and radium should prevail.

For the specific purpose of determining the validity of this condition N. Issac and E. Picciotto of the Centre de Physique Nucleaire de Brussels, have evolved a method for the direct determination of ionium in sediments, (Issac and Picciotto, 1953). The method involves adding a beta emitting thorium isotope (Th^{234}) to a solution of the sediment sample, separation of the cations (including radium and uranium) from the thorium by base exchange, and measurement of the yield by beta counting and the ionium concentration by detecting the alpha particles of ionium by nuclear emulsion techniques. The authors report that this method allows for measurement of ionium at concentrations between 10^{-9} and 10^{-10} grams of ionium per gram of sediment to within ten per cent. To date the data of only five samples have been published. The results are listed in Table 12. The authors state that these values should be considered only preliminary, subject to revision, and that the results are too few to allow any general conclusions to be drawn.

Table 12

Ra-Io Equilibrium in Sediment

1 Sample No.	2 Core No.	3 Depth No.	4 Radium (10^{-12}g/g)	5 Ionium (10^{-10}g/g)	6 $R = \lambda RaNRa/\lambda IoNIo$
4	83	3.5-4.5	27.9	14	1
5	83	31.5-32.5	46.4	10	2.3
11	86B	11.5-13	38	20	1
12	86B	16.5-17.5	52	13	2
13	86B	48-49	19.1	$\ll 1$	$\gg 1$

It should however be pointed out that all of the five numbers of the last column are either equal to or greater than unity. That is, in the three cases where the results do not indicate equilibrium between radium and ionium, radium appears to be in excess. In none of the results is ionium in excess. This seems to indicate the possibility of a recurring error. Since the radium values of column four were determined by direct fusion of the sediment, it would be expected that essentially all of the trapped radon was released and measured. The efficiency of radium measurement by this method has been discussed earlier. The measurements of ionium however, necessitated putting the samples into solution. This offers the possibility of an error due to the difficulty of dissolving the silicate fraction of the sediment. Any error of this sort would tend to give lower ionium concentrations, which in turn would tend to make the values in the last column of Table 12 greater than unity. If condition (2) were truly not valid, a comprehensive study of the relative concentrations of ionium and radium should yield as many values of R less than unity as are found greater. Thus, with the reservation that not nearly enough data is available, perhaps the absence of R values less than unity suggests an experimental error.

Condition 3 - Only "normal" sedimentation processes must have been responsible for the emplacement of the material of the core, and no subsequent external factors have influenced or disturbed the original sediment column.

The existence of eroding and depositing bottom currents, turbidity currents, and submarine slumps, has been realized for some time. Their nature and effects are being actively studied by the Geophysics and Oceanography group at the Lamont Observatory, under the direction of Professor M. Ewing, (Ericson, Ewing and Heezen, 1951; Heezen, Ewing and Ericson, 1951; Ericson, Ewing and Heezen, 1952; Heezen and Ewing, 1952). These authors studied a large number of deep ocean cores from a variety of locations in the Atlantic Ocean including the Hudson Submarine Canyon, Bahamas, Bermuda, Caribbean, Puerto Rico trough and the North America Basin. Among their conclusions, they state, "in the North Atlantic, most of the samples taken from the floors of the main basins will have a large proportion of sediment deposited by turbidity currents". Although they believe that Pacific Ocean sediments are probably affected much less by this agent, because of its size and its being bordered by effective sediment traps, "... one must not overlook the possibility that a specific sample may contain a serious amount of reworked material".

On the basis of these studies it is quite clear that condition (3) is very critical in the Ionium Method of Age Determination. It is probably the violation of this condition which made it impossible to date most of the Atlantic Ocean cores in this study. Figure 30 is a bathymetric sketch of the western North Atlantic Ocean modified after Heezen, Ewing and Ericson (1955). The locations of the Atlantic cores which have been studied are plotted on the figure. It can be seen that although none fall within the Abyssal Plains they are all in areas somewhat susceptible to sedimentation disturbances. Core A-152-118 as described earlier (Fig. 26) clearly was affected by

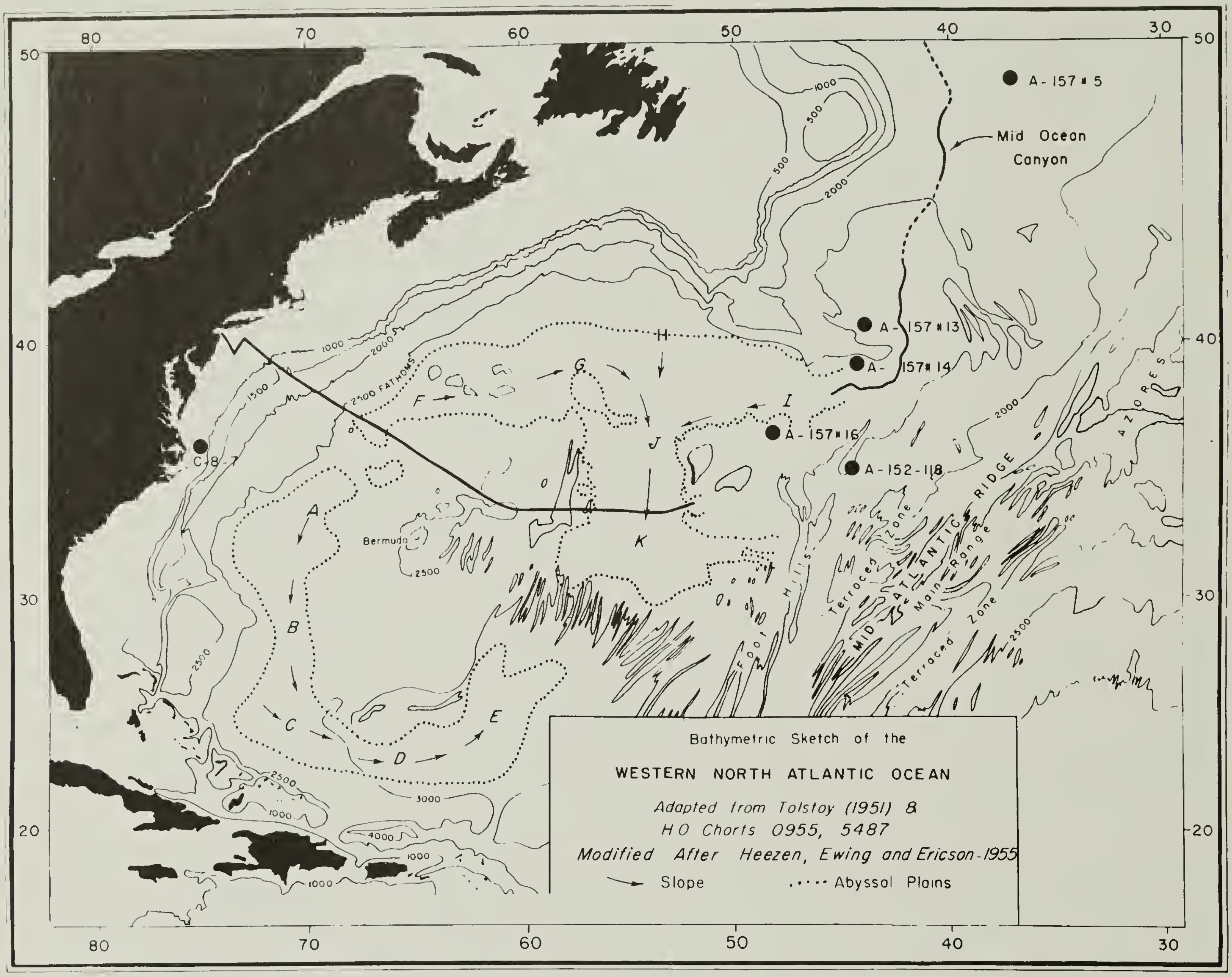

Bathymetric Sketch of the
WESTERN NORTH ATLANTIC OCEAN
Adapted from Tolstoy (1951) &
H O Charts 0955, 5487
Modified After Heezen, Ewing and Ericson-1955
Slope
Abyssal Plains
A-157 # 5
Mid Ocean Canyon
A-157 # 13
A-157 # 14
A-157 # 16
A-152-118
C-8-7
Bermuda
MID-ATLANTIC RIDGE
Terraced Zone
Main Range
Terraced Zone
Foot Hills
AZORES
2500 FATHOMS
A
B
C
D
E
F
G
H
I
J
K
80
70
60
50
40
30
50
40
30
20
500
1000
1500
2000
2500
3000
4000

Figure 30

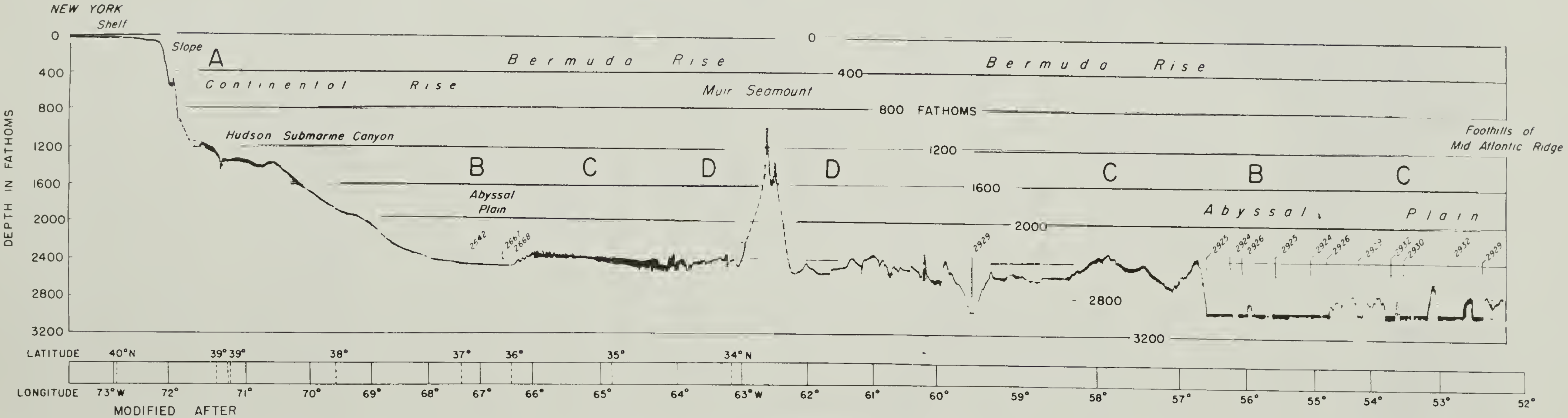
slumping. Core A-157-16 was probably affected by much the same type of disturbance, while the two cores from flanks of the Southeast Newfoundland Ridge (A-157-13, A-157-14) contain evidence of sub-marine erosion and slumping. Core A-157-5 was in all probability disturbed by a turbidity current from the slopes of the Mid Atlantic Ridge.

The other two cores studied, P-137, from the Caribbean Sea; and N-2 from the Pacific Ocean do not show lithologic evidence of abnormal deposition. The radium versus depth curves for these two cores indicate the undistrubed inequilibrium relationships predicted by the theory. Apparently condition (3) was therefore satisfied and the method is applicable.

It seems evident therefore that the ocean bottom topography is quite critical in deciding where to take cores that may be suitable for ionium dating. Figure 31 is a precision depth profile modified after Heezen, Ewing and Ericson (1955). The traverse of this section is indicated on the map, Figure 30. From the available data on ocean floor topography it appears that condition 3 may be satisfied for only small areas in the Atlantic but for sizeable areas in the Pacific.

Condition 4 - The sedimentary material must be homogeneous throughout the length of the core, specifically with regard to its chemisorption properties.

The two factors which control the effectiveness of chemisorption or base exchange capacity of a sediment are its mineral composition and its surface area. Variations in either of these factors would produce



MODIFIED AFTER

HEEZEN, EWING AND ERICSON 1955

VERTICAL EXAGGERATION 40:1 - 50:1

PRECISION DEPTH RECORDER PROFILE

Western Mid Atlantic Ridge to New York

Figure 31

Sediments on the continental slope (A), or abyssal plains (B), will have a high probability of having been eroded and/or deposited by turbidity currents. Sediments from any of the hilly areas (C) will very likely have been disturbed by slumps and submarine erosion, except in an occasional case. The area of the Bermuda Rise (D), would be most likely to yield a core entirely "normal" in its deposition, except if taken close to the actual slope.

discontinuities in the radium versus depth curve.

The validity of condition (4) in particular cores may be tested by means of surface area measurements and mineralogical studies, of the material along the length of the cores. Most of the cores used in this study were analyzed in this way, as described in the section on experimental results. A definite correlation of surface area with sediment type has been found. Averaging the data by sediment type, the following values have been found:

Continental slope, green clay	12.6 M^2/g
Globigerina ooze, foraminiferal green to gray clay	21.9 M^2/g
Red Clay	32.8 M^2/g

These values were obtained from samples representative of each sediment type, thus variations of the concentration of any of these major constituents will affect the surface area of a specific sample accordingly.

It is of course self evident that an intimate connection between conditions (3) and (4) must exist in many cases. The turbidity or slump deposited material which may occur in cores where condition (3) has been violated will in many cases differ in surface area and lithic character from the normally deposited sediment at the site. Thus in addition to a history of heterogeneous sedimentation, the core will commonly be variable in lithologic character along its length. Dating by the ionium method will be impossible in this case.

In the case where only condition (4) is violated as a result of normally fluctuating sedimentation conditions, it is still theoretically possible to employ the ionium method. If surface area alone is changing this factor can be measured experimentally, and the curve normalized to constant surface area. If well defined lithologic layering occurred, the homogeneous layers could be dated independently of the intervening portions. This situation has not been encountered in any of the cores of this study, but a similar analysis was attempted by Urry (1949) and Hough (1953) on one of the Pacific cores exhibiting fluctuating lithology. A detailed discussion of these studies follows in Chapter VII.

The importance of condition (4) is borne out by the results presented in the previous chapter. The Pacific core N-2 exhibited extreme lithologic uniformity and the surface area measurements as described earlier were in the main constant. The radium and total alpha activity data are thoroughly in accordance with the theory of the method. In contrast, the Atlantic Ocean cores studied, varied considerably in sediment type along the core length, lacked consistency in surface area and resulted in radium data incompalible with the theory.

It appears therefore, that of the four necessary conditions upon which the Ionium Method is based, only conditions (3) and (4) are apt to be violated in deep ocean cores. Since the relative fullfillment of these conditions can be defined either by a careful lithologic study or surface area measurements of the core material, it should be possible to select suitable material prior to extensive radium analysis.

Discussion

Pettersson (1953) suggested that the erratic radium versus depth curves obtained from cores measured at the Oceanografiska Institutet, Göteborg were due to migration of radium in the sedimentary column subsequent to deposition. However, in a discussion at the University of Chicago in the spring of 1954, Dr. Pettersson stated that he had abandoned this theory and concurred that the multiple peaks in the radium versus depth curves were probably due to depositional interferences as outlined in condition (3).

More recently, Kröll (1954) has reached a similar conclusion concerning the theory of radium migration, i.e., "observations indicate that there is no important diffusion of radium or ionium".

In the same paper Kröll attempts to explain the multiple maxima obtained in some cores as being due to changes in the rate of accumulation of ionium. This supposedly comes about because of variations in the concentration of ionium in the sea water through geologic time.

The main argument offered by Kröll for this hypothesis is based upon a calculation which indicates that the present rate of accumulation of ionium is equal to the supply of ionium due to decay of the uranium in the sea water. Since in several cores Dr. Kröll claims to have found a higher value of ionium supported radium than corresponds to the present uranium content in the water column above the core, he maintains that "the uranium content in the sea water is not a constant in time and that no unsupported ionium is carried to the sea at present". There are a number of objections to this hypothesis.

(1) Consideration of condition (3) of this chapter indicates that there may be considerable sections of cores containing radium unsupported by ionium. Should a core be composed largely of recent turbidity current material, or slumps, this is precisely the radioactive relationships that

would be predicted. Further, this unsupported radium may reach rather high concentrations as it approaches equilibrium with the ionium as the data of core N-2 indicates.

(2) Experimental determinations of the equilibrium chemisorption of ionium ions in very dilute solution, (Holland and Kulp, 1954) similar to sea water, make it clear that "all" of the ionium in a column of water through which a particle falls, will not be removed. Rather, the particles will tend to equilibrate with the ionium concentration of the water near the surface and remain essentially constant as it falls through the water column. Since the ocean is mixed rapidly relative to the time scale of the ionium method, the concentration of ionium in the open ocean far from land must change only very slowly and be proportional to the average world-wide sedimentation rate. This relation would not explain the multiple maxima with intervening minima that differ by a factor of ten.

(3) In their studies of the distribution of these radioelements in the oceans and sediments, Holland and Kulp (1954) further conclude that the rate of influx and deposition of ionium with pelagic sediments appear to greatly exceed the rate of radioactive production. Presumably the rate of influx would be proportional to the total rate of sedimentation.

If in some cores it is experimentally demonstrated that there are multiple peaks of unsupported ionium, the next step would be to make detailed mineralogical, chemical and surface area measurements. This would prove whether or not condition (3) was satisfied, and reveal differences in chemisorption properties. Only if none of these data explain the radium versus depth curves should a more complicated and seemingly less likely hypothesis be adopted. Finally, if the rate of accumulation of ionium is generally variable as it would have to be if Kröll's suggestion is correct, it is difficult to account for the smooth curves with single maxima, such as N-2 and P-137.

VI. Age Analysis

To define the precision that may be obtained by the use of the ionium method, the data from cores N-2 and P-137 will be thoroughly evaluated. These cores were chosen for this analysis because they have yielded radium versus depth curves which are seemingly consistent with the theory. Following the age analysis, attention will be given to the ultimate source of errors. From this study limits of the precision of the method under the best conditions can be set.

Core N-2. Urry never published an actual set of ages for core N-2, although the rate of deposition of the material of this core was published (Urry-1948). A complete age analysis was made on the original radium data published by Urry (1949), carried out as described in the section on theory. Because of the difficulty of extrapolating the radium curve to the ordinate, Θ_1 was obtained by the alternate mathematical method. The values of the two constants were found to be $\Theta_1 = 1.72$, $\Theta_2 = 0.086$. Table 13 lists the ages obtained using these constants. Since by definition these constants are respectively the initial amounts of uranium and ionium, expressed as ratios of the amounts which would be in equilibrium with the initial amount of radium, they are in effect each composed of two other constants. To simplify the symbols, let:

Ra_o = Radium content at t_o

Ra_U = Amount of radium in equilibrium with the uranium content at t_o

Table 13

Ages of Samples From Core N-2
Based on data of Urry (1949)

Sample Depth (cm.)	Age (years x 10^3)
1.0	0.6
2.0	1.1
3.0	1.6
4.0	2.4
5.0	3.3
6.0	4.7
7.0	6.5
8.0	9.5
9.0	11.2
10.0	15.0
15.0	35
20.0	60
25	87
30	116
35	146
40	182
45	214
50	252
60	350

Ra_I = Amount of radium in equilibrium with the ionium content at t_o

Then:

$$\Theta_1 = Ra_I/Ra_o$$

$$\Theta_2 = Ra_U/Ra_o$$

In the case of core N-2, the constants Ra_o and Ra_U could be read off the curve of experimental data quite accurately; Ra_o from the youngest radium content, and Ra_U from the average radium content of the deep end of the core where the ionium content had reached equilibrium with the uranium. The Ra_I constant however, is not easy to find because it requires extrapolating the up-swinging curve to zero depth. Despite this difficulty, Ra_I can be calculated since Θ_1 may be found mathematically, and Ra_o is known. Figure 32 shows the values of these three constants relative to the radium curve.

It seems quite clear that the value of Ra_I could never have been arrived at by extrapolation. Yet according to the definition, this value is proportional to the ionium content at zero depth, thus the ionium content must change down the core approximately as indicated by the dashed line on the figure. The change in slope of this dashed line indicates a changing rate of deposition. Thus the accuracy of the line is critical in the determination and interpretation of the depositional rate. Urry's curve on the rate of deposition of the material of core N-2 is reproduced in figure 33. It may be seen from this figure that over the period of from about 5,000 years ago to the present, the rate of deposition has increased by almost

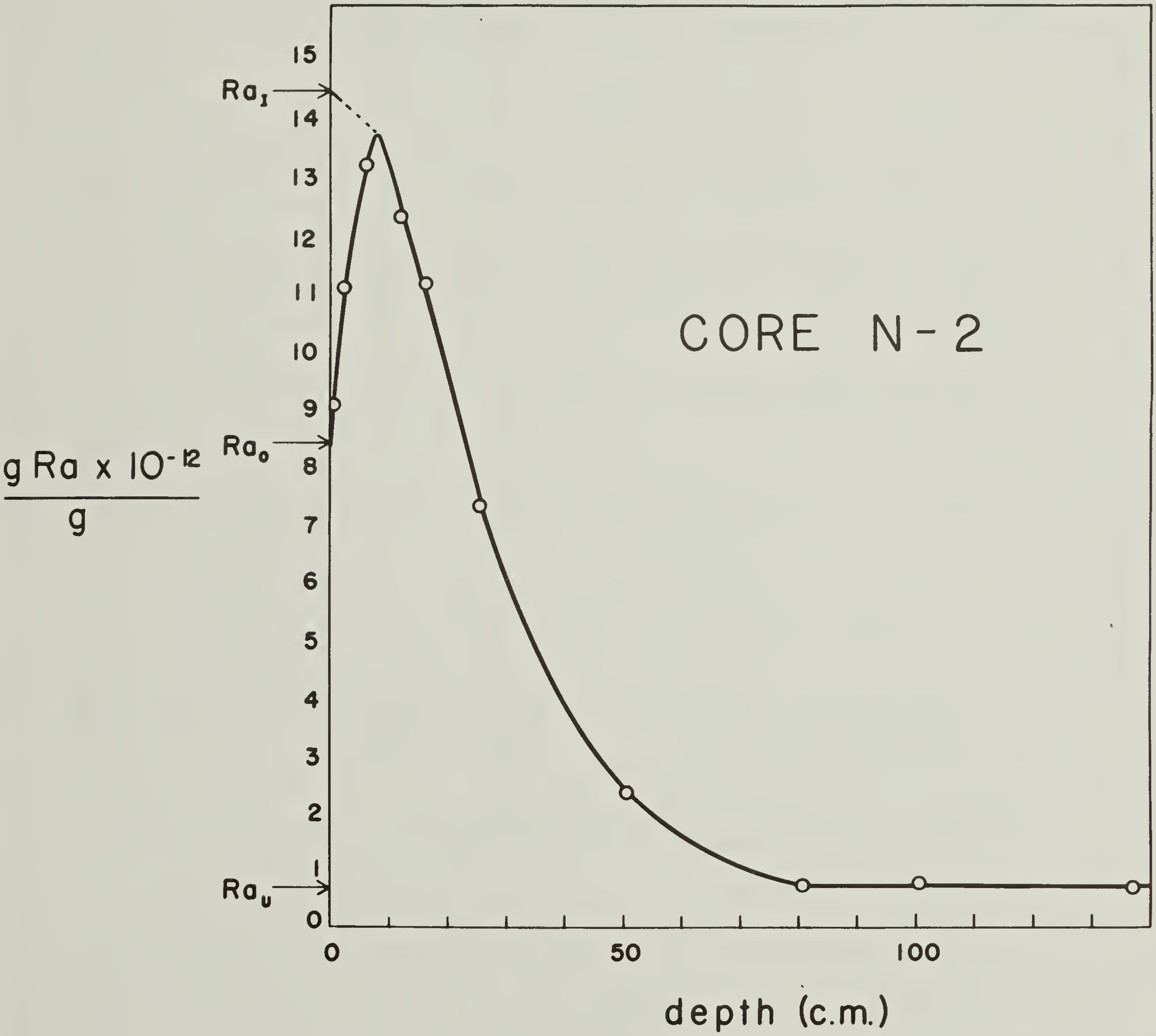


Figure 32. Analysis of the constants, core N-2.

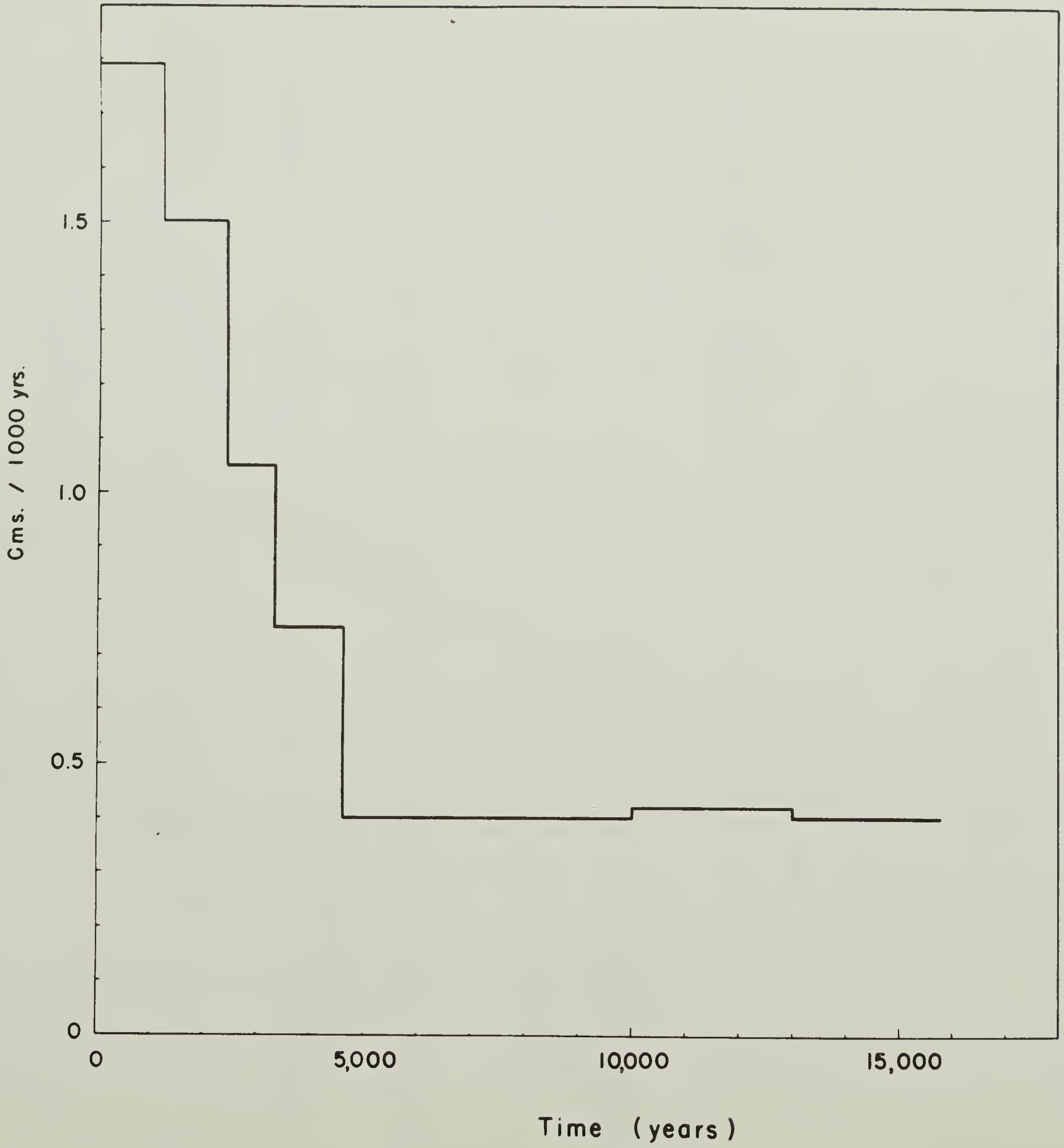


Figure 33. Rate of deposition as a function of time, core N-2.

a factor of four. This very large increase and the point in time where the increase became significant are of great geological importance as discussed in a later section. Therefore the accuracy of both the magnitude and position in time of this increased rate must be critically examined.

Referring to figure 32 it is obvious that the greatest change in slope of the dashed curve coincides with the peak in the radium curve. Thus in this case the peak defines the time of rapid change in deposition rate, and ambiguity in the position of this peak may greatly alter the interpretation. Reference to figure 32 indicates that for core N-2 the radium values do not clearly define the peak. The peak was evidently drawn by Urry as a smooth curve, but this is not necessarily valid. The smoothness of the curve depends directly on the deposition rate, and there seems no reason to assume constancy of this rate. It thus appears that both the position and magnitude of the peak as drawn by Urry is only one of many possibilities, and therefore the set of ages for the upper 15 centimeters of the core may not be correct.

Another analysis of the same data has been made. Figure 34 indicates the radium contents of the measured points of core N-2 without the smooth curve of Urry connecting them. The points are connected instead by straight lines. It is interesting to notice that a natural peak occurs in this curve at point 3, which is at 6.5 cm. depth. This point is some 2 cm. below the peak drawn by Urry. There seems to be no reason for placing the peak of the curve deeper than point 3 other than to obtain a smooth curve. If the curve is drawn solely on the

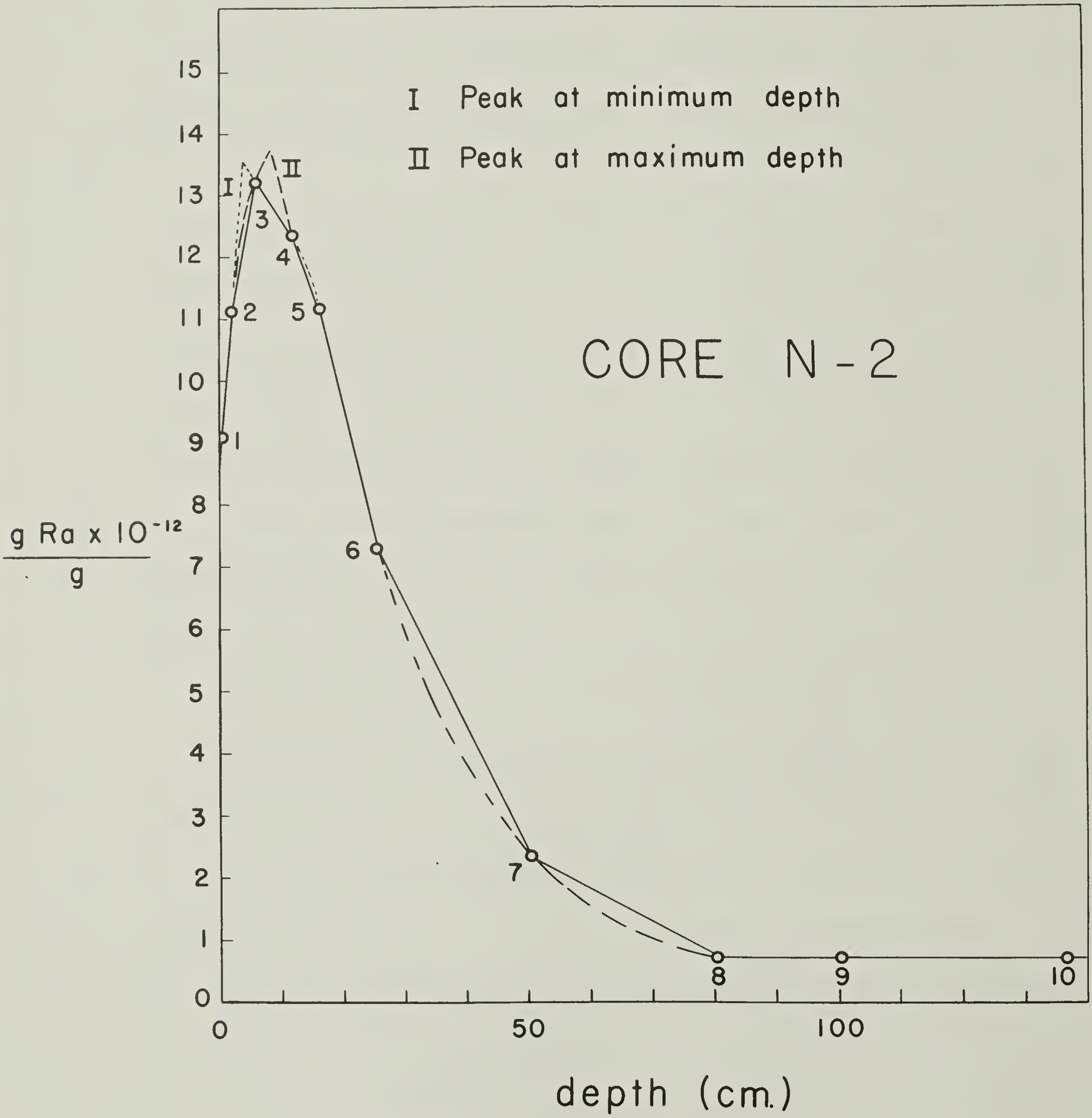


Figure 34. Age analysis, core N-2.

basis of the available data, that is, no assumptions of depositional rate are made, it seems clear that the peak for core N-2 may occur at any point between about 4.5 and 8.5 cm. These two extremes are shown in Figure 34, as dashed lines. In both cases Ra_O and Ra_U are quite well defined by the experimental data. For curve I, Ra_I is obtained by extrapolation to the ordinate of the straight line between points 3 and 4. Once the three constants Ra_O, Ra_I, and Ra_U are known, the peak of the curve is automatically set and may be obtained from a plot of Ra_t/Ra_O versus time, i.e. equation 9 in the theory. Knowing this peak radium value, its position on the abscissa is determined since it must lie on the extrapolation line between points 3 and 4, and may be plotted on the curve. The radium curve may now be drawn in for curve I, and ages determined in the usual way. Curve II it may be seen is essentially identical to that drawn by Urry, reproduced in Figure 33, thus the ages for this case have been described earlier. For comparison the two sets of ages indicating the limits depending upon the positioning of the peak are listed in Table 14. It is apparent that the age may be off by as much as a factor of two in the range of 2-10,000 years but that beyond 50,000 the disagreement between ages based on the two assumptions is trivial.

From the foregoing discussion it seems clear that with the available data, a completely unambiguous set of ages are not attainable for core N-2. The reason for this is primarily the uncertainty in the constant Ra_I, brought about by the lack of definition of the peak of the radium curve in the region of the peak. This difficulty may be easily overcome

Table 14

Ages of Samples from Core N - 2(years x 10^3)

Sample Depth (cm.)	Peak drawn at Maximum depth	Peak drawn at Minimum depth
1.0	0.6	0.5
2.0	1.1	1.8
3.0	1.6	2.3
4.0	2.4	3.7
5.0	3.3	7.0
6.0	4.7	8.2
7.0	6.5	10.6
8.0	9.5	12.1
9.0	11.2	14.2
10.0	15.0	15.3
15.0	35	27
20.0	60	55
25.0	87	81
30.0	116	113
35.0	146	143
40.0	182	180
45.0	214	214
50.0	252	247
60.0	350	338

by a series of closely spaced radium measurements to accurately define this peak.

The calculations which produced the ages in Table 13 were based on the original curve of radium versus depth as published by Urry, assuming constant surface area down the length of the core. As shown in Table 4 this is actually not the case for core N-2. The points at 25 and 50 centimeters were found to have higher surface areas than the others measured, which were quite constant. If the radium curve is normalized (see Fig. 19) to constant surface area, and the ages recalculated, the effect of surface area variation is evident.

Using the minimum peak as the most probable interpretation the ages are unaffected from the surface to about 15 cm. in depth since the surface areas are constant for this interval. Below 15 centimeters, due to the corrections to the radium data at 25 and 50 centimeters, the curve (Fig. 19) must necessarily be drawn with a much steeper slope, indicating a much slower depositional rate. Table 15 compares the ages for points along core N-2 after correction for surface area with the uncorrected values of Table 14. It is clear that this correction in the ages, below the depth of 20 centimeters is of first order importance. Thus even where a smooth single-peaked radium versus depth curve is found, surface areas must be run to insure constancy in adsorption potential.

An analysis of the curve of gas phase radon versus depth (described in chapter IV) may also be made. If the fraction of radon in the gas phase is an accurate index of the total radium, this fraction must be constant

Table 15

Ages of Sample, Core N - 2

Depth	Age (years x 10^3)	
	Uncorrected	Corrected for Surface Area
15	27	27
20	55	62
25	81	145
30	113	208
35	143	254
40	180	293
45	214	337
50	247	~ 400
60	338	$\gg 400$

Table 16

Fraction of Radon in the Gas Phase - Core N - 2

Sample Depth (cm.)	Ra_t	Ra_g	Ra_g/Ra_t
0.0 - 0.5	9.08±0.09	5.18±0.03	0.57±0.02
6.0 - 6.5	13.19±0.13	7.12±0.04	0.54±0.01
16 - 16.5	11.16±0.11	5.49±0.03	0.49±0.01
25 -26	7.30±0.07	3.87±0.02	0.53±0.01
50 -51	2.35±0.02	1.34±0.02	0.57±0.01
100 -101	0.76±0.01	0.31±0.01	0.41±0.02
137 -138	0.69±0.01	0.27±0.01	0.39±0.02

All radium values are in units of g Ra x 10^{-12}/g sed.

Ra_t = Total radium content (measured by Urry, 1949) with ± 1% error assumed.

Ra_g = Radium in equilibrium with radon in the gas phase along the length of the core. If this fraction is constant, then an identical set of ages would result from either total radium or gas phase radon analysis. Table 16 shows the fraction of radon in the gas phase for core N-2 obtained from the total radium measurements by Urry and the gas phase radon measurements from this study. It is seen that for core N-2 the average fraction of radon in the gas phase is about 0.50, thus enough radon escapes to make the measurements feasible. In the upper part of the core the condition of constancy is nearly satisfied within the experimental error. The lowest two points are not in agreement. It is possible that these inconsistencies are experimental because the measurements were made in different laboratories, and they occur in the lower concentration range where errors are greatest. Further work is required before the equilibrium gas phase radon can be used with confidence to determine the ionium age curve.

Core P-137. An age analysis has also been carried out on core P-137. Figure 22 illustrates the radium versus depth data as measured by Urry (1942). Although an actual set of ages has never been published, a diagram showing the rate of deposition for this core was contained in a later paper. For core P-137 the experimental data defines the curve in much greater detail than in the case of core N-2, especially in the very critical area of the peak. However, an analysis similar to the one made on core N-2, may be carried out for this core.

The constants necessary for the age analysis were obtained as follows: Ra_o is well-defined by the experimental data of Urry (Fig. 22) and is taken as 1.40×10^{-12} g Ra/g. Ra_U was found by directly measuring the uranium concentration at several points in the core. Urry (1941) made three measurements at 0, 19 and 188 centimeters in depth. The maximum spread of these data was about 50%, within the experimental error of his measuring technique. The average value expressed as equilibrium radium concentration is found to be 0.30×10^{-12} g Ra/g. Qualitatively this is in good agreement with the value obtained by smoothly extrapolating the original data of Figure 22 to depth in the core. Ra_I was obtained by the mathematical method of finding Θ_I as described in the theory. Although the peak area in the radium curve of this core is much better defined then in core N-2, the data are still not definitive enough to precisely pinpoint it. Thus the analysis was made on this core following the method used for core N-2, i.e. choosing a maximum and minimum depth for the occurrence of the peak, based on the available experimental data. The two peaks fall respectively at 20 and 15 centimeters. It may be pointed out that again the peak used by Urry is almost equal to the maximum depth position. Table 17 lists the ages of various depths in core P-137, based on the peak at maximum and minimum depth respectively.

As in the case for core N-2, the correction in ages due to re-plotting of the radium peak appreciably affects only portions younger than about 40,000 years. For this core however, the deviations are not as great as found in N-2, this being due to the much better definition of the curve by the data. Here only sections between about 3000 and 20,000 years are affected by more than 10%.

Table 17

Age of Samples from Core P - 137(years x 10^3)

Sample depth (cm)	Peak drawn at:	
	Maximum depth	Minimum depth
1	0.1	0.1
3	0.5	0.5
5	1.0	1.0
7	1.7	1.7
9	2.6	2.6
11	3.5	3.7
12	4.0	3.8
13	4.6	4.2
14	5.7	4.8
15	8.0	5.4
16	9.2	5.9
17	9.8	7.0
18	10.3	7.3
19	10.6	7.5
20	10.8	8.0
23	12.5	10.5
30	19.6	17.8
50	44	43
80	85	84
100	116	114
120	140	140
140	166	166
160	204	204
180	253	253

Table 18

Fraction of Radon in the Gas Phase - Core P - 137

Depth (cm)	Ra_t	Ra_i	$1 - Ra_i/Ra_t$
0	1.40±0.02	0.80±0.02	0.43±0.02
8	2.21±0.04	1.34±0.03	0.39±0.03
13	2.34±0.03	1.35±0.03	0.42±0.02
59	1.88±0.02	0.84±0.02	0.55±0.02
105	1.21±0.02	0.72±0.02	0.40±0.02
144	0.90±0.01	0.51±0.01	0.43±0.02
188	0.54±0.01	0.31±0.01	0.43±0.03

All radium values in units of g Ra x 10^{-12}/g sed.

Ra_t = Total radium content (measured by Urry, 1942)

Ra_i = Radium content in equilibrium with internal radon.

A series of samples were measured for internal radon content, i.e. all of the radon not in the gas phase. From these data the fraction of radon in the gas phase was calculated. Table 18 summarizes the analysis. Again as in core N-2 it can be seen that the fraction in the gas phase is high enough to be easily measurable. This fraction appears to be constant except for the point at 59 cm. This anomaly may be either in the experimental measurements (since the total radium and internal radon were measured in different laboratories), or in the sampling of the core at one point.

Errors

The absolute accuracy of dating by the ionium method is subject to a variety of possible errors. These may be listed as due to:

(1) accuracy of radium measurements,

(2) loss of surface material from the top of core in handling,

(3) distortion of the core due to friction in the coring tube,

(4) compaction of the sediment by overlying material on the ocean floor.

The errors in the absolute accuracy of radium measurements have been discussed in the section on procedures. It is concluded that with the techniques now employed, radium measurements may be made rather routinely with an accuracy of better than 2%.

Loss of material from the top of the core may in some cases constitute a rather serious limit on the validity of any ages obtained for that core. Because of the very fluid state of the top few centimeters of the sediment column in many areas, unless extreme care is taken in handling to preserve this section it will run or slump out of the coring tube. Thus the point of zero depth for these cases is unknown and an age analysis is impossible. It has been estimated by D. B. Ericson (private communication) that as much as 8 to 10 centimeters of the tops of many cores have been lost in this way. The chief cause of this loss is the swinging of the core to the horizontal position as it is pulled on to the ship. This is necessitated by the extreme lengths of core now being taken. Mr. Ericson pointed out, however, that if the core were kept vertical and if liners were employed, the top of the column would probably be kept intact. The two cores discussed in detail in the first part of this chapter, P-137 and N-2, were probably not subject to this error. They were relatively short cores apparently handled with considerable care and were taken in plastic liners. Thus it is believed that in both of these cases the tops are well-defined and errors due to loss of top material are negligible.

The effect of the coring mechanism on the material of the core has been discussed by Piggot and Urry (1942) and Urry (1948). Experiments carried out with the Piggot core sampler in varved clay pits near Hartford, Connecticut, demonstrated that the shift of the peak in the radium versus depth curve due to this effect is negligible. The only important correction is a reduction in the slope of the ionium decay curve below the peak, i.e., an increase in the apparent rate of deposition. Urry further points out that for the particular cores under consideration i.e., P-137 and N-2, "the effect of distortion is negligible . . . for the upper six tenths of the total core length". In core P-137, the effect below .6 of the core length increases to a maximum error of about 50%

in rate of deposition at the very bottom of the core. This effect is insignificant in considering the other sources of error at that depth in the core.

D. B. Ericson (private communication) suggests that with the use of the piston corer now being employed by the staff of the Lamont Geological Observatory, distortion is negligible throughout the entire length of the core. This conclusion is based upon his very careful studies of the condition, positioning and shape of such features as bedding and burrows. Distortion due to coring would tend to make flat bedding planes appear concave downward in the coring tube, and elongate the normally round burrows common in many cores.

The effect of compaction of the core material due to load likewise appears to be unimportant in evaluating the errors in age determinations. Piggot and Urry (1942) measured the specific gravity of numerous samples from core P-137 to a depth of about 200 centimeters. The results showed no regular increase with depth as would be predicted for a homogeneous core if compaction were appreciable. The values appear to change randomly with a maximum variation of about 15%.

D. B. Ericson (private communication) has measured the specific gravity and porosity of a number of Atlantic cores obtained recently by the Lamont Observatory group. Some data typical of the results are listed in Table 19.

Table 19

Specific Gravity and Porosity of an Atlantic Ocean Core

Core No.	Depth (cm.)	Specific Gravity	Porosity
C - 8#4	top	1.35	72%
	223	1.48	65%
	490	1.58	64%

On the basis of the foregoing discussion it appears that the absolute accuracy of dating by the ionium method is limited by the errors in measurement of the radium concentrations. The effect of these errors on the ages obtained in an analysis is summarized in Table 20. This table has been compiled for the data of core P-137 since it most closely approaches the ideal case of any of the cores studied. It has been further assumed in preparing this table that the peak in the radium curve is very well defined at the minimum possible depth (see Table 17), i.e., that the parameter θ_1 is closely known. Thus Table 20 represents the best case obtainable with the presently available techniques.

It should be pointed out that in dating by the ionium method ages are determined solely on an absolute scale, based on the decay characteristics of the radioelements and the length of the core. There is no single error aside from the half life of ionium which could make all of the ages older or younger either by a fixed or proportional amount. Thus relative ages cannot be more accurate than absolute ages for this method.

Accuracy of dating by the ionium method may be materially improved by greater precision in the absolute measurement of radium. This improvement will be approximately linear. Thus radium measurements to .50% error would diminish the error in the most sensitive section of the core to about ±6%, and the remaining 95% of the core would have errors of less than 2%. Radium measurements to .50% accuracy appear feasible if larger samples encompassing shorter time spans could be

Table 20

Errors in Absolute Ages, Core P-137

	Error	
Age of Sample (yrs.)	± (years)	± (%)
2000	~100	~5
4000	~200	~5
6000	600	10
7000	1000	14
8000	1900	24
10,000	1700	17
12,000	1500	12
15,000	1500	10
20,000	1400	7.0
30,000	1400	4.6
40,000	1300	3.3
60,000	1400	2.4
100,000	1500	1.5
150,000	1500	1.0
200,000	2000	1.0
250,000	2500	1.0
300,000	3000	1.0

obtained. Thus cores of possibly 6 or 8 inches diameter would allow closer spacing of samples and great improvement in accuracy of dating.

VII. Geological and Cosmological Applications

Rate of Deep Sea Sedimentation

In the study of past geological history by the stratigraphic and and sedimentation methods, the most important parameter is the rate of accumulation of marine sediments. This may be divided into the sedimentation on the continental shelves and on the deep ocean floor.

The indirect methods to estimate the sedimentation rate in the deep sea are outlined in The Oceans, (Sverdrup, Johnson and Fleming, 1942). These methods fall into two general categories, the supply method and the stratigraphic method.

The supply method is based on the rate of supply of sedimentary material to the sea. Clarke, (1924), estimated the total annual supply of dissolved solids into the oceans and derived a figure of $23 \pm 1 \times 10^8$ metric tons deposited annually. This corresponds to a layer 0.25 cm. per thousand years if evenly distributed over the ocean floors. This figure really tells little about the rate of sedimentation on the ocean floor since (a) it does not consider detrital or volcanic material and (b) a sizable fraction of the sediment is deposited near the coast line.

Kuenen, (1937), considering erosion since the Cambrian, and supply from terrestrial volcanoes, estimated total deep sea deposition at a rate of about 0.33 centimeters per thousand years. In a later revision, Kuenen, (1941), reduced his estimate to 0.1 cm. per thousand years for red clay and 0.2 cm. per thousand years for globigerina ooze.

Other estimates based on the supply method by Lohmann (1909) of 0.1 to 0.2 cm./thousand years and by Revelle and Shepard (1939) of 0.25 cm./thousand years are much too general for use other than as an indication of an order of magnitude for the particular sediment type studied.

The stratigraphic method of estimating mean rates of deposition may be applied when it is possible to determine the thickness of a deposited accumulation in a given time interval. Schott (1939) calculated the rate of accumulation of globigerina ooze, blue mud and red clay in the equatorial Atlantic Ocean, by assuming that certain foraminiferal forms were deposited only since the last glacial period, 20,000 years ago. The corrected values are:

Blue mud	0.59 cm./thousand years
Globigerina ooze	0.40 " " "
Red clay	0.29 " " "

These results have little meaning due to the uncertainty of the assumption of the end of the glacial period. Other values for mean sedimentation rates have been published (Moore, 1931 ; Strom, 1936) for restricted localities. It is concluded that the use of the sediment column as a time scale is a complex affair at best.

Estimation of the rate of deposition of deep sea sediment by use of the Ionium Method is of course limited in accuracy by the validity of ages obtained by the method. Urry (1948) discussed in detail these deposition rates for all of the cores studied at the Geophysical Laboratory. His chief conclusions were (a) deposition in most of the cores is more rapid at present than the average of the last half miooion years, (b) the general rate of deposition was not appreciably affected by the repeated climate changes of the ice age, and (c) the average rates of deposition are in generally good agreement with the estimates made earlier by other methods.

Utilizing the data and theory outlined in the previous chapter on age analysis, rates of deposition for red clay (core N-2) and globigerina ooze (core P-137) may be determined for these specific localities.

An average rate for this sediment type can be approximated from restricted localities since by its lithologic properties the material from these localities is representative of a much larger sample of the ocean floor.

Red Clay

It may be recalled that in analyzing the data of core N-2 the spread in the ages was defined by the ambiguity of the experimental data. (Table 14). Figure 35 illustrates the rate of deposition of the material of core N-2 for each of the two limiting cases. It is clear that no appreciable difference in the apparent rate of deposition over most of the core is found due to the assumptions made in the age analysis. The average rate of deposition for more than 90% of this red clay core is about -.15±0.05 cm./1000 years. This value is in substantial agreement with the estimates of red clay accumulation by both the supply (0.1 - 0.2 cm./1000 years) and stratigraphic (0.29 cm./1000 years) methods but is probably the more quantitative.

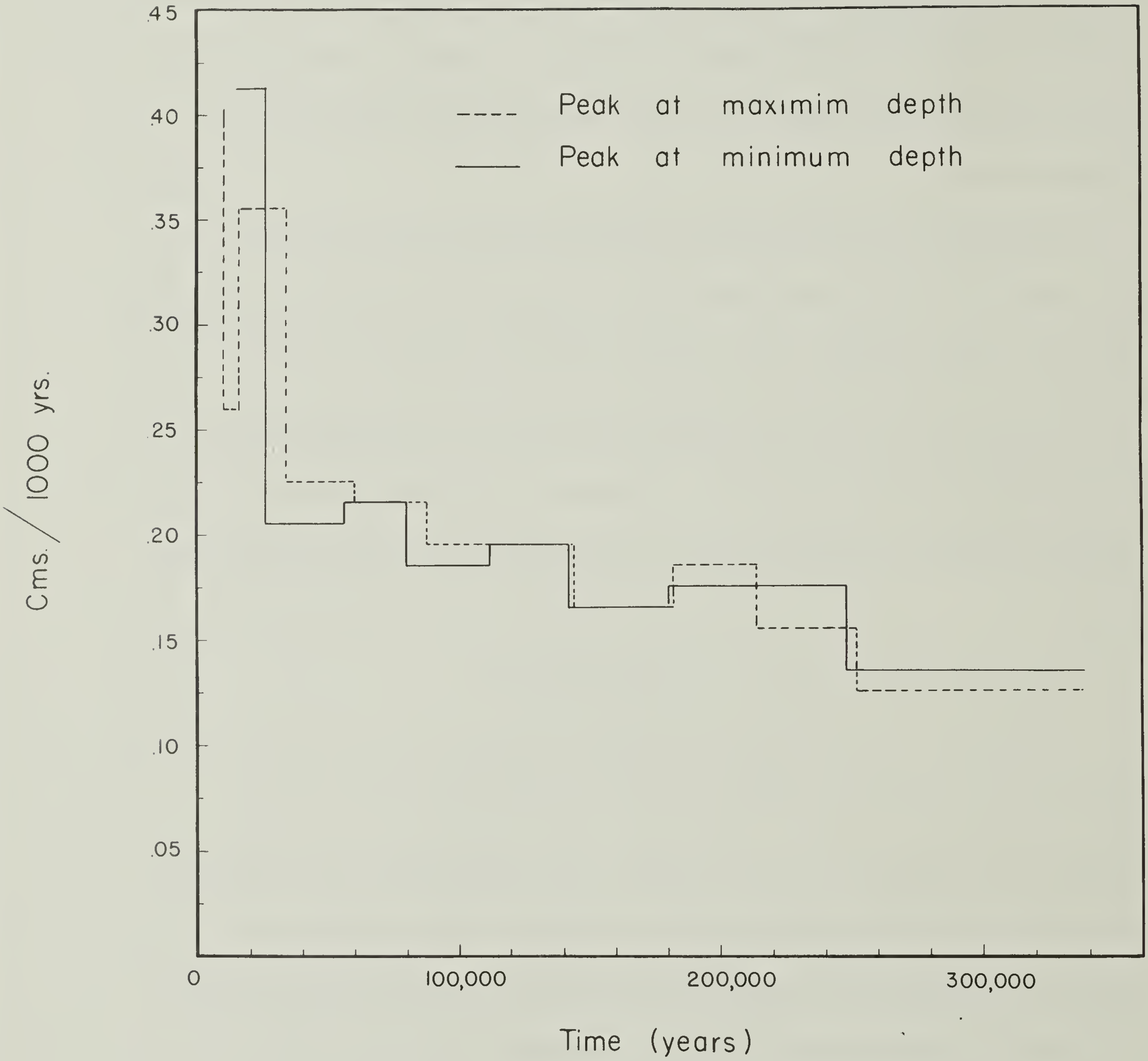


Figure 35. Limits of the rate of deposition, core N-2.

The increasing rate of deposition of red clay occurring in the last 30,000 years, reaching about a factor of 3 over the general average, is of extreme geologic importance. Discussion of this will be deferred to a later section.

Globigerina Ooze

The rate of deposition of the material of core P-137 is illustrated in Figure 36. The calculation was based on the ages developed in the last chapter. It is seen that no appreciable differences occur due to the various assumptions in the age analysis. The average rate of deposition for more than 90% of the material of this core is 0.6±0.2 cm./1000 years. This value is somewhat higher than Kuenen's 0.2 cm./1000 years for globigerina ooze estimated by the supply method, and Schott's 0.40 cm./1000 years obtained from stratigraphic considerations. However, the rate obtained from the ionium method is probably the most quantitative in that it is based on radioactive decay and permits assignment of a numerical error.

Again as in the red clay core N-2, the rate of deposition appears to have increased in the last 20,000 years, in this case by about a factor of three.

Recent Increase in Depositional Rate

The increase in the apparent rate of deposition of both red clay and globigerina ooze in the last 20,000-30,000 years cannot be explained by either a compaction phenomenon or systematic experimental error as noted in chapter VI. Thus it appears necessary to accept these high

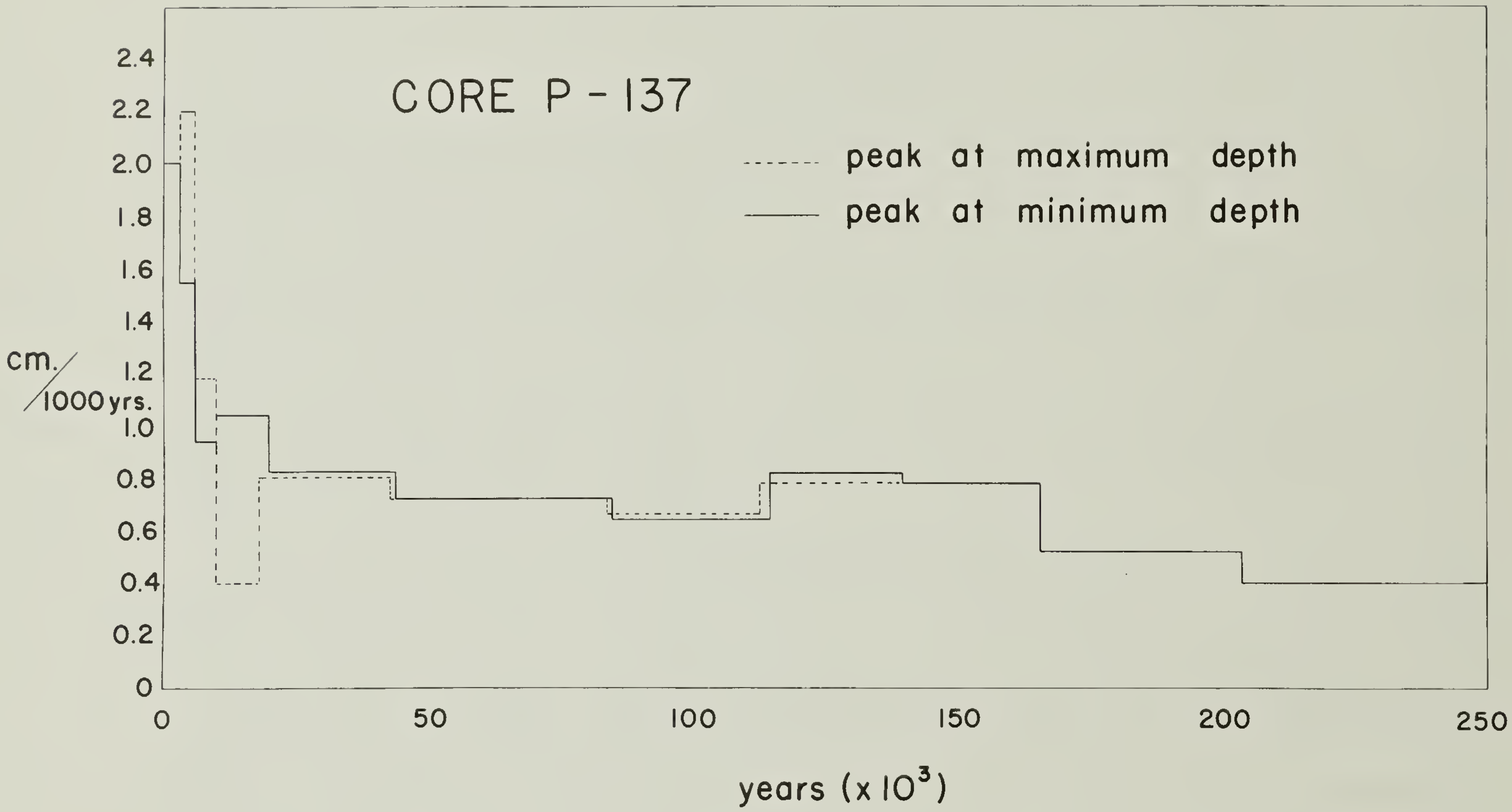


Figure 36. Limits of the rate of deposition, core P-137.

rates and explain them on geological grounds.

The most obvious world-wide event centered on this time is the Wisconsin glaciation and the subsequent Recent interglacial stage. The world-wide retreat of the Wisconsin ice sheet may be considered to have extended from about 40,000 years to 5000 years ago. This is based on the gradual rise in sea level dated by radiocarbon measurements in the Mississippi delta area (Kulp; 1952, Fisk and McFarlan; 1954). It appears that the increased deposition was initiated sometime in the latter half of Wisconsin time. With retreat of the ice sheet, the resulting increased erosion rate due to the greater volume of water feeding to the seas and the excess rock debris produced by moving rock, would tend to increase the deposition rate of the inorganic red clay sediment. Simultaneously, the general rise in mean world temperature would bring about an increase in population of organic life in the oceans, leading to higher rates of deposition of organic remains in the globigerina ooze sediments. It thus appears plausible to explain the measured high rates of deposition in late and post-Wisconsin time as due to the changes associated with the retreat of the ice.

On this hypothesis, however, similar increased deposition rates should be in evidence for the time of retreat of the Iowan and Illinoian glacial ice. The absence of any large change in the rate of sedimentation curve may be more experimental than real. Not only is the ionium decay curve relatively insensitive to such changes beyond 70,000 years ago, but also the absence of closely spaced radium analyses make it impossible to recognize such changes. None of the cores studied to the present have been analyzed this closely. For example, in core P-137 the two deepest points measured for radium content (144 cm. and 189 cm.) give ages of 173,000 years and 282,000 years respectively. Thus all of the interpretation of deposition rate for more than 100,000 years between these points is based on a smooth line connecting them. It is clear that this interpretation may be seriously in error. A factor of 2 increase in the deposition rate may be assumed for the period between about 210,000 years and 250,000 years (e.g., Illinoian?) with a slight modification in the curve drawn between the lowest two experimental points.

In future measurements of cores by the Ionium Method careful attention should be given to the spacing of the samples if detailed interpretations of depositional rates are to be valid.

Pleistocene Geochronology

Ocean cores taken from the great depths may reveal a detailed record of lithologic changes which in turn may reflect world-wide climatic changes. Since the Ionium Method of age determination is applicable in principle over the last one half million years, the existence of this method makes it possible to define the broad phases of the Pleistocene period. In practice this is no simple affair, for not only must cores be obtained that fit the criteria of chapter V, but the definition of a glacial marine deposit is not always unambiguous. Further, the most homogeneous cores which may yield smooth ionium decay curves are least interesting in terms of showing climatic changes; whereas the cores which contain layers of glacial marine deposits seldom yield ionium curves that can be interpretated with certainty. Probably the most satisfactory application is through examination of the pelagic micro-fauna be means of the oxygen thermometer ($0^{18}/10^{16}$) in a homogeneous core which yields a smooth ionium curve.

Some preliminary attempts to read Pleistocene history from Ionium Method analyses of deep sea cores have been made. Piggot and Urry (1942) discussed the chronology of three cores from the North Atlantic and one from the Caribbean Sea. They concluded, "(1) the effects of glaciation on the continents are contemporaneous equivalent effects on the type of deposit in the ocean bottom; and (2) that the effects of glaciation on the type of ocean sediment are widespread, extending in the northern hemisphere at least to the Caribbean Sea". It should be pointed out that in the data upon which these conclusions were based no cognizance was taken of the errors outlined in chapter VI with the exception of distortion due to coring. Considering (a) the general location of three of these cores, i.e., from areas of the North Atlantic Ocean highly susceptible to bottom disturbances; (b) the extremely inhomogeneous nature of the sedimentary material comprising the three North Atlantic cores; and (c) the errors inherent in the radium determinations, it seems that the conclusions may have been premature.

Hough (1953) described in great detail the "Pleistocene climatic record in a Pacific Ocean core sample". The core (N-1) analyzed by Hough in this paper was obtained from the southeastern Pacific Ocean during the same expedition in which core N-2 was taken. The core was analyzed by Urry (1949) but the time-depth curve was not published. Lithologically the core exhibited alternate layering of red clay and globigerina ooze. In this core Urry had hoped to obtain two radium vs. depth curves, i.e., one for each sediment type, which would be independently analyzed for time. However, the distribution of the material was such that red clay predominated in the upper 30 centimeters and globigerina ooze was found mainly below 20 centimeters in depth. Thus it was impossible to date the two materials independently. It should be pointed out that there were several samples which were considered mixtures of red clay and globigerina ooze. The data for this core are reproduced in Figure 37. The solid lines drawn through the points are apparently the bases for the age analysis carried out.

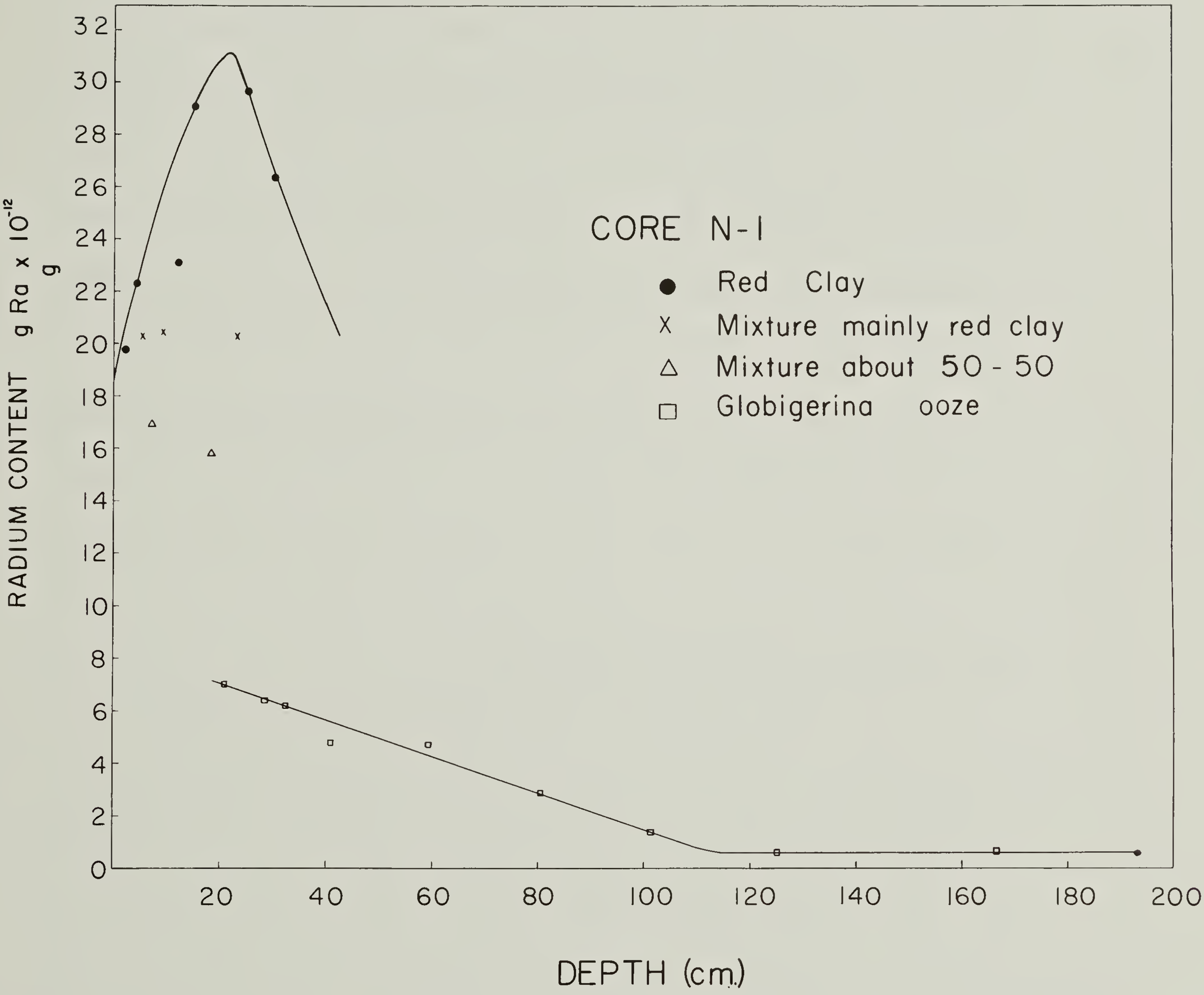


Figure 37. Radium content, core N-1.

There are suggestions of the predicted decay curve, especially in the lower portion of the core. On the basis of the earlier discussions of errors and age analysis, however, it does not seem possible to arrive at anything more than some qualitative estimates of ages in this core. This means that none of the dates in years tabulated by Hough along the length of core N-1 possess quantitative significance. Unfortunately in Hough's paper the entire interpretation of geologic and climatic events occurring during the Pleistocene is based on these unreliable dates.

Thus, although the Ionium Method may make a major contribution to Pleistocene chronology in the future, a satisfactory test case has not yet been made.

The Constancy of the Cosmic Ray Flux

One of the two major assumptions of the Carbon-14 Method of age determination is the constancy of the integrated cosmic ray flux. An experiment was devised to indicate flux variations from the present back to the maximum of the Wisconsin glaciation, (estimated at 40, 000 years ago). This span of recent earth history displays about one half of the greatest mean annual temperature fluctuation since the Cambrian period (500, 000, 000 years ago). Thus if the cosmic ray flux (integrated over a few centuries) was constant in this interval, and if it is related in any way to the total energy received by the planet, it would appear that the integrated cosmic ray flux has remained constant over most of geologic time.

The experiment involves dating layers of mud in a deep sea core by both the Carbon-14 and Ionium Methods. From a consideration of all of the earlier discussion it may be realized that samples applicable to dating by both methods are limited and must be chosen with great care. For carbon-14 dating the core samples must be (a) young enough to be dated, i.e., not over about 30,000 years old, (b) large enough, and of sufficient calcium carbonate content, to yield a minimum of about three grams of black carbon. For ionium dating, all of the conditions mentioned in chapters V and VI must be fulfilled for reliable ages to be obtained.

Four core samples were found to be applicable for this study. All came from cores used by Urry in his ionium age studies. The ionium ages were recalculated with careful consideration of all of the possible errors, and have been plotted with these errors indicated by the height of the boxes in Figure 38. The carbon-14 ages were then obtained on these samples and reference to the figure indicates that the errors as shown by the length of the boxes were rather large. These errors are mainly due to the very small amount of sample which was available in each case. Also plotted on Figure 38 are six samples of known historical age, versus the carbon-14 age for each sample. From the data it seems certain that the cosmic ray flux has not varied by more than 20% over the last 20,000 years. A hypothetical curve on the figure shows the relation if the cosmic ray flux was half its present value during the ice age.

New developments in the technique of C^{14} dating by the use of CO_2 proportional counters may make it possible to go back to 50,000 years ago with rather high precision and with smaller samples than were used in the preliminary study described above. This improvement along with the possibility of taking larger diameter cores and therefore larger samples, may permit the definition of variation of the integrated cosmic ray flux to 5% over the last 40,000 years.

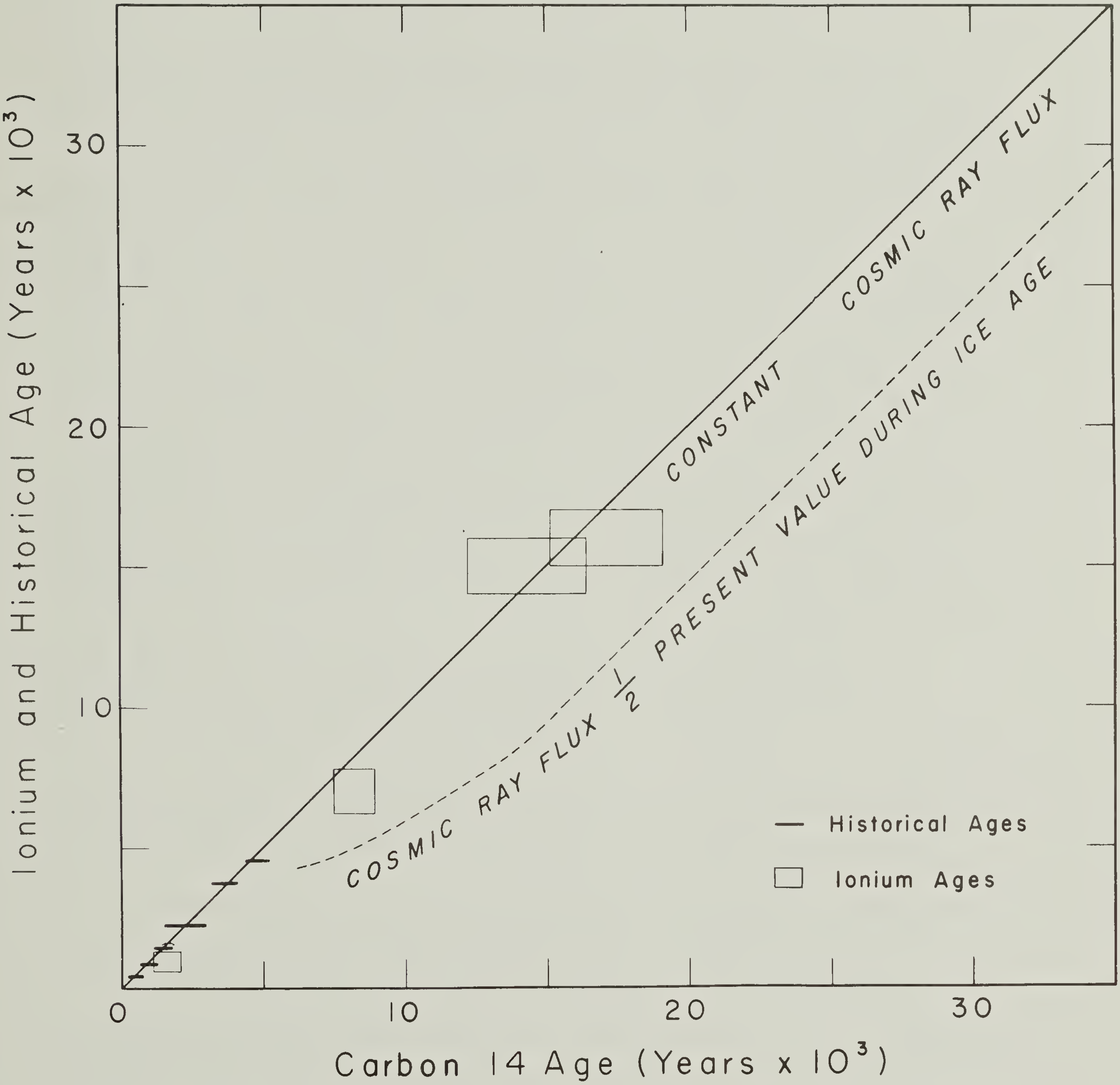


Figure 38. Correlation of radiocarbon and ionium ages.

VIII. Conclusions

A detailed study of the Ionium Method of age determination has been carried out. Emphasis has been placed on an examination of the assumptions and limiting conditions upon which the method is based. A number of deep ocean cores from the Atlantic and Pacific Oceans and Caribbean Sea were measured for radium content, radon in the gas phase, total alpha activity and surface area. Age analyses on the two cores applicable for dating were carried out along with a thorough evaluation of the errors involved in this method. Based on the results of the age analyses certain geological and cocmological interpretations have been made.

The main conclusions drawn by this investigation may be listed as follows:

(1) Application of Ionium Method dating is limited to cores possessing certain favorable characteristics:

(a) A chronologically undisturbed sediment column;

(b) Homogeneity with regard to adsorption potential.

(2) The accuracy of dates obtained by the Ionium Method is limited by:

(a) The accuracy of the radium determinations;

(b) The frequency of samples chosen along the length of the core, for radium determination.

(3) The average rates of deposition of a red clay core from the Pacific Ocean and a globigerina ooze core from the Caribbean Sea were determined. For a time interval of at least 200, 000 years, except for the most recent 20, 000-30, 000 years, these rates were essentially constant with values of

Red Clay	0.15±0.05 cm./1000 years
Globigerina Ooze	0.60±0.20 cm./1000 years

(4) The high rate of deposition in the recent past exhibited by both of the cores mentioned above may be explained as due to the increased erosion rate and world-wide temperature rise since the peak (40,000 years ago) of the Wisconsin glaciation. The lack of evidence of similar sedimentation rate increases in Iowan and Illinoian time is probably due to inaccurate experimental data and the insensitivity of the method to changes in rate of sedimentation for relatively short intervals occurring at times greater than 70,000 years ago.

The Ionium Method holds a great deal of promise as a quantitative dating tool if the conditions and restrictions on its application are understood. With an improved coring apparatus of much larger diameter, e.g. 6-8 inches, selective choosing of coring sites based on studies of ocean bottom topography, careful studies of lithology and micropaleontology in the laboratory and greatest possible accuracy in radium measurement, valuable information on the detailed chronology of the Pleistocene period, rates of deposition of oceanic sediments, and further clarification of cosmic ray flux variations in the past, may be obtained.

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