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Radiocarbon Dating

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By

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PREFACE

IT IS a real pleasure to acknowledge the invaluable contributions of my collaborators, Drs. E. C. Anderson and James R. Arnold, in the development of the dating method. Certainly nothing would have been done without them. Dr. A. V. Grosse and his collaborators at the Houdry Process Corporation concentrated the methane samples which first established the existence of radiocarbon in nature and laid a firm foundation for the program.

The Committee on Carbon 14 of the American Anthropological Association and the Geological Society of America, consisting of Frederick Johnson, chairman, Donald Collier, Richard Foster Flint, and Froelich Rainey, in selecting the samples for measurement, advising on priorities, and lending a friendly ear in troubled periods, have indeed earned our most heartfelt gratitude. We hope that the results of the research may in some small measure repay them for their efforts.

It is also a privilege to thank the Wenner-Gren Foundation for Anthropological Research, formerly The Viking Fund, Inc., and its director, Dr. Paul Fejos, for the financial support of this research with two grants totaling some $35,000 in the years 1948, 1949, and 1950. A small unexpended balance remains from these funds, which will be used over the years for occasional further measurements. This foundation, together with the University of Chicago, furnished the principal financial support for the entire research. We are very grateful indeed for this assistance.

We also are indebted to the Air Force (Wright-Patterson Air Force Base, Contract AF 33[038]–6492) for a contract for the development of low-level counting techniques during the year 1949, the results of which were put to immediate use in the radiocarbon dating research.

It is hoped that the present publication will contain the answers to most of the questions which will occur to an investigator con-

structing and operating equipment for the measurement of dates by the radiocarbon technique. It is realized, however, that certain important details may have been omitted, and we would be pleased to try to assist in the solution of any difficulties which other groups may encounter.

W. F. LIBBY

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CHAPTER I

PRINCIPLES

THE discovery of cosmic radiation by V. F. Hess in 1911 led to repeated conjectures as to possible permanent effects this radiation might have on the surface of the earth. The energy received by the earth in the form of cosmic radiation is commensurate with that received as starlight. It is therefore really quite small in terms of the solar energy. The specific energy, that is, the energy per constituent particle, is very much higher than for any other type of radiation, averaging several billions of electron volts (1 electron volt is 1.6×10^{-12} ergs, which is the average energy of motion of a gas molecule at 10,000° C.). It is conceivable, therefore, that the cosmic radiation will alter the earth's atmosphere in detectable ways.

It was discovered shortly after the neutron itself had been discovered that neutrons were present in the higher layers of the atmosphere probably as secondary radiations produced by the primary cosmic rays. Measurements by cosmic-ray physicists have clearly established that the population in the atmosphere rises with altitude to a maximum somewhat above 40,000 feet and then falls.[1] This proves the secondary character of the radiation—that it is not incident on the earth from interstellar space but is a product of the impact of the true primary radiation on the earth's atmosphere. A corroborating point in this connection is the recent demonstration that the neutron is truly radioactive with a lifetime of about 12 minutes, which of course removes any possibility of the neutrons having time to travel any considerable distance in interstellar space, though the trip from the sun could be made without complete decay to hydrogen.

Consideration of possible nuclear transmutations which the cosmic rays might effect leads one immediately to consider what the neu-

1. H. M. Agnew, W. C. Bright, and Darol Froman, *Phys. Rev.*, **72**, 203 (1947) (this paper contains references to many earlier measurements); J. A. Simpson, Jr., *Phys. Rev.*, **73**, 1389 (1948); L. C. L. Yuan, *Phys. Rev.*, **74**, 504 (1948); L. C. L. Yuan and R. Ladenburg, *Bull. Am. Phys. Soc.*, **23**, No. 2, 21 (1948); L. C. L. Yuan, *Phys. Rev.*, **76**, 1267, 1268 (1949); L. C. L. Yuan, *Phys. Rev.*, **77**, 728 (1950).

trons known to be produced by the cosmic rays might be expected to do to the earth's atmosphere. In the laboratory many studies have been made of the effects of neutrons of various energies on all the ordinary elements and especially on nitrogen and oxygen, the constituents of the air. In general, the results are that oxygen is extraordinarily inert but that nitrogen is reactive. It appears certain that, of the two nitrogen isotopes, N^{14}, of 99.62 per cent abundance, and N^{15}, of 0.038 per cent abundance, N^{14} is the more reactive. With neutrons of thermal velocity the reaction

$$N^{14} + n = C^{14} + H^1 \qquad (1)$$

is dominant, the cross-section of the N^{14} atom for a room temperature thermal neutron being in the vicinity of 1.7×10^{-24} cm.[2], whereas the thermal neutron cross-section for reaction with O^{16} is of the order of 0.1 per cent of this. It is therefore quite certain that thermal neutrons introduced into ordinary air will react according to Equation (1) to form the radiocarbon isotope of mass 14 and half-life of 5568 $\pm$ 30 years.

The neutrons in the air being formed by the energetic cosmic rays possess energy themselves, probably of the order of 5–10 mev (million electron volts) on the average when first formed. After birth they then collide with the air molecules and lose their energy by collision, either elastic or inelastic, either reacting on one of these collisions and so being absorbed or finally attaining thermal energies where they are quite certain to be absorbed to form radiocarbon by Reaction (1). Laboratory studies of the effects of energetic neutrons on air again indicate that the nitrogen is the more reactive constituent. Reaction (1) is still dominant, though a second reaction,

$$N^{14} + n = B^{11} + He^4, \qquad (2)$$

occurs.[2] The latter reaction becomes dominant at energies above 1 mev but even at the most favored energies attains cross-sections of only 10 per cent of that of nitrogen for thermal energies. Reaction (1), on the other hand, goes with considerable probability in the region of 0.4–1.6 mev.

A third type of reaction of high-energy neutrons with nitrogen,

$$N^{14} + n = C^{12} + H^3, \qquad (3)$$

2. C. H. Johnson and H. H. Barschall, *Phys. Rev.*, 80, 819 (1950).

has been reported in the laboratory.[2] The nature of the laboratory experiment was such that it was difficult to estimate the cross-section for the reaction, but the reported value was 10^{-26} cm.[2], to an accuracy of about a factor of 5. It is certain from the masses of the atoms involved in Reaction (3) that neutrons of not less than 4 mev are involved, since the reaction is endothermic to this extent. The hydrogen isotope in Reaction (3) is the radioactive hydrogen called tritium, of 12.46 years half-life, which decays to form the stable isotope of helium, He^3, which occurs in atmospheric helium in an abundance of 1.2×10^{-6} parts He^3 per ordinary helium in atmospheric air.[4] It is thought that this value is accurate to about 30 per cent. The abundance of He^3 in ordinary helium from terrestrial sources varies widely from undetectably small values in uranium ores, where an excessively large amount of He^4 is found, to the values of 12×10^{-6} parts for certain Canadian rocks. In general, however, the He^3 content of helium from the earth's crust is not over one-tenth as large as that of atmospheric helium. Since tritium produced by Reaction (3) lasts such a short time, one knows that any tritium produced by Reaction (3) will introduce an equivalent amount of He^3 into the earth's atmosphere, so that one possible effect of the cosmic-ray bombardment of the earth's atmosphere could be the introduction of He^3 into the atmospheric helium. It is seen that this may be the case, since it is observed that atmospheric helium is richer in He^3 than terrestrial helium.

Summarizing the three most probable reactions, only the first and third lead to radioactive isotopes. It is therefore to be expected that the neutrons produced by the cosmic radiation may produce these radioactive materials in the earth's atmosphere. After these points were made,[5] a search in nature for both radioactivities was instituted. Both have since been found[6] in amounts and concentrations corresponding roughly to those expected.

3. R. Cornog and W. F. Libby, *Phys. Rev.*, 59, 1046 (1941).

4. L. T. Aldrich and A. O. Nier, *Phys. Rev.*, 74, 1590 (1948).

5. W. F. Libby, *Phys. Rev.*, 69, 671 (1946).

6. E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirshenbaum, and A. V. Grosse, *Science*, 105, 576 (1947); E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirshenbaum, and A. V. Grosse, *Phys. Rev.*, 72, 931 (1947); A. V. Grosse, W. H. Johnston, R. L. Wolfgang, and W. F. Libby, *Science*, 113, 1 (1951).

Therefore, we now have more confidence in the basic postulates made in the arguments outlined above—that the behavior of the cosmic-ray neutrons in the air is predictable from the observed behavior of laboratory neutrons on nitrogen and oxygen and that the possibility of the neutrons having higher energy than laboratory neutrons appears not to confuse the issue appreciably.

The prediction of the expected amounts of radiocarbon and tritium can be made only on the basis of some information about the relative probabilities of Reactions (1), (2), and (3). Reaction (1) is so much more probable, however, that it is clear that the yield of radiocarbon will be nearly equal to the total number of neutrons generated by the cosmic rays, a number which we shall call Q in units of number per square centimeter per second. The tritium yield, due to Reaction (3) only, is taken to be of the order of the ratio of these cross-sections, or about 1 per cent of Q. The latter will be considerably more uncertain than the yield of radiocarbon, since the cross-section for Reaction (3) is much more uncertain than that for Reaction (1) and more specifically than the dominance of Reaction (1). If we integrate the data for the neutron intensity as a function of altitude from sea-level to the top of the atmosphere, to obtain the total number of neutrons, Q, produced per square centimeter per second, and average this over the earth's surface according to the observed variation of neutron intensity with latitude,[7] we obtain a figure for Q, the average number of neutrons generated per square centimeter of the earth's surface per second by the incidence of cosmic radiation. If we further assume that the cosmic-ray production of radiocarbon is an ancient phenomenon in terms of the 5600-year half-life of radiocarbon (i.e., the cosmic rays have remained at essentially their present intensity over the last 10,000 or 20,000 years), we can conclude that there is some place on earth enough radiocarbon to guarantee that its rate of disintegration is just equal to its rate of formation. Evaluation of Q from the experimental data available gives 2.6 as a most likely value. Since the earth's surface has 5.1×10^{18} cm.^{2}, the radiocarbon inventory must be such that 1.3×10^{19} beta disintegrations occur per second.

$$C^{14} = \beta^- + N^{14+}. \tag{4}$$

7. J. A. Simpson, Jr., *Phys. Rev.*, **73**, 1389 (1948); L. C. L. Yuan, *Phys. Rev.*, **76**, 1267, 1268 (1949).

Since laboratory measurement of the specific disintegration rate of radiocarbon[8] gives 1.6×10^{11} disintegrations per second per gram, dividing we obtain 8.1×10^7 grams, or 81 metric tons, as the predicted inventory for radiocarbon on earth. This is equivalent to 365 million curies (1 curie is that quantity of radioactivity which gives a disintegration rate of 3.7×10^{10} per second). Reasoning similarly, we predict a tritium inventory of about 3 million curies in nature.

The question remains as to where the radiocarbon will occur. A moment's thought answers this, however. We consider the problem of the ultimate fate of a carbon atom introduced into the air at a height of some 5 or 6 miles. It seems certain that within a few minutes or hours the carbon atom will have been burned to carbon dioxide molecule. It is true that there are points of interest to discuss in the question of the kinetics of combustion of atomic carbon in the air, and research is necessary to supply definite answers for the many questions which would arise in such a discussion. It seems probable, however, that the carbon will not long remain in any condition other than carbon dioxide. Postulating that this is so (i.e., the absorption of cosmic-ray neutrons by nitrogen of the air is equivalent to the production of radioactive carbon dioxide), we can proceed to an immediate answer to the question as to where natural radiocarbon should occur on earth. Radioactive carbon dioxide will certainly mix with considerable speed with the atmospheric carbon dioxide, and so we conclude that all atmospheric carbon dioxide is rendered radioactive by the cosmic radiation. Since plants live off the carbon dioxide, all plants will be radioactive; since the animals on earth live off the plants, all animals will be radioactive. Thus we conclude that all living things will be rendered radioactive by the cosmic radiation. In addition, there is another carbon reservoir for the natural radiocarbon, and this is the inorganic carbon in the sea present as dissolved carbon dioxide, bicarbonate and carbonate, for it is known that an exchange reaction occurs between carbon dioxide and dissolved bicarbonate and carbonate ions. The time for radioactive carbon dioxide in the air to distribute itself through this reservoir

8. A. G. Engelkemeir, W. H. Hamill, M. G. Inghram, and W. F. Libby, *Phys. Rev.*, **75**, 1825 (1949); W. M. Jones, *Phys. Rev.*, **76**, 885 (1949); W. W. Miller, R. Ballentine, W. Bernstein, L. Friedman, A. O. Nier, and R. D. Evans, *Phys. Rev.*, **77**, 714 (1950); A. G. Engelkemeir and W. F. Libby, *Rev. Sci. Inst.*, **21**, 550 (1950).

probably is not in excess of 500 years. This is the so-called "turn-over" time for the life-cycle which has been widely discussed by geochemists. The estimates vary quite widely, but it does seem that this time can hardly exceed 1000 years. Since this is a time short as compared to the lifetime of radiocarbon, we conclude that any given radiocarbon atom will make the round trip several times in its lifetime, and we therefore predict that the distribution of radiocarbon throughout the reservoir will be quite uniform, there being little vertical or latitudinal or longitudinal gradients left. One has some cause to suspect that there might be variations in intensity over the earth's surface, for the reason that it is known that the cosmic-ray neutron component varies by a factor of about 3.5[9] between equa-

TABLE 1

CARBON INVENTORY

Source	Amount (Gm/Cm²)
Ocean "carbonate"	7.25
Ocean, dissolved organic	0.59
Biosphere	0.33
Atmosphere	0.12
Total	8.3

torial and polar regions, the intensity being greater in the polar regions.

As expected, however, on the basis of the probable brevity of the turn-over time as compared to the lifetime of radiocarbon, it has been found that the distribution is uniform. Materials have been selected from various points on the earth's surface and from various altitudes, and the specific radioactivity has been found to be identical within the error of measurement, which amounts to some 3–5 per cent.

In order to predict the specific radioactivity of living carbon, the amount of carbon in the exchange reservoir must be estimated. Careful consideration of the complex biochemical questions involved leads us to the numbers given in Table 1.

The dominance of the inorganic material dissolved in the sea is obvious from these numbers. This has the immediate consequence that variations in living conditions which will lead to variations in

9. J. A. Simpson, Jr., *Phys. Rev.*, 73, 1389 (1948); L. C. L. Yuan, *Phys. Rev.*, 76, 1267, 1268 (1949).

the amount of living matter on earth will not appreciably affect the total carbon in the reservoir. Or, conceivably, the only possible significant variations of the quantity of carbon in the reservoir must involve changes in the volume, the temperature, or the acidity (pH) of the oceans. This probably means that the reservoir has not changed significantly in the last few tens of thousands of years, though there is the point to consider of the effect of the glaciation on both the volume and the mean temperature of the oceans. If the numbers in Table 1 are correct, there are some 8.3 grams of carbon in exchange equilibrium with the atmospheric carbon dioxide for each square centimeter of the earth's surface, on the average, and since there are some 2.6 neutrons incident per square centimeter per second, we must expect that these 8.3 grams of carbon will possess a specific radioactivity of 2.6/8.3 disintegrations per second per gram, or $2.6 \times 60/8.3$ disintegrations per minute per gram. This number, 18.8, is to be compared with the experimentally observed value of 16.1 ± 0.5.[10] The agreement seems to be sufficiently within the experimental errors involved, so that we have reason for confidence in the theoretical picture set forth above.

The agreement between these two numbers bears on another point of real importance—the constancy in intensity of the cosmic radiation over the past several thousand years. If one were to imagine that the cosmic radiation had been turned off until a short while ago, the enormous amount of radiocarbon necessary to the equilibrium state would not have been manufactured and the specific radioactivity of living matter would be much less than the rate of production calculated from the neutron intensity. Or, conversely, if one were to imagine that the intensity had been much higher in the past until very recently, the specific radioactivity would greatly exceed that calculated from the observed neutron intensity. Since 5568 ± 30 years will be required to bring the inventory halfway to any new equilibrium state demanded by the change in cosmic-ray intensity, we find some evidence in the agreement between these numbers that the cosmic-ray intensity has remained essentially constant for the last 5000–10,000 years. This does not mean that it could not exhibit hourly, daily, or even annual fluctuations. It does mean, however, that the intensity averaged over 1000 years or so has not changed.

10. E. C. Anderson, Ph.D. thesis, University of Chicago (1949); E. C. Anderson and W. F. Libby, *Phys. Rev.*, **81**, 64 (1951).

There is the slight possibility that an approximately compensating change in the carbon inventory has occurred, but for the reasons mentioned above the buffering action of the great reservoir in the sea makes this very remote.

A further point of interest in connection with the inventory and the observed specific assay is that the carbon isotopes apparently are fractionated in being incorporated into the biosphere from the inorganic world. This effect was discovered some time ago[11] for the isotope C^{13}, which has a mean abundance of 1.1 per cent in ordinary carbon. It was found that the ratio of the abundance of C^{13} in inorganic carbon to that in biological carbon is 1.03. On the basis of this, one would expect a value of 1.06 for the analogous ratio for C^{14}, radiocarbon. Since the mass spectrographic measurements of the C^{13} abundance are quite accurate and the theory on which one calculates the 1.06 ratio from the observed 1.03 ratio for C^{13} is quite rigorous, we are inclined to multiply our assay of biological material by 1.06 rather than to take the mean value of the small number of measurements we have made on inorganic carbon. The mean of the biological assay is 15.3 ± 0.1. Multiplying by 1.06, we obtain 16.2 for inorganic carbon; then, averaging according to the weight factors given in Table 1, we derive the average 16.1 for the carbon inventory as a whole. One must remember, however, that wood or other biological material will present an assay of 15.3 and that modern seashell will present an assay of 16.2.

If the cosmic radiation has remained at its present intensity for 20,000 or 30,000 years, and if the carbon reservoir has not changed appreciably in this time, then there exists at the present time a complete balance between the rate of disintegration of radiocarbon atoms and the rate of assimilation of new radiocarbon atoms for all material in the life-cycle. For example, a tree, or any other living organism, is in a state of equilibrium between the cosmic radiation and the natural rate of disintegration of radiocarbon so long as it is alive. In other words, during the lifetime the radiocarbon assimilated from food will just balance the radiocarbon disintegrating in the tissues. When death occurs, however, the assimilation process is abruptly halted, and only the disintegration process remains.

11. A. O. Nier and E. A. Gulbranson, *J. Am. Chem. Soc.*, **61**, 697 (1939); B. F. Murphy and A. O. Nier, *Phys. Rev.*, **59**, 771 (1941).

It has been known for many years that the rate of disintegration of radioactive bodies is extraordinarily immutable, being independent of the nature of the chemical compound in which the radioactive body resides and of the temperature, pressure, and other physical characteristics of its environment. The reason for this is that the
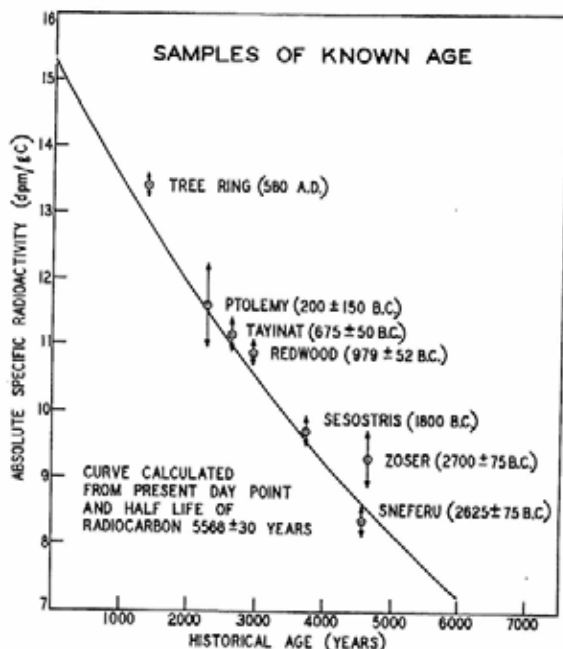

FIG. 1.—Predicted versus observed radioactivities of samples of known age

transformation is a nuclear phenomenon involving energies very much larger than those corresponding to the chemical bonds and to the various physical influences to which matter might conceivably be subjected. Therefore, we conclude that the rate of disappearance of radioactivity following death corresponds to the exponential decay law for radiocarbon as represented by the solid curve in Figure 1, in

which the world-wide assay of 15.3 for biological materials corresponds to zero time, and the predicted specific radioactivities for various times thereafter are given by the curve. The equation for the curve is

$$I = 15.3 \exp\left(-0.693 \frac{t}{5568}\right) \qquad (5)$$

or

$$I = 15.3 \; 2^{(-t/5568)}, \qquad (5')$$

in which t is the age of the organic material in years, age being defined as the time elapsed since death occurred. The experimental points shown in Figure 1 are the observed assays for various samples of known age, discussed later. In so far as the points fit the curve, we have reason to believe that the method is sound and gives the correct ages. The errors indicated on the experimental points are standard deviations, and it appears that the results are favorable as judged statistically.

It is obvious that we must be careful in selecting samples to choose materials that contain the original carbon atoms present at the time death occurred. In other words, samples must not have been preserved with organic materials containing carbon of age different from that of the sample. Care must also be taken that chemical changes have not led to replacement of the carbon atoms. In a general way, organic materials consisting mainly of large molecules, such as cellulose and charcoal, are favored. An example of questionable material is shell, for it is quite conceivable that shell which is powdery and chalky in appearance has had its carbonate atoms replaced.

CHAPTER II

WORLD-WIDE DISTRIBUTION
OF RADIOCARBON

FUNDAMENTAL to the radiocarbon dating method is the question of the contemporary assay of the exchange reservoir for radiocarbon and the uniformity over the earth's surface of this assay.[1] Organic material, principally wood, was collected from widely scattered points over the earth's surface, and measurements of the specific radioactivity were made. One group of samples was concentrated near the geomagnetic equator, where the neutron flux is at a minimum; another in high latitudes, where the neutron flux is at a maximum. The variation in neutron intensity with latitude, as observed by Simpson at 30,000 feet, is presented in Figure 2.[2] Some consideration was given to the archeological importance of the region with the thought that, if no uniformity were demonstrated, these data might be utilized in age measurements where the original assay would vary from region to region. Fortunately, this has not proved to be necessary. Owing to the known extreme variation of neutron intensity with altitude, shown in Figure 3, in which the data of Yuan and Ladenburg taken at Princeton, New Jersey,[3] are given, two samples from high altitudes were measured. It might be suspected that the specific radioactivity would be higher at higher altitudes. However, the height of the timber line was of course very small indeed compared with the 30,000-foot altitude at which the principal radiocarbon production occurs.

The experimental results are given in Tables 2 and 3, in which the type of sample, the donor, the geomagnetic latitude, and the observed specific radioactivity in absolute disintegrations per minute

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1. The material on this subject has been taken largely from the doctoral thesis of E. C. Anderson, presented to the Division of Physical Sciences, University of Chicago, in partial fulfilment of the requirements for the Ph.D. degree.

2. *Ibid.*

3. *Phys. Rev.*, 74, 504 (1948); 76, 1267, 1268 (1949); 77, 728 (1950); *Bull. Am. Phys. Soc.*, 23, No. 2, 21 (1948).
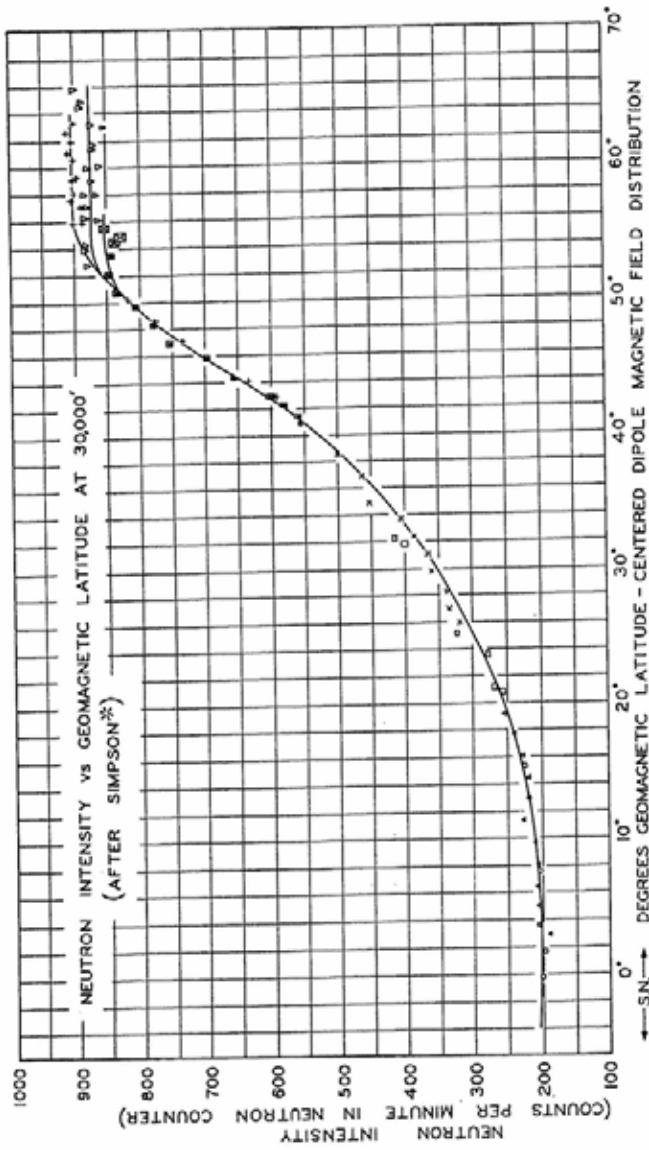
Fig. 2.—Latitudinal variation of cosmic-ray neutron intensity. (After J. A. Simpson, Jr., *Phys. Rev.*, **73**, 1389 [1948])

per gram of carbon are recorded, Table 2 applying to the biosphere and Table 3 to the inorganic.

The associated error is the standard deviation calculated from the counter statistics only. Naturally, since other errors are involved, the true error will be somewhat larger. However, similar treatment of the more numerous data quoted later on samples measured for age determination seem to indicate that the scatter appears to be
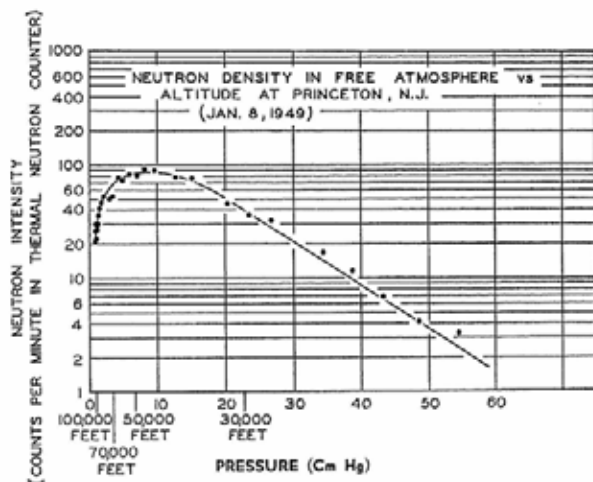

Fig. 3.—Altitudinal variation of neutron intensity

little more than would be expected from this source alone. So perhaps one can conclude that this nearly represents the true standard deviation of the measurement. The terrestrial distribution of the samples is shown in the map in Figure 4, each dot corresponding to a particular sample. It is of course to be realized that the geomagnetic latitude and the ordinary latitude are not identical. The geomagnetic latitude is taken as being more significant in Table 2, since the variation in neutron intensity with latitude shown in Figure 2 correlates with it.

TABLE 2

ACTIVITY OF TERRESTRIAL BIOSPHERE SAMPLES

Source	Geomagnetic Latitude	Absolute Specific Activity (Dpm/Gm)
White spruce, Yukon (Frederick Johnson)	60° N.	14.84 ± 0.30
Norwegian spruce, Sweden (Donald Collier, Chicago Natural History Museum)	55° N.	15.37 ± 0.54
Elm wood, Chicago (authors)	53° N.	14.72 ± 0.54
Fraxinus excelsior, Switzerland (Donald Collier)	49° N.	15.16 ± 0.30
Honeysuckle leaves, Oak Ridge, Tennessee (C. H. Perry, Clinton Laboratory)	47° N.	14.60 ± 0.30
Pine twigs and needles (12,000-ft. alt.), Mount Wheeler, New Mexico (Robert Fryxell)	44° N.	15.82 ± 0.47
North African briar (John Hudson Moore, Inc.)	40° N.	14.47 ± 0.44
Oak, Sherafat, Palestine (Donald Collier)	34° N.	15.19 ± 0.40
Unidentified wood, Teheran, Iran (M. Hessaby)	28° N.	15.57 ± 0.34
Fraxinus mandshurica, Japan (Donald Collier)	26° N.	14.84 ± 0.30
Unidentified wood, Panama (John Simpson)	20° N.	15.94 ± 0.51
Chlorophora excelsa, Liberia (Donald Collier)	11° N.	15.08 ± 0.34
Sterculia excelsa, Copacabana, Bolivia (9000-ft. alt.) (Donald Collier)	1° N.	15.47 ± 0.50
Ironwood, Majuro, Marshall Islands (Donald Collier)	0°	14.53 ± 0.60
Unidentified wood, Ceylon (Donald Collier)	2° S.	15.29 ± 0.67
Beech wood ('Nothalagus'), Tierra del Fuego (Junius Bird)	45° S.	15.37 ± 0.49
Eucalyptus, New South Wales, Australia (Donald Collier)	45° S.	16.31 ± 0.43
Seal oil from seal meat from Antarctic (Byrd Expedition through H. J. Deason)	65° S.	15.69 ± 0.30
Average		15.3 ± 0.1*

* Error of calibration of counter raises error on absolute assay to 0.5.

TABLE 3

ACTIVITY OF CONTEMPORANEOUS SHELL SAMPLES

Source	Assay
Murex shell, Florida west coast	17.1 ± 0.5
Freshly deposited ocean sediments, 1150-meter depth, Bermuda (J. Lawrence Kulp)	17.4 ± 0.6
Oyster shells, Chesapeake Bay	15.1 ± 0.5*
Average	16.5 ± 0.5

* This sample had a high ash (22 per cent), so the number is less reliable than the counting error indicated.
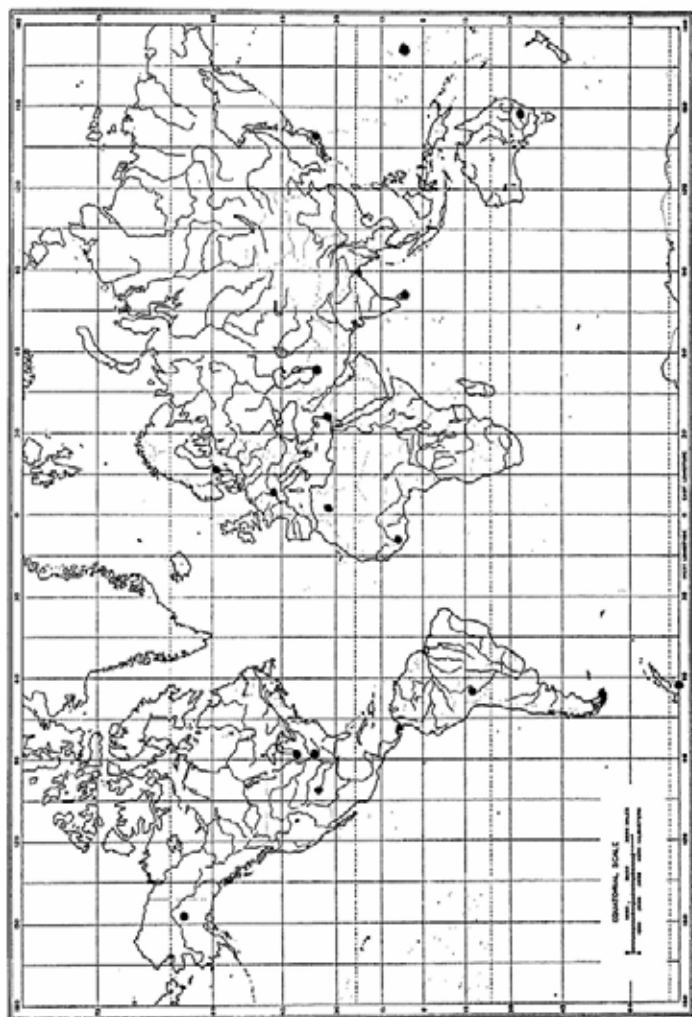
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FIG. 4.—Distribution of contemporaneous samples

The average specific activity of all the biosphere samples is found[4] to be 15.3 ± 0.5 absolute disintegrations per minute per gram. The data seem to show no scatter appreciably larger than the expected statistical fluctuations, indicating that the samples involved would indeed have specific activities identical within the error of measurement. The data presented in Table 3 for shell reveal that shell is definitely more radioactive than organic material. This difference is to be expected, since it has been shown[5] that fractionation of the stable isotopes of carbon, C^{12} and C^{13}, occurs in these systems. The ratio of the C^{14} content of carbonate to that of organic material which is found here is 1.09 ± 0.03. On the basis of the fractionation factor 1.03 found for C^{13} against C^{12}, one would expect a value of 1.06 for C^{14}. The difference between this value and the one found in the present investigation is not outside the experimental error; and, since the accuracy of the estimation of the fractionation factor is better than the precision of our measurements of the shell activity, we take the observed value to be 16.2 ± 0.5, derived by multiplication of the mean of the organic specific activity by 1.06. It seems that a further investigation of the fractionation factor would be worth while and that further measurement of contemporaneous shell samples is definitely desirable.

The estimation of the amount of carbon in exchange with the atmospheric carbon dioxide is a difficult task. It is, however, necessary to the striking of a balance between the observed specific activity and the cosmic radiation intensity. The results have been given in Table 1.

The carbon in the exchange reservoir is obviously of three principal origins; namely, that dissolved in the oceans, the carbon of living organisms, and atmospheric carbon dioxide itself. We shall find that the latter two are so small as to be nearly negligible in comparison with dissolved material in the sea, principally carbonate and bicarbonate. Let us consider first the amount of carbon dissolved in the oceans as some species of carbonic acid. This amount can be calculated from a knowledge of two factors: the alkalinity and the

4. Earlier publications have given 12.5 for this number. The counters have been recalibrated for absolute efficiency since then, and the new value is derived from the old one by correction for the more accurately determined efficiency.

5. A. O. Nier and E. A. Gulbranson, *J. Am. Chem. Soc.*, **61**, 697 (1939); B. F. Murphy and A. O. Nier, *Phys. Rev.*, **59**, 771 (1941).

pH of the ocean water. The alkalinity is the excess of positive ions over the anions of strong acids. This difference must be made up by the ionization of weak acids in order to preserve electrical neutrality. Since carbonic acid is the principal weak acid in the ocean, the situation is fairly simple. The total amount of dissolved carbon is not uniquely determined by the alkalinity alone, because of its variable equivalent nature due to the possibility of its existence in the neutral, monobasic, and dibasic forms: H_2CO_3, HCO_3^-, and CO_3^{--}. The ratio of the amounts in these forms must therefore be specified, and this ratio is, of course, determined by the pH. The necessary equations are

$$\frac{(H^+) \cdot (HCO_3^-)}{(H_2CO_3)} = K_1 \qquad (6)$$

$$\frac{(H^+) \cdot (CO_3^{--})}{(HCO_3^-)} = K_2 \qquad (7)$$

$$A = (HCO_3^-) + 2\,(CO_3^{--}) \qquad (8)$$

$$S = (H_2CO_3) + (HCO_3^-) + (CO_3^{--}), \qquad (9)$$

where A is the alkalinity due to carbonic acid, and S is the total amount of carbon present in the forms indicated. These equations can be combined to give

$$S = \frac{A}{1 + \frac{2K_2}{(H^+)}} \left[\frac{(H^+)}{K_1} + \frac{K_2}{(H^+)} + 1 \right]. \qquad (10)$$

We must now consider the values to be adopted for the four constants in this equation; namely, the alkalinity, the hydrogen-ion concentration, and the two ionization constants of carbonic acid.

The average value of the alkalinity of the ocean seems to be well established as a result of numerous measurements by many investigators and has a value of 2.43 milliequivalents per liter.[6] The alkalinity is due almost exclusively to carbonate and bicarbonate, the amounts of phosphorus, arsenic, silicon, and other elements capable of forming weak acids being completely negligible. A slight correction can be made for the amounts of boron known to be present.

6. H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans* (New York: Prentice-Hall, 1946), p. 208.

Using only the first ionization constant of boric acid and taking the pH of the ocean as 8.0, we find the alkalinity due to boron to be 0.06 milliequivalents per liter.[7] The alkalinity due to carbon is therefore 2.37 milliequivalents per liter.

The variation in pH throughout the ocean is surprisingly small, and the average value is about 8.0.[8] The small amount of variation found throughout the greater portion of the water map is graphically illustrated by the north-south section of the Atlantic Ocean given by Sverdrup et al. as taken from Wattenberg.[9] It is clear that over the major portion of the ocean the variation is only 0.1 pH units.

It is of interest to compare the observed pH of ocean water with that calculated assuming complete equilibrium with the carbon dioxide of the atmosphere. The deep water which constitutes by far the largest fraction of ocean water is formed at high latitudes by the cooling of water of high salinity. Therefore we will assume Arctic conditions for the equilibration. For the apparent ionization constants of carbonic acid we will use experimental values which will be discussed below. These are $K_1' = 8.3 \times 10^{-7}$, and $K_2' = 6.3 \times 10^{-10}$, and are applicable to water of chlorinity 19.0 per mil at a temperature of 4° C. We will assume an alkalinity of 2.37 milliequivalents per liter and a partial pressure of CO_2 in the polar air of 0.23 mm. of mercury.[10] For the solubility of CO_2 in sea water we will use the data given by Sverdrup et al.[11] The result of this calculation is a pH of 8.10 for the water while at the surface. On sinking to the average depth of the oceans (3800 meters), the pH will change to 8.01 as a result of changes of K_1' and K_2' with pressure. These results are in very satisfactory agreement with the observed pH of the deep ocean, namely, 8.0.

Because of the high ionic strength of sea water, namely, 0.9 molal, and the lack of knowledge of the activity coefficients of the species involved, it is necessary to use apparent ionization constants rather than thermodynamic constants for carbonic acid. Fortunately the values of K_1' and K_2' have been carefully investigated by a number

7. Ibid., p. 199.

8. Ibid., p. 208.   9. Ibid., p. 210, Fig. 43.

10. K. Buch, Acta Acad. Aboensis, Math. et Physica, 11, No. 12 (1939).

11. Op. cit., p. 191.

of investigators[12] as a function of pH, salinity, temperature, and pressure in both natural and artificial sea water. In general, the agreement among the several investigators is excellent, and the results appear to be very reliable.

The relations which were found for the normal range of composition of sea water are

$$pK_1' = 6.47 - 0.100 \ (Cl)^{1/2} \tag{11}$$

at 20° C. with a temperature coefficient of -0.008 per °C. and a pressure coefficient of -4.8×10^{-5} per meter of depth; and

$$pK_2 = 10.35 - 0.498 \ (Cl)^{1/2} \tag{12}$$

(where pK is the negative logarithm, base 10) at 20° C. with a temperature coefficient of -0.011 per °C. and a pressure coefficient of -1.8×10^{-5} per meter. Taking (Cl) as 1.95 per cent, the temperature to be 4° C., and a depth of 3800 meters (the mean depth of the ocean), we find that for average ocean water

$$K_1' = 1.26 \times 10^{-6} \tag{13}$$

$$K_2' = 7.41 \times 10^{-10} . \tag{14}$$

From Equation (10) it is possible to calculate the errors which will be introduced into the value of the total carbon by errors in K_1', K_2', and pH. If we substitute the following numerical values in Equation (10), $K_1' = 1.20 \times 10^{-6}$, $K_2' = 7.41 \times 10^{-10}$, and $(H^+) = 10^{-8}$, we find

$$S = \frac{A}{1 + 0.148} (0.0082 + 0.074 + 1) . \tag{15}$$

It is clear that K_1' has a completely negligible effect on S, since it contributes only 0.8 per cent to the last term.

Dropping K_1' and expanding Equation (10) in terms of powers of $[K_2'/(H^+)]$, and dropping higher powers than the first, we have, to a good approximation,

$$S = A \left(1 - \frac{K_2'}{(H^+)}\right) = A \ (1 - 0.074) . \tag{16}$$

12. E. G. Moberg, D. M. Greenberg, R. Revelle, and E. C. Allen, *Bull. Scripps Inst. Oceanogr., Univ. Calif., Tech. Ser.*, 3, 231 (1934); K. Buch, *Acta Acad. Aboensis, Math. et Physica*, 11, No. 5 (1938); Sverdrup *et al., op. cit.*, p. 250.

The entire effect of K'_2 is only 7.4 per cent. If for the possible error in K'_2 we allow the amount of the full range between K_2 and K'_2, we will estimate the possible error in S from this source as 7 per cent.

The error introduced in the value of S by an error in pH can be calculated by differentiating Equation (10) with respect to $-\log (H^+)$. In this way we find

$$\frac{dS}{d\,(pH)} = -3.42 \times 10^{-9} \frac{(H^+)}{(H^+ + 2K'_2)^2}. \qquad (17)$$

At pH 8 a change of one pH unit gives a change of 0.36 in S, or 16 per cent. If we assume that the uncertainty in the exact average pH of the ocean is 0.5 pH unit, we place an error of 8 per cent on the amount of dissolved carbonate.

The variations in alkalinity which have been observed in water from various sources by different investigators amount to about 4 per cent. We may take this as a measure of the uncertainty in A. Combining the errors from K'_2, pH, and A, by the square root of the sum-of-squares method, we place an uncertainty of 11 per cent on the value of S.

Using the values of $K'_1 = 1.26 \times 10^{-6}$, $K'_2 = 7.41 \times 10^{-10}$, pH = 8.0, and $A = 2.37$, the solution of Equation (10) gives for S a value of 26.2 milligrams of carbon per kilogram of sea water, or 7.25 gm/cm^2 of earth's surface. This corresponds to a total mass of 3.7×10^{19} grams of carbon. In addition to the dissolved inorganic carbon, there is found in solution in the ocean a considerably smaller amount of organic carbon (not living). The best value for this appears to be about 2 mg. per liter, according to Sverdrup et al.[13] This corresponds to 0.59 gram of carbon per square centimeter of the earth's surface.

The amount of carbon in living material is difficult to estimate and appears to have been grossly overestimated by some writers in the past. We will base our estimate on the rate of fixation of carbon by photosynthesis, a quantity which appears to be fairly well established.[14] Fortunately it can be shown that biosphere carbon is small compared with ocean carbonate, and therefore an error in the estimation of it will not be of great importance to our use of this quantity.

The total rate of fixation of carbon by land plants has been in-

13. Op. cit., p. 250.

14. E. Rabinowitch, *Photosynthesis and Related Processes* (New York: Inter-Science Publishers, Inc., 1945), chap. i.

vestigated by Schroeder,[15] who concluded that the average annual fixation by this source is 1.63×10^{16} grams, or 3.2 mg/cm² of the earth's surface. Riley[16] made an investigation of the fixation by ocean plankton and arrived at a figure of 30.5 mg/cm² of earth's surface for the average annual rate. Rabinowitch[17] estimates that on the basis of the solar energy flux, reflection losses, and photosynthetic efficiency, not more than 60 mg/cm² of earth's surface could be fixed annually, indicating that Riley's figures could not be too low by any large factor. On the other hand, it appears that the estimate of Vernadsky,[18] who gives 2000 mg/cm² for the carbon content of the biosphere, with renewal several times a year, is energetically impossible. We will use the sum of the values given by Schroeder and by Riley as the total annual rate of fixation of carbon; namely, 33 mg/cm² of the earth's surface.

The total amount of carbon contained in the biosphere at any time will be given by the fixation rate times the average length of time a given carbon atom spends in the biosphere, if a steady state exists. An estimation of this time is somewhat easier than might appear on first glance, since 90 per cent of the fixation is by ocean plankton, which are minute organisms of very short life. Furthermore, even the carbon contained in longer-lived organisms does not in general have a time of residence in the organism equal to the life of the organism but rather less because the material of the organism is replaced a number of times during its lifetime. A maximum value for the average time the carbon atom spends in the biosphere seems to be a few years. Since carbon in the biosphere is such a small fraction of the total exchange reservoir, a more exact treatment appears unnecessary. Taking 10 years for the average carbon life, our calculated biosphere inventory will be 0.33 gm/cm² of the earth's surface, which will prove to be only some 4 per cent of the total in the exchange reservoir, as has been shown in Table 1.

We may check this estimate against measurements which have been made of the ratio of living matter to dissolved organic carbon

15. G. Schroeder, *Naturwiss.*, **7**, 8, 96 (1919).

16. G. A. Riley, *Bull. Bingham Oceanogr. Coll.*, **1**, 1 (1941), quoted by Rabinowitch, *op. cit.*, p. 6.

17. *Op. cit.*, p. 6.

18. W. J. Vernadsky, *Geochemie in ausgewählten Kapiteln* (Leipzig: Akademische Verlagsgesellschaft, 1930).

in the ocean. A number of such measurements have been made by several observers,[19] and the ratio of dissolved to living matter has been determined to vary between 300:1 and 2:1. The low figures are found only in relatively small areas near shore where there is intense biological activity. The larger ratio, which was established for the deep water of the open ocean, was probably considerably nearer the average for the ocean as a whole. The estimates which we have chosen for these two quantities give a ratio of 2:1, again indicating that we have not underestimated the amount of carbon in the biosphere.

The most likely way of appreciably increasing the holdup of the biosphere is by the assumption that a considerable portion of this material spends many years in slow decay as humus or ocean sediments before it is recirculated. The available evidence for the ocean sediments seems to be that the major part of the dead material dissolves during the settling process and that little of it ever reaches the ocean floor.[20] This makes it unlikely that this factor could increase appreciably the importance of biosphere carbon to the size of the exchange reservoir.

The amount of carbon dioxide in the atmosphere has been determined by several people. The values are: Buch,[21] 0.12 (polar) to 0.13 (tropical and continental); Paneth,[22] 0.12; and Vernadsky,[23] 0.12. We will use 0.12 gm/cm^2 of the earth's surface for the amount of carbon in atmospheric carbon dioxide. This is equivalent to CO_2 partial pressure of 0.21 mm. of mercury, or a concentration of 0.028 per cent.

In addition to the dilution of cosmic radiocarbon by the carbon of the exchange reservoir, some is being removed constantly by incorporation in sedimentary rocks as they form. This rate of loss of radiocarbon will be estimated. The rates of deposition of calcium carbonate in the sea are not at all well established. Various estimates can be made on the basis of the total amount of calcium carbonate that has been deposited, the bicarbonate contents of rivers emptying

19. Sverdrup *et al.*, *op. cit.*, p. 250.   20. *Ibid.*, p. 1012.

21. K. Buch, *Acta Acad. Aboensis, Math. et Physica*, 11, No. 12 (1939).

22. F. Paneth, quoted by G. P. Kuiper, *The Atmospheres of the Earth and Planets* (Chicago: University of Chicago Press, 1949), p. 1.

23. *Op. cit.*

into the sea, and the direct observation of the rate of formation of ocean sediments. For example, Brown[24] has calculated the following inventory of carbon in the sedimentary rocks: in shale, 5.45×10^{21} grams; in sandstone, 0.20×10^{21} grams; and in limestone, 3.67×10^{21} grams—a total of 9.3×10^{21} grams of carbon. If we assume uniform deposition over a 2-billion-year period, we have a yearly loss rate of 5×10^{12} grams, which would remove only 6 grams of the 9800 grams of radiocarbon produced each year. This may be low because recycling may be important, and the other methods give somewhat higher figures; but it seems likely that the total removal by formation of sedimentary deposits is probably less than about 3 per cent.

We may consider now the question as to whether or not the various portions of the exchange reservoir are sufficiently well mixed so that they are completely efficient in the dilution process. The uniform distribution of radiocarbon throughout the reservoir will result only if the various mixing processes are complete in a time short compared with the average life of radiocarbon (8033 years; the average life is longer than the half-life by $1/\ln 2$). From the estimated photosynthetic fixation rate given above and the total material in the exchange reservoir, it can be calculated that a time of the order of 250 years would suffice to turn over all the carbon through the biosphere. This insures that the thin layer of the reservoir at the surface of the earth and of the ocean will be well mixed. The main question is whether or not the depths of the ocean and the upper reaches of the atmosphere are mixed.

Considering the latter first, we note that the radiocarbon is produced at great heights (Fig. 3), the neutron intensity reaching a maximum at about 40,000 feet and falling off considerably by 70,000 feet. At this altitude the air pressure is 3.5 mm. of mercury. Excellent and rapid mixing is well established in the troposphere, the adiabatic portion of the atmosphere in which most weather phenomena occur. In the meteorological "standard atmosphere" the tropopause, or boundary between the adiabatic troposphere and the isothermal stratosphere, is assumed to be[25] at 10.8 km. (36,000 feet).

24. H. S. Brown, private communication.

25. H. R. Byers, *General Meteorology* (New York: McGraw-Hill Book Co., 1944), p. 171.

However, the height of the tropopause varies considerably with the season and with latitude, reaching 18 km. (58,000 feet) in the winter at 40° N. latitude, while in summer it may be found at 16 km. (52,000 feet) as far north as 60° N. geomagnetic latitude.[26] Thus the tropopause is actually above the altitude of maximum neutron intensity some of the time each year. Even the isothermal stratosphere is not without vertical mixing.[27]

The situation with regard to oceanic mixing is much less obvious. Very little indeed is known about the quantitative rates of convective mixing of the deep ocean basins. Diffusive mixing is of course so extremely slow as to be out of the question.

From studies made of the circulation of the Atlantic Ocean[28] a very rough estimate of the mixing time can be made. These figures indicate that the rate of flow southward between South America and Africa at the equator is about 6×10^6 cubic meters per second at 3000 meters depth. This flow has been identified with North Atlantic Deep Water produced in the Arctic regions, and much of it reaches the Antarctic to replace water subsiding at the Antarctic Convergence. The situation is greatly complicated by the presence of some six water masses interacting in an involved circulatory pattern, but we may take this figure to represent the gross exchange of water between the North and South Atlantic at great depths. The shallower water is mixed more rapidly by local complexities in the circulation pattern, and the surface water is characterized by well-developed patterns of rapid currents. The Antarctic Bottom Water, which fills the deepest parts of most of the Atlantic, moves slowly north below the southward current and is presumably returned to the Antarctic by gradual mixing with the North Atlantic Deep Water. The rate of the return is not known, but the northward flow at the equator is estimated at 1×10^6 cubic meters per second.

Taking the volume of the Atlantic Ocean as 3.24×10^{17} cubic meters, we find the calculated time of circulating the entire ocean through the entire Deep Water current to be 1700 years. About 18 per cent of the Atlantic is below 4000 meters. If this water has a

26. C.-G. Rossby, in *The Atmospheres of the Earth and Planets*, ed. G. P. Kuiper (Chicago: University of Chicago Press, 1949), p. 21.

27. L. Spitzer, Jr., *ibid.*, p. 221.   28. Sverdrup *et al.*, *op. cit.*, pp. 629 and 747 ff.

circulation rate of 1×10^6 cubic meters per second, the time required to circulate it is 1800 years. Less is known about the Pacific circulation, but it is thought to be somewhat slower than that of the Atlantic.

For isolated seas for which the annual inflow and outflow are known, it is possible to calculate a renewal time. Some of the figures so obtained are: Mediterranean, 80 years; Arctic Mediterranean, 165 years; and Black Sea, 2500 years. The volume of such seas makes their importance in a general mixing process small, but the figures given are an indication of the order of magnitude of the time scale involved.

A further argument in favor of complete mixing of the ocean basins may be based on the following considerations: It is known that heat is being liberated from the earth's crust at the rate of about 30 calories per square centimeter per year.[29] Presumably the evolution of heat from the bottom of the sea is of a similar magnitude, as indeed recent measurements by Revelle and associates in the deep Pacific have shown.[30] Owing to this heat evolution, one might expect regions of temperature inversion to develop near the ocean bottom, especially in areas of poor circulation. To transfer this amount of heat by molecular conduction would require a thermal gradient of 8×10^{-4} °C. per centimeter, assuming the conductivity of water to be 0.0013. If a layer 1000 meters thick at the bottom were cooled only by molecular conduction, a temperature difference of 80° C. would be required. Naturally, turbulent eddy circulation patterns would be set up at much lower gradients, and a more effective mechanism of eddy conduction would operate to remove the heat. Such eddy circulation would be equally efficacious in the transfer of dissolved carbonate, and a very efficient method of maintaining the radiocarbon equilibrium would arise. It can be calculated, for example, that a temperature gradient of 1.6×10^{-6} °C. per centimeter would require a coefficient of eddy conduction some five hundred times the molecular coefficient for the transfer of the postulated amount of heat. This is quite small as eddy coefficients go, since they often range up to 10^8 or more times the molecular co-

29. E. C. Bullard, *Nature*, **156**, 35 (1945).

30. Roger Revelle and associates, private communication. They find 38 calories per square centimeter per year.

efficients. Such an eddy circulation operating at a depth below 4000 meters can be shown to be adequate to mix the ocean depths sufficiently so that the assay of radiocarbon at 6000 meters would be 90 per cent of normal with an integrated effect of only 1.4 per cent on the value of the specific activity.

Few cases of temperature inversion in the deep ocean have been established. The inversion gradient shown in the above calculation is that observed in the Mindanao Trench[31] and is almost exactly equal to the gradient which would be produced by adiabatic compression; that is, there is no density inversion, the density of the water being constant with depth. However, the smaller the thermal gradient, the larger the coefficient of eddy conduction required to transport the heat. Without specifying the nature or source of the circulation, we merely point out that if 30 calories per square centimeter per year are being evolved from the ocean floor, a certain minimum rate of circulation must exist in order to prevent the development of large thermal gradients. The above arguments are of course qualitative, since turbulent eddy circulation is not amenable to calculation. However, if the assumption of the specified heat evolution is correct, the absence of appreciable thermal inversions near the ocean bottom would seem to indicate that the mixing is very good indeed on our time scale.

It has not been possible to obtain samples of dissolved carbon from the very deep ocean, so that experimental evidence on the mixing time is not at hand. It would appear that measurements of this kind might be of considerable oceanographic interest and might shed some light on the problem of circulation in the deep basins. It is to be noted that collection of the deep water must be done with care, so that particulate material on transit from the top to the bottom and probably in equilibrium with the biosphere will not be taken as part of the sample proper. It seems likely that matter falling through the deep water would not come into exchange equilibrium with dissolved material.

We arrive finally, therefore, at the numbers given in Table 1 and a total figure of 8.3 gm/cm² of the earth's surface for the carbon in the exchange reservoir. The uncertainty in this value for the total

31. Sverdrup *et al.*, *op. cit.*, p. 739.

carbon in the reservoir we place at about 15 per cent, most of this error being in the estimated uncertainty in the value for ocean carbonate, since it is the largest single item in the reservoir. It is interesting to compare our numbers with a similar set given by Rubey.[32] Dr. Rubey's numbers are 7.85 gm/cm^2 for the total, consisting of 6.95 for ocean and fresh water, 0.125 for the atmosphere, and 0.775 for living organisms and undecayed organic matter.

We shall turn now to the question of the present production rate of radiocarbon as judged from the observed neutron intensity in the atmosphere, assuming essentially quantitative conversion of atmospheric neutrons to radiocarbon by Equation (1). As stated previously and shown in Figure 3,[33] the neutron intensity increases with altitude from sea-level up to about 40,000 feet in an exponential fashion, with a half-thickness of about 1 meter of water equivalent. Above 40,000 feet a maximum is reached, followed by a rapid decrease, indicating very low intensity at the very top of the atmosphere, in agreement with the principle that the neutrons are secondary in origin, being produced by the impact of the primary cosmic radiation on the atmosphere. In addition to the altitude dependence, the neutron intensity shows a strong dependence on geomagnetic latitude (Fig. 2),[34] the intensity at high latitudes being about four times that at the geomagnetic equator.

The measurements on neutron intensity which we use for our calculations of total intensity have been on the thermal component as defined by cadmium absorption for a boron detector. We shall take this to mean that that fraction of the neutron spectrum lying below 0.4 ev has been measured, and, in order to calculate the total number of neutrons per square centimeter, Q, and its world-wide average, $\bar{Q}$, we must determine theoretically the probable ratio of the total intensity to the thermal intensity. Bethe, Korff, and Placzek[35] and Placzek[36] have considered the problem in detail. Fol-

32. W. W. Rubey, "Geological Evidence Regarding the Source of the Earth's Hydrosphere and Atmosphere," *Science*, 112, 20 (1950); and autumn, 1950, meeting of the National Academy of Sciences.

33. L. C. L. Yuan, *Phys. Rev.*, 74, 504 (1948); 76, 1267, 1268 (1949); 77, 728 (1950); L. C. L. Yuan and R. Ladenburg, *Bull. Am. Phys. Soc.*, 23, No. 2, 21 (1948).

34. E. C. Anderson, Ph.D. thesis, University of Chicago (1949).

35. H. A. Bethe, S. A. Korff, and G. Placzek, *Phys. Rev.*, 57, 573 (1940).

36. G. Placzek, *Phys. Rev.*, 69, 423 (1946).

lowing them and using the later data of Melkonian[37] together with
the data in the Massachusetts Institute of Technology volume,[38] we
shall assume that in the range 0.4 ev to 0.5 mev the total cross-
section in units of 10^{-24} cm.^{2} for air is given by

$$\sigma_t = 8.56 + (0.266/E^{1/2}), \qquad (18)$$

and that the capture cross-section is given by

$$\sigma_c = 0.266/E^{1/2} . \qquad (19)$$

The expression for the ratio of the total number of neutrons gener-
ated to the number which reach the thermal range is e^y, where y is
given by

$$y = \frac{1}{0.124} \int_{0.4}^{5 \times 10^5} \sigma_c dE / \sigma_t E , \qquad (20)$$

where the number 0.124 is the fractional energy loss in elastic col-
lision with the average air atom, the bond strength being neglected.
Integration and substitution give 0.79 for the integral and the calcu-
lated ratio of total production to thermal population of 2.20. It is
clear, however, that one must consider the effect of the very strong
bonds in the nitrogen and oxygen molecules on the cooling process.
Study of the analogous problem of the effect of binding on the neu-
tron elastic and inelastic cross-sections for hydrogen[39] leads us to
expect that no large error is made in neglecting the binding for cool-
ing down to the cadmium cut-off of 0.4 ev, which is 1.5 vibrational
quanta for the average air molecule.

It is necessary to make a correction for the absorption above 0.5
mev. It has been shown by Barschall and Battat,[40] Johnson and
Barschall,[41] and others,[42] that resonance production of radiocarbon
occurs in this range at cross-sections rising to a maximum of 0.1×10^{-24} cm.^{2} and falling to about 0.01×10^{-24} cm.^{2} in the range 0.5
mev to 2.0 mev. To obtain a probable upper limit for the capture
contribution in this high-energy range, we assume that only elastic

37. E. Melkonian, *Phys. Rev.*, **76**, 1750 (1949).

38. *Science and Engineering of Nuclear Power* (Cambridge, Mass.: Addison-Wesley
Press, 1947), 1, 408-11.

39. H. A. Bethe, *Rev. Mod. Phys.*, **9**, 122-27 (1937).

40. H. H. Barschall and M. E. Battat, *Phys. Rev.*, **70**, 245 (1946).

41. C. H. Johnson and H. H. Barschall, *Phys. Rev.*, **80**, 819 (1950).

42. *Science and Engineering of Nuclear Power*, 1, 408-11.

scattering occurs and that an average capture cross-section of 0.035×10^{-24} cm.² applies throughout the high-energy interval. This gives an additional contribution of 7 per cent to the ratio of total to thermal neutron population. The corrected ratio is 2.36. The value of Q is now to be obtained at any given latitude by integrating the observed intensity under the intensity versus altitude curve (e.g., Fig. 3) and multiplying this observed intensity by the number 2.36. For this purpose we choose the data of Yuan and Ladenburg,[43] Figure 3, obtained at Princeton, New Jersey, which give 1.9 as the number of slow cosmic-ray neutrons absorbed per second per square centimeter of earth's surface at that latitude. Using Simpson's data[44] (Fig. 2) for the variation of Q with latitude, and integrating over the surface of the earth, we find for the average thermal flux 1.1 thermal cosmic-ray neutrons per square centimeter per second. Finally, multiplying by the ratio of total production to thermal neutron population, we obtain 2.6 as the most likely value for Q, the average total production of cosmic-ray neutrons per square centimeter of earth's surface per second. Considering the various sources of error in this figure, it seems that it probably is good to about 20 per cent, though there is, of course, considerable possibility that the error is somewhat larger or smaller than this.

If the figure 2.6 for the average total production of cosmic-ray neutrons per square centimeter of earth's surface per second, $\bar{Q}$, is correct, and this intensity has remained constant over the last several half-lives of radiocarbon, we can calculate an expected specific activity for the carbon in the exchange reservoir of $(2.6 \times 60)/8.3$, or 18.8 ± 5 disintegrations per minute per gram of carbon. This is to be compared with the observed mean value (Table 2) of 16.2 ± 0.5. Both of these numbers are for the average carbon in the inventory and are very close to the number expected for carbonate carbon, which is some 6 per cent higher in its radiocarbon content than biological carbon. The agreement between these two values is gratifying and suggests that no major factors contributing to the situation have been overlooked, although it does seem possible that the agreement may be due in some part to cancellation of errors.

The possibility that the amount of carbon in the exchange reser-

43. L. C. L. Yuan and R. Ladenburg, *Bull. Am. Phys. Soc.*, **23**, No. 2, 21 (1948).
44. E. C. Anderson, Ph.D. thesis, University of Chicago (1949).

voir has altered appreciably in the last 10,000 or 20,000 years turns almost entirely on the question as to whether the glacial epoch, which as we will see later appears to reach into this period, could have affected the volume and the mean temperatures of the oceans appreciably. Antevs,[45] Daly,[46] and Flint[47] give 90, 85, and 102 meters, respectively, for the lowering of the seas below the present level during the last Ice Age. This is to be compared with the mean depth of 3800 meters, so we may expect a decrease in the volume of the sea by about 5 per cent during this period, the actual magnitude depending on the extent of the continental shelf in shallow regions in this sea. This effect in itself would lead to an increase in the specific activity of carbon formed during the glacial epoch by about this same percentage. In addition, there is the question of the mean temperature of the oceans and whether this has varied appreciably. An increase in mean temperature would act to increase the carbon in the reservoir, and a decrease in mean temperature would decrease the inventory. Bearing in mind that both of these effects will be unimportant unless the altered conditions last for a time of the order of magnitude of the mean life of radiocarbon (8033 ± 50 years), we find it difficult at this stage to make correction for these effects. It does seem possible, however, that the certain decrease in volume and the possible slight decrease in temperature might raise the specific activity of carbon in the exchange reservoir during the glacial maximum by 5 or 10 per cent, causing an error in the direction of making glacial material appear somewhat too young. We can estimate from the decay equation

$$I = I_0 e^{-t/\tau}, \tag{21}$$

in which I_0 is the original specific activity and τ is the mean life, that the error in the age will be given by

$$\Delta t = \tau \sqrt{\left(\frac{\Delta I}{I}\right)^2 + \left(\frac{\Delta I_0}{I_0}\right)^2}, \tag{22}$$

in which ΔI is the error in the determination of the specific activity of the ancient material and ΔI_0 is the error made in assuming that

45. *Am. Geog. Soc., Res. Ser.*, No. 17, pp. 74–82 (1928).

46. *Changing World of the Ice Age* (New Haven: Yale University Press, 1934), p. 46.

47. *Glacial Geology and the Pleistocene Epoch* (New York: John Wiley & Sons, 1947), p. 435.

I_0 has the modern value of 15.3 for organic matter or 16.2 for shell and inorganic material. From this we see that a 10 per cent error in I_0 would make our glacial ages too young by some 800 years. As further information becomes available on the chronology of the recent ice ages, it should be possible to make a more accurate correction for this effect. It is to be hoped that Professor Urey's determination of prehistoric temperatures by the O^{18} content of fossil shell[48] will give quantitative information on the mean temperature of the oceans in recent glacial times. With such data one then can calculate the expected change in the principal item in the inventory, the inorganic carbon in the sea. The data available at present suggest that the temperature correction will not be large, though it must be borne in mind and considered to be a source of uncertainty.

It seems quite likely that the amount of living matter on earth will not seriously affect the specific activity, for the reason that it constitutes such a small fraction of the total inventory in the reservoir and probably has always held this minor position. The situation would appear to be similar for the other two items in the inventory, the dissolved organic material in the ocean and atmospheric carbon dioxide.

The question of the constancy of the cosmic radiation intensity is much more difficult to answer. One feels that it is not unlikely that the intensity has remained constant in the sense we demand; namely, variations in the average intensity over periods commensurate with the lifetime of radiocarbon, since it appears to be a phenomenon originating in the cosmos and therefore probably tied to a time scale similar to that controlling the intensity of solar radiation. However, it is not obvious a priori that this is true, and we must admit the possibility of variations having occurred. About the only sources of information on this point discovered so far have been the agreement between the specific activity of the present-day inventory and the observed present rate of production and observation that ancient materials of historically known age appear to

48. H. C. Urey, *Science*, **108**, 489 (1948); J. M. McCrea, *J. Chem. Phys.*, **18**, 849 (1950); S. Epstein, R. Buchsbaum, H. A. Lowenstam, and H. C. Urey, "The Carbonate-Water Isotopic Temperature Scale," *Bull. Geological Society of America*, **62**, 417 (1951); H. C. Urey, H. A. Lowenstam, S. Epstein, and C. R. McKinney, "Measurement of Paleotemperatures and Temperatures of the Upper Cretaceous of England, Denmark and the Southeastern United States," *Bull. Geological Society of America*, **62**, 399 (1951).

exhibit the radiocarbon content calculated on the assumption that
their original assay was identical with that of the modern reservoir.
We have seen how uncertain the experimental information on the
present rate of production is and are therefore forced to conclude
that agreement between this rate and the radioactivity of modern
material, which of course reflects the production rate as of some
8000 years ago—since the carbon atoms now found in modern wood,
for example, are 8000 years old on an average—is not a very firm
proof of the constancy and intensity of the cosmic radiation. It does,
however, agree with this postulate. The rather satisfactory agree-
ment between the predicted and observed radiocarbon contents of
organic materials of historically known age (Fig. 1) is somewhat
more reassuring. Taking the oldest materials with an age of some
4000 years, we observe their radiocarbon content, which was of
course due to an average production some 8000 years previous to
their existence, or some 12,000 years before the present, appears
within the experimental error to have been the same as at present.
This of course assumes that the size of the reservoir has not changed
simultaneously and in a compensating manner. However, for the
reasons given above we do not think that a significant factor of this
sort is very likely. Considering the matter empirically, we are ap-
parently justified in saying that, whatever the reasons, the specific
activity of living matter has not changed significantly in historic
times, and the problem resolves itself into consideration of possible
variations restricted to the prehistoric period encompassed by the
radiocarbon dating method.

HALF-LIFE OF RADIOCARBON

T HE half-life of radiocarbon has been measured several times. Table 4 gives the results obtained, together with the method of measurement. It is clear at a glance that the early measurements in which the amount of radiocarbon in the sample being measured was based on estimated bombardment yield gave high values. The later measurements based on mass spectrometric assays divide into three groups, according to the method of measurement: (a) counting of solid barium carbonate with thin window counters; (b) gas counting with the carbon disulfide–carbon dioxide mixture described by Miller and Brown;[1] and (c) gas counting with CO_2 either as a small additive to the standard argon–alcohol counter gas or as CO_2–methane mixture in the proportional counter. Miller et al.[2] have given evidence that the latter group is more nearly correct. It seems on first principles that the point of 100 per cent efficiency for ionizing radiations is most definitely settled in the case of standard argon–alcohol gas mixtures and probably in the case of the proportional counting technique. The first group, using the solid barium carbonate technique, seems to be subject to more errors in that more serious corrections for scattering and absorption are involved. The second group presents answers which are not clear in their significance, and the discussion of Miller et al.[3] casts considerable doubt on the validity of the results obtained by this technique. Therefore, in seeking the most probable value for the half-life of radiocarbon, we select the three values determined by the gas-counting technique with ordinary gas mixtures. They are 5580 ± 45;[4] $5589 \pm$

1. W. W. Miller, *Science*, 105, 123 (1947); S. C. Brown and W. W. Miller, *Rev. Sci. Inst.*, 18, 496 (1947).

2. W. W. Miller, R. Ballentine, W. Bernstein, L. Friedman, A. O. Nier, and R. D. Evans, *Phys. Rev.*, 77, 714 (1950).

3. *Ibid.*

4. A. G. Engelkemeir, W. H. Hamill, M. G. Inghram, and W. F. Libby, *Phys. Rev.*, 75, 1825 (1949); A. G. Engelkemeir and W. F. Libby, *Rev. Sci. Inst.*, 21, 550 (1950).

TABLE 4

SUMMARY OF THE PREVIOUSLY PUBLISHED VALUES
FOR THE HALF-LIFE OF RADIOCARBON

Half-Life (Years)	Method for Isotopic Composition of Sample	Method for Radioactivity of Sample	Reference*
$10^2 - 10^4$	Estimated bombardment yield	Solid carbonate counting: $CaCO_3$ in screen-wall counter	[1]
$26,000 \pm 13,000$	Estimated bombardment yield	Gas counting: CO_2 in counter	[2]
$21,000 \pm 4000$	Estimated bombardment yield	a) Solid sample counting: sample with thin window counter b) Gas counting: CO_2 in counter	[3]
4700 ± 470	Mass spectrometer (1.71 per cent)	Solid carbonate counting: $BaCO_3$ with thin window counter	[4]
5300 ± 800	Mass spectrometer (3.23 and 3.35 per cent)	Solid carbonate counting: $BaCO_3$ in low absorption counter	[5]
5100 ± 200	Mass spectrometer (3.23 and 3.35 per cent)	Solid carbonate counting: $BaCO_3$ in low absorption counter	[6]
7200 ± 500	Mass spectrometer	Solid carbonate counting: $BaCO_3$ with thin window counter	[7]
6400 ± 200 or 6100 ± 200	Mass spectrometer	Gas counting (Miller technique)	[8], [9], [10], [11], [12]
5580 ± 45	Mass spectrometer	Gas counting; small amount of CO_2 in argon-alcohol gas	[13], [14]
5589 ± 75	Mass spectrometer	Gas counting; small amount of CO_2 in argon-alcohol gas	[15]
5513 ± 165	Mass spectrometer	Proportional counting of methane-CO_2 mixture	[16]
6360 ± 200	Mass spectrometer	Gas counting (Miller technique)	[8], [9], [16]
$5360 \pm (200)$†	Mass spectrometer	Gas counting (Miller technique)	[8], [9], [17]

* [1] S. Ruben and M. D. Kamen, *Phys. Rev.*, **59**, 349 (1941); [2] M. D. Kamen, *Manhattan Project Literature*, A-316; [3] A. S. Langsdorf, Jr., and R. L. Purbrick, *Manhattan Project Literature*, CP-G-3272; [4] A. V. Reid, J. R. Dunning, S. Weinhouse, and A. V. Grosse, *Phys. Rev.*, **70**, 431 (1946); [5] L. D. Norris and M. G. Inghram, *Phys. Rev.*, **70**, 772 (1946); [6] L. D. Norris and M. G. Inghram, *Phys. Rev.*, **73**, 350 (1948); [7] L. Yaffe and Jean Grunlund, *Phys. Rev.*, **74**, 696 (1948); [8] W. W. Miller, *Science*, **105**, 123 (1947); [9] S. C. Brown and W. W. Miller, *Rev. Sci. Inst.*, **18**, 496 (1947); [10] R. C. Hawkings, R. F. Hunter, W. B. Mann, and W. H. Stevens, *Phys. Rev.*, **74**, 696 (1948); [11] R. C. Hawkings, R. F. Hunter, W. B. Mann, and W. H. Stevens, *Can. J. Research*, **B,27**, 545 (1949); [12] R. C. Hawkings, R. F. Hunter, and W. B. Mann, *Can. J. Research*, **B,27**, 555 (1949); [13] A. G. Engelkemeir, W. H. Hamill, M. G. Inghram, and W. F. Libby, *Phys. Rev.*, **75**, 1825 (1949); [14] A. G. Engelkemeir and W. F. Libby, *Rev. Sci. Inst.*, **21**, 550 (1950); [15] W. M. Jones, *Phys. Rev.*, **76**, 885 (1949); [16] W. W. Miller, R. Ballentine, W. Bernstein, L. Friedman, A. O. Nier, and R. D. Evans, *Phys. Rev.*, **77**, 714 (1950); [17] G. G. Manov and L. F. Curtis, *Abstracts*, *118th Meeting, Am. Chem. Soc., Chicago, Sept., 1950*, p. 5p.

† The error quoted here is twice that listed in the reference and results from discussion at the meeting at which the paper was presented.

75;[5] and 5513 ± 165;[6] for a weighted average of 5568 ± 30, where the weighting was taken according to the inverse square root of the errors quoted.

In order to exhibit evidence as to the reliability of the half-life we choose, we shall discuss in a little detail the methods used in our laboratory[7] to obtain the value 5580 ± 45. These of course are very similar to the method used by Jones[8] at Los Alamos also. The first point is the evidence for the ability of the standard argon–alcohol-filled Geiger counter to record any ionization event occurring in the gas phase except for the small volumes near the end where the electrical field is reduced; in other words, the evidence for 100 per cent efficiency as one moves from the wire to the very wall of the counter. The proof is not completely rigorous, but the evidence strongly favors this conclusion. In the first place, it has been known since the discovery of Geiger counters that a counter can be made to record photoelectrons emitted from the wall if the wall is made of the proper materials. Photoelectrons cannot well have over 2 or 3 volts of kinetic energy and therefore have an extremely small range of their own and no ability to ionize the gas molecules. We therefore conclude that single electrons introduced right at the wall are recorded with a not negligible efficiency by a good Geiger counter. Further evidence on this point is that counters made with appropriate materials such as cesium-coated walls must be cooled to avoid an extraordinarily high background which is presumably due to the emission of thermionic electrons from the wall. These electrons of course have even lower energies than the photoelectrons, ranging around 0.03 ev, so again we see that electrons introduced at the very wall with energies below ionization energies can be recorded in these instruments. Neither of these arguments shows that the instrument records in the low-energy range in the wall region with 100 per cent efficiency. It does show, however, that the efficiency is not zero for even the lowest energies.

The argument as to efficiency rests almost entirely on two lines

5. W. M. Jones, *Phys. Rev.*, **76**, 885 (1949).

6. W. W. Miller, R. Ballentine, W. Bernstein, L. Friedman, A. O. Nier, and R. D. Evans, *Phys. Rev.*, **77**, 714 (1950).

7. A. G. Engelkemeir *et al.*, *Phys. Rev.*, **75**, 1825 (1949); A. G. Engelkemeir and W. F. Libby, *Rev. Sci. Inst.*, **21**, 550 (1950).

8. *Phys. Rev.*, **76**, 885 (1949).

of evidence. The first is an experiment in which three counters are set in a line with their axes parallel and connected electrically so that, when the first and third counters fire simultaneously, observation is made as to whether the middle counter fires.[9] The simultaneous firing of the first and third counters is due to a penetrating radiation which passes through both instruments, presumably in a straight line, and therefore certainly passes through the middle counter. These observations show that the middle counter does fire. The middle counter then is displaced in a direction perpendicular to the line joining the first and third by a small amount, and the observation repeated. The displacement is continued until the very edge of the counter just is in line with the very edges of the first and third counters. It is then found that there is a very abrupt disappearance of sensitivity of the middle counter. Further evidence has been obtained in our own researches, as described later, in which we shield the counter measuring our samples from penetrating cosmic radiation by surrounding it with a single layer of counters in tangential contact. In a typical experiment we find that without the shielding counters connected our central working counter records a rate of some 120 counts per minute, whereas the rate is reduced to about 7 counts per minute by connecting the shielding counters. The residual 7 counts per minute may well be due to contamination in our central counter or to radiation coming in the ends where our shielding-counter array affords incomplete coverage. We thus conclude that at least 95 per cent and probably more nearly 100 per cent of the radiations passing through the counter bundle are recorded by the counter bundle and thereby written off the record. More to the point, however, is that experiments in which we have added a second layer of counters have not significantly reduced this background. This seems to have the interpretation that counters in tangential contact possess nearly a 100 per cent efficiency throughout their volume.

The second general line of evidence is the internal consistency obtained in the measurements on the half-life of radiocarbon by using counters of various diameters, as discussed later. If the basic assumption of limited efficiency were not true, it seems clear that the consistency would be reduced. The assumption therefore was made in

9. K. Greisen and N. Nereson, *Phys. Rev.*, **62**, 316 (1942).

these researches that a standard brass-wall Geiger counter filled with argon and ethyl alcohol at typical pressures of 7 cm. of mercury pressure of argon, and 1.2 cm. of mercury pressure of ethyl alcohol would record any ionizing event that involved so much as a single ion pair in any part of the volume between the counter wire and the very surface of the brass wall.

With this assumption the task of measuring the half-life of radiocarbon is reduced to three parts. The first is to determine the end loss, that is, the effective volume at the ends of the counter where the field is so weak that radiations appearing in the gas are not recorded. The second task is to make correction for the case in which a radioactive carbon atom expels its beta ray in the direction of the wall but lies so close to the wall that it does not succeed in ionizing the counter gas before entering the wall, and then the ray enters the wall and remains in it without ejecting secondary ions from the wall. This is called the wall correction. The third task is of course to measure out a known number of radiocarbon atoms into the counter and to observe the disintegration rate. Correcting for the end and wall losses, one then can calculate the absolute disintegration rate and half-life.

The method used to obtain the end-loss correction is the obvious one of taking a set of counters of a given diameter but of different lengths, filling them with a given pressure of radioactive carbon dioxide, and observing the count rates. One then takes the difference between the rates observed for counters of two different lengths as the rate one would observe for a counter of length equal to the difference in length but with no end loss and from this calculates the end loss observed in the two counters. Using this technique and counters with flat ends made of lucite plastic plugs, so the construction of duplicate counters would be simple and the observed end corrections generally applicable, we have found that the end corrections are primarily dependent on the length-to-diameter ratio. For example, a counter 12 inches long and 2 inches in diameter has nearly the same percentage end loss as one 6 inches long and 1 inch in diameter. In addition, the correction is extraordinarily independent of energy for beta emitters up to 0.74 mev upper energy limit. Three substances were used for this study: A^{37}, which emits 2.8 kev Auger electrons; C^{14} with a beta spectrum with a 154 kev upper limit;

and Kr^{85} with a beta spectrum of 740 kev upper limit. The results are shown in Figure 5. The correction can be expressed empirically by the equation

$$y = K/(L/D - K),\qquad(23)$$

where K has a value of 0.275 ± 0.1.[10]

The second correction on the count arises from the possibility that a radioactive carbon dioxide molecule that happens to disintegrate near the wall and to fire its disintegration electron in the direction of the wall will either fail to produce a free electron in the
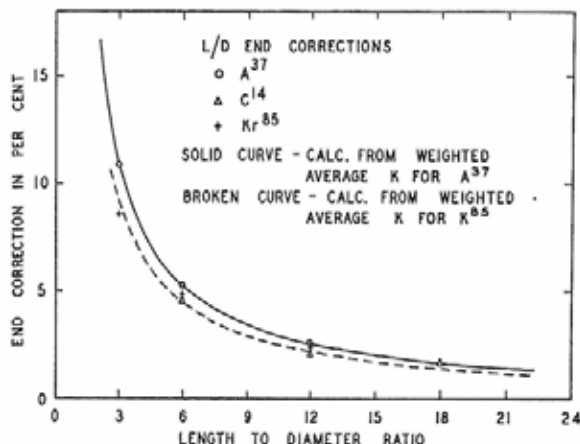

FIG. 5.—End-loss corrections for flat-ended gas counters

gas itself or fail to dislodge one or more from the wall. At first glance this seems unlikely to be a serious effect, and it is indeed a small effect, but one large enough to require a correction. It is clear that the effect is proportional to the surface-to-volume ratio or should vary inversely as the diameter of the counter. One therefore can compare the observed count rates as a function of the diameter of the counter after the rates have been corrected for the end loss and empirically determine the magnitude of the effect. Measurements with Kr^{85} have given[11] a correction of 6.9 ± 1.1 per cent for 1-inch

10. Engelkemeir and Libby, Rev. Sci. Inst., 21, 550 (1950).   11. Ibid.

diameters, 4.6 ± 0.7 per cent for 1.5-inch diameters, and 3.4 ± 0.5 per cent for 2-inch diameter counters. It is also clear that the effect should increase with the energy of the radiation emitted, since the number of ions formed per unit length of path decreases as the energy increases. In keeping with this, no wall loss was found for the very soft 2.8-kev radiation from A^{37}. We therefore can expect that for radiocarbon with energy intermediate between these two substances the correction should be of the order of 2–4 per cent depending on the diameter of the counter. The C^{14} data themselves indicate this to be so: for 1-inch diameter counters 3.5 ± 1.2 per cent; for 1.5-inch diameters 2.3 ± 0.8 per cent; and for 2-inch diameters 1.8 ± 0.6 per cent are the values found.

TABLE 5

CALCULATED WALL CORRECTIONS

	WALL LOSS CORRECTION	
ISOTOPE	For Diameter = 1 Inch	For Diameter = 2 Inches
A^{37}	0	0
C^{14}	$3.1\% \pm 0.8$	$1.5\% \pm 0.4$
Kr^{85}	7.1 ± 1.4	3.5 ± 0.7

It is possible to estimate the magnitude of this correction semi-empirically by considering the data for the density of ionization produced by beta rays of various energies.[12] Using these data and averaging over the known beta spectrum of radiocarbon, one calculates the mean thickness of the gas near the wall which fails to count. This is a fictitious physical concept, of course, since part of the gas even next to the wall will fire its beta rays into the main body of the counter and certainly record a count. The second component of the semi-empirical calculation is the effect of splashing-out of secondary electrons by the electron incident on the wall. Data for this phenomenon are known for brass surfaces,[13] since they are of great importance in the operation of the standard photomultiplier tube. The results of this calculation are given in Table 5.

It is interesting to see how well the semi-empirically calculated corrections agree with those observed experimentally. The first half-

12. *Ibid.*   13. *Ibid.*

life published on the basis of the data obtained was 5720 ± 47 years,[14] in which the wall correction had not been made. The reality of this correction was revealed by later research,[15] and a correction of some 2.5 per cent was made to lower the value to 5580 ± 45 years.

The radioactive carbon dioxide used in the determination was obtained from the Isotopes Division of the Atomic Energy Commission, and four master-samples of carbon dioxide of different isotopic composition were prepared. These were carefully analyzed for the C^{14} contents on the mass spectrograph. The four masters were then diluted by various factors to provide seven working samples. Since the original compositions were in the range of from 1 to 6 per cent, dilution factors of several thousand fold were necessary to lower the specific radioactivity of the carbon dioxide to a measurable value. The dilution was accomplished by allowing part of the master-sample to expand from its storage bulb into a McLeod gauge. A 0.3281-cc. bulb had been sealed to the capillary of the McLeod, and the radioactive CO_2 was forced into this bulb by raising the mercury. The vacuum line was thoroughly evacuated and the pressure of CO_2 in the bulb measured. Inert CO_2 was then used to flush the vacuum line, and a pressure of inert CO_2 was allowed to build up so that, as the mercury was lowered, inert CO_2 was forced through the mercury into the McLeod to a pressure of 40 or 50 cm. of mercury. The vacuum line then was evacuated, and the total pressure in the 503.1-cc. McLeod volume was measured. After allowing to stand to mix, the diluted sample was stored in a bulb by condensation into a trap attached to the bulb using liquid nitrogen. The temperature of the room was recorded throughout the process, and it was considered that no significant error was introduced in the dilution step.

The diluted working sample was introduced into the counter in a number of different ways. The most satisfactory of the procedures was to introduce a known pressure into a rather large bulb to which a known pressure of argon was then added. After thorough mixing, this gas mixture was then introduced into the counter, to which some 1.2 cm. of ethanol vapor had previously been added. The count rate then was determined to a fraction of a per cent error, external standards being used to check that the counter was operating with its usual efficiency and corrections being made for loss due to a count

14. Engelkemeir *et al.*, *Phys. Rev.*, **75**, 1825 (1949).
15. Engelkemeir and Libby, *Rev. Sci. Inst.*, **21**, 550 (1950).

occurring while the counter was busy with the preceding count (this correction in general was quite small). Somewhat over a hundred measurements of this sort were made in the course of a two-year period, resulting in the value 5580 ± 45 mean solar years.

The agreement between our determination and those of Jones[16] and Miller et al.[17] is gratifying and leads us to believe that the weighted mean of these three determinations, 5568 ± 30, is probably accurate to within 50 years and almost certainly to within 100 years. The importance of an accurate value for the half-life to the radiocarbon dating technique is obvious, it being true that a 1 per cent error in the half-life appears immediately as a 1 per cent error in the absolute age of any given sample. For example, a 10,000-year-old sample could never be measured to better than 100 years under such conditions. It is also equally clear that a chronology could be developed in which the radiocarbon half-life was defined to be 5568, and questions of simultaneity would not be incorrect even though the half-life were indeed quite erroneous.

A further point in favor of a half-life somewhere between 5000 and 6000 years is the result obtained with ancient samples of historically known age (Fig. 1). One cannot use these data to decide definitely between the various determinations of the half-life given in the latter part of Table 4. It is conceivable that a careful research devoted entirely to the most careful measurement of the specific activity of the historically dated samples would give data of such accuracy as to distinguish between these values. Our own experience has been that the fit of the data we obtained when we thought the life to be 5720[18] was not any worse than the one obtained at present with the new life 2.5 per cent lower.[19]

It is to be hoped that further measurements on the half-life of radiocarbon will be made, preferably by entirely different techniques, since considerable agreement by the present technique we favor has already been obtained. This is important not only for the radiocarbon dating technique but for many problems in nuclear physics and radiochemistry, where methods of measuring absolute disintegration rates rather than relative rates are of vital importance.

16. *Phys. Rev.*, **76**, 885 (1949).
17. *Phys. Rev.*, **77**, 714 (1950).
18. W. F. Libby, E. C. Anderson, and J. R. Arnold, *Science*, **109**, 227 (1949).
19. J. R. Arnold and W. F. Libby, *Science*, **110**, 678 (1949).

CHAPTER IV

PREPARATION OF THE SAMPLE
FOR MEASUREMENT

ONE of the principal requirements of the radiocarbon dating technique is that the material measured contain the original carbon atoms present in the sample at the time it died or was deposited from the exchange reservoir. This means, of course, that the chemical form in which the carbon is bonded may have real bearing on the validity of the result obtained. Chemical experience clearly indicates that the covalently bonded molecules which constitute the organic world are less susceptible of replacement of the carbon atoms by direct exchange than are the inorganic molecules such as the carbonates. One therefore does not fear particularly the possibility that the carbon in carbonate, bicarbonate, or carbon dioxide will exchange with the carbon atoms in organic structures such as wood or flesh or cloth or charcoal. One does worry considerably, however, about the possibility that underground waters washing over shell would cause an exchange.

On the other hand, putrefaction and chemical alteration are possible with organic systems, and one has to worry about whether a given sample has been so altered. Of course it is obvious that in a rich find where materials of various chemical forms exist one has an excellent opportunity to test whether alteration has occurred by observing whether the radiocarbon ages obtained from the various chemicals present in the site agree. It is clear that, if agreement is found, alteration has not occurred, for it is extremely unlikely that shell and wood would be altered to the same degree, the chemical reactions involved being so different in character.

If one examines the nature of putrefaction reactions, one observes that, by and large, they involve a degradation of molecular weights. That is, large molecular structures are reduced in size, and certain structures are so large as to not be involved. Among these latter, charcoal is most important. One does not anticipate that charcoal will be altered by any sort of attack of organic systems. About all

that can conceivably happen is that it would be burned to gaseous carbon monoxide and carbon dioxide and so escape, but it seems clear that, if one does find carbonized material and carefully removes other material from it, alteration in the residual carbon is extremely unlikely from a chemical and biochemical point of view. Materials such as wood, grass, and frozen flesh are most debatable. However, wood consists largely of very large cellulose molecules, and, if one were to take care to separate the smaller molecules from wood, it seems very likely that alteration would be definitely excluded. Likewise similar processing of fibrous materials such as grass would be a good precaution.

In the case of shell material there is no chemical guaranty that the material has not been altered. It does appear, however, from results of ours on radiocarbon content in ancient shells found together with organic matter, and results of Professor Urey on the O^{18} content of the oxygen in the carbonated shells,[1] that shells which appear well preserved physically have a good chance of being authentic. More work is needed on this point, however, and at the present time it is difficult to say of any given case whether shells will give reliable results. We look for evidences of alteration such as a powdery appearance or chalky consistency.

Our experience on woods and grasses and even peat material has been quite favorable in that we have very few evidences of alteration and some rather striking examples of organic matter such as twigs and leaves which have lain in the ground for over 10,000 years and been bathed by the underground waters, which apparently give reliable results in that they check with well-preserved pieces of wood found with them and also with the general stratigraphy and chronology built up by the whole set of dates. We are therefore inclined to recommend the materials normally found in about the following order:

1. Charcoal or charred organic material such as heavily burned bone
2. Well-preserved wood
3. Grasses, cloth, and peat
4. Well-preserved antler and similar hairy structures
5. Well-preserved shell

1. H. C. Urey, *Science*, **108**, 489 (1948); J. M. McCrea, *J. Chem. Phys.*, **18**, 849 (1950); S. Epstein *et al.*, *Bull. Geological Society of America*, **62**, 417 (1951); H. C. Urey *et al.*, *Bull. Geological Society of America*, **62**, 399 (1951).

We have had no experience with bone as such and believe that it is a very poor prospect for two reasons: the carbon content of bone is extremely low, being largely in inorganic form in a very porous structure; and it is extremely likely to have suffered alteration. It is barely conceivable that measurements on bone might reveal that some reliability could be obtained. However, because the quantities required are so large, and there usually are other acceptable materials associated with a find of bone, it does not seem to be an urgent matter to pursue.

It is to be realized of course that our experiences with various types of samples must be taken in the light of the actual chemical processing we have used in the preparation of the samples for measurement. A description of this process follows.[2]

1. The first step in each instance is carefully to examine the sample and to separate out as well as possible by physical methods the material desired. For example, a piece of wood will usually be dirty and is cleaned physically as well as possible, and perhaps the surface removed by sawing or cutting so the danger of contamination is reduced. In the case of finely divided charcoal from camp fires, it is necessary carefully to remove intrusive rootlets and other matter which might introduce modern carbon into the material. It is hoped that eventually physical separation methods may be developed to the point where rather low carbon-containing soils can be examined.

2. The physically cleaned sample is then tested with hydrochloric acid solution for calcium carbonate which may have been deposited in the cracks and internal fissures by underground waters. If any effervescence of carbon dioxide is observed on this test, the sample then is treated for several hours with about $1 \, N$ hydrochloric acid until effervescence ceases, after which it is carefully washed and dried in a laboratory oven. This is a particularly important part of the processing and should be conducted with real care. In the case of materials containing considerable extraneous matter other than the desired organic substances, the acid treatment frequently works to purify the sample. For example, burned bone is treated with $1-3 \, N$ hydrochloric acid for 24 or 48 hours until the bone structure is dissolved, and the residual carbon, which of course does not dissolve in acid, is then removed by filtration. In one or two cases colloidal

2. E. C. Anderson, J. R. Arnold, and W. F. Libby, *Rev. Sci. Inst.*, **22**, 225 (1951).

organic substances formed as a result of treatment of charred bone, and this material was separated by dialysis of the acid solution which concentrated the colloidal organic material and allowed separation and drying and use of this fraction.

This acid treatment probably guarantees to a considerable extent against the incorporation of putrefaction products in that it would heavily weigh against small organic molecules in that they would be dissolved out as gases or resist the filtration or dialysis steps.

3. This step consists of the controlled combustion of the sample, if it is organic in character, to form carbon dioxide, or the addition of hydrochloric acid to evolve carbon dioxide if the sample is shell.
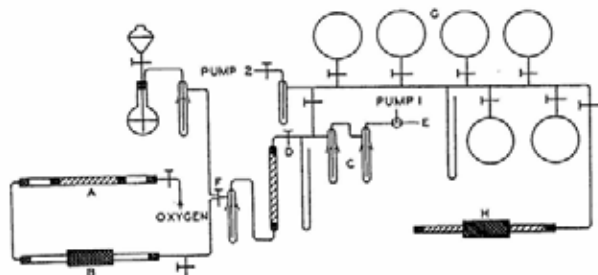
Fig. 6.—Combustion and reduction line assembly

Figure 6 displays the apparatus in which the present step and several of the subsequent steps in the procedure are conducted. The combustion of the sample is carried out in the Vycor tube (A). Oxygen from a standard commercial cylinder is passed over the sample at a pressure slightly below 1 atmosphere, and the combustion gases are carried through hot copper oxide heated in a Vycor tube by a furnace (B) to complete the oxidation by converting carbon monoxide and possibly other gases to carbon dioxide. The gas stream then is led through a dry-ice trap and Drierite tube to remove residual water. Following this the gas is led through a controlling stopcock (D) into two successive liquid nitrogen traps (C), in which the carbon dioxide is condensed. The combustion is begun by setting the flow rate with the control stopcock (D) while air is

passing through the system such that the pressure in the trap system is about 10 cm. of mercury with the high vacuum exhaust pump (1) full on. Oxygen then is admitted and the flow adjusted through a needle valve to maintain the pressure in the combustion system at slightly below 1 atmosphere. The oxidation is begun by igniting the sample with a torch applied externally. Some of the early combustions were conducted in an apparatus different from the Vycor tube (A),[3] in which the sample was placed on the top of a vertically traveling screw adjustable in position and the fire started on the top end of the sample and the screw rotated to bring fresh sample into the flame zone as combustion proceeded. The whole assembly was inclosed in a glass bulb to which the product oxygen was fed and from which the product gases were removed continuously. The oxygen was introduced with little jets near the flame zone. This apparatus is a slight modification of a standard apparatus used for ashing samples of organic matter for the detection of traces of iodine.[4] The important feature of the device is that only the portion of the sample actually burning is heated appreciably and that the hot gases do not pass over the unburned portions of the sample. It was particularly valuable in the combustion of flesh and similar materials. However, the bulk of the samples are handled in the Vycor tube (A).

The amount of material selected for combustion, or acidification in the case of shell, is determined by the carbon content of the material. It must be such as to yield between 10 and 12 grams of elementary carbon, which is equivalent to some 24 liters of carbon dioxide gas. In the case of pure charcoal, of course, 10 or 12 grams would be sufficient. Actually the charcoal is rarely this pure; something like a half-ounce or more is usually taken. In the case of pure shell in which the acidification procedure is used, some 100 grams is the minimum. As a rough rule we suggest that in the case of materials of high carbon content at least 1 ounce per sample (28 grams) be submitted and preferably several ounces. If the carbon content is doubtful and no accurate analysis is available, at least a pound or more should be collected.

4. The material condensed in the trap system at the conclusion

3. E. C. Anderson, Ph.D. thesis, University of Chicago (1949).

4. G. M. Karns, *Ind. Eng. Chem., Anal. Ed.*, 4, 299 (1932); H. van Kolnitz and R. E. Remington, *Ind. Eng. Chem., Anal. Ed.*, 5, 38 (1933); F. X. Gassner, *Ind. Eng. Chem., Anal. Ed.*, 12, 120 (1940).

of a run consists not only of carbon dioxide but also of the oxides of nitrogen, sulfur, products of incomplete combustion, and any radon that may have been present in the sample. Radon is a noble gas of rather high boiling point which is a radioactive disintegration product of uranium, the ubiquitous parent of most of the radio-activity in soils and rocks. This might well follow through the sub-sequent steps of the procedure and lead to a falsely radioactive final product if chemical purification were not used. The chemical purifi-cation therefore accomplishes the removal of the bulk of contamina-tion consisting of oxides of nitrogen and sulfur and the trace radio-chemical contamination by radon. The purification is accomplished in the following manner: A 1-liter flask containing 500 cc. of 6 N NH_4OH is attached to the stopcock at point E. After the traps have been pumped down at liquid nitrogen temperature, the Dewars are removed and the carbon dioxide is evolved, using a flame to speed up the process. When the pressure reaches 60 cm. of mercury, the trap system is connected to the flask. A rapid absorption of the gas takes place. The evolution of the gas is continued, and the flask is shaken to insure absorption until the traps are empty. The pressure at this point should be about 70 cm. of mercury, and the solution should be quite hot. A second solution consisting of 180 grams of $CaCl_2 \cdot 2H_2O$ in 180 cc. of water is heated near to boiling. The flask is removed from the line, and the hot calcium chloride solution is added slowly from a separatory funnel. Rapid precipitation of cal-cium carbonate takes place. It is essential that this step be carried out in such a way that the final temperature of the combined solu-tion be higher than 70° C. Otherwise a flocculent, poorly filterable precipitate results. The precipitate is filtered and washed free of ammonia, the washings being made with distilled water. It is then removed from the Buchner funnel used for the filtration and washed into a clean 1-liter flask. At this point all the oxides have been left behind in the form of soluble salts, and the radon has been lost either by gaseous evolution or in the aqueous solution.

Carbon dioxide now is removed from the precipitate, using the same system employed in the combustion. A separatory funnel con-taining 250 cc. of concentrated hydrochloric acid is placed in the flask. A second lead is attached to the drying and collection system at F. It is important that the tube from the separatory funnel reach nearly to the bottom of the flask to prevent the accumulation of acid

and uneven reaction. In the beginning of this operation the gas-flow rate is set as in the combustion operation. The stopcock leading to the flask is opened, and acid is added at a rate sufficient to keep the pressure in the flask slightly below 1 atmosphere.

The gas is dried carefully and collected in the traps (C) and then allowed to evaporate into a system of 5-liter bulbs (G), where it is stored ready for the reduction step.

5. Reduction is carried out in an iron tube (H), which is filled with about 85 grams of magnesium turnings together with 1 gram of cadmium powder or turnings as a catalyst. An 8-inch movable electric furnace capable of reaching 1000° C. is placed around the tube. The ends of the tube are sealed with rubber stoppers and deKhotinsky wax, and the reduction system evacuated and tested for freedom from leaks.

Carbon dioxide is now admitted to the tube up to a pressure approaching 1 atmosphere and external heat applied with a torch at one end of the magnesium filling. When a temperature near the melting point of magnesium (660° C.) is reached, the reaction begins rather violently and produces sufficient heat to maintain itself if gas is admitted at a moderate rate from the bulbs. The chemical reaction involved is

$$2 \text{ Mg} + CO_2 = 2 \text{ MgO} + C . \qquad (24)$$

Since the reaction involves no gaseous products, no circulation is required, and care must be taken because the heat evolved is so large that, unless the inflow of carbon dioxide is controlled, the reaction will melt the iron tube. It is a practice to run in gas from one bulb in a controlled fashion. The carbon dioxide in the storage bulbs is introduced into the reduction chamber one bulb at a time until pressure is reduced to about 20 cm. of mercury in each. In this way five or six bulbs of gas can be reacted smoothly before the other end of the magnesium filling is reached. To complete the reduction, the remaining gas is condensed in the trap (J) and may either be expanded into a single bulb or reacted directly. It is necessary to apply external heat using the furnace to start the fire again after this collection of the residual carbon dioxide in the various bulbs. When the reaction is complete, no more than 1 or 2 cm. of mercury pressure should remain in the manifold system, and the bulbs should be com-

pletely empty. The reduction tube then is allowed to cool, and the carbon, magnesium oxide, and unreacted magnesium are removed from the tube, using an iron rod as a ram.

6. The material taken from the reduction tube is placed in a clean 3-liter beaker. Sufficient distilled water is added to dampen, and the mixture is allowed to stand 15 minutes until the hydrocarbons which are formed in small yield, presumably by the impurities in the magnesium metal, are decomposed and evolved. Concentrated hydrochloric acid then is added as rapidly as possible without bubbling over. The proper rate for this is about 25 cc. every 5 minutes. After about 100 cc. have been added in the first 20 minutes, an additional 700 cc. is added rapidly. It is well to have a spare 3-liter beaker handy in case of overflow at this point.

The acid solution is allowed to stand overnight in a hood so the fumes evolved are exhausted from the room. It is then placed on a hot plate with an asbestos pad over the plate at "high" heat. After the acid is brought to a boil, about 1 liter of distilled water is added, and the solution brought to a boil and allowed to boil for about 15 minutes. It then is filtered by the insertion of a sintered glass "filter stick" made by taking a coarse sintered glass suction funnel and cutting off the rim normally used to hold the solution in the funnel down to the level of the sintered glass plate, sealing a piece of glass tubing about 6 inches long on the end of the funnel, and connecting the rubber hose to a good aspirator. This device has the advantage of removing the obnoxious acid solution without mechanical lifting and dispersing it in the sewer system immediately after dilution. It also has the merit that no new glass apparatus has to be brought into the process with its consequent danger of introducing contamination.

After sucking the black carbon residue dry, 1.5–2 liters of distilled water are added and the system again brought to a boil and allowed to boil about 15 minutes. The filtration step is then repeated, and distilled water added again and brought to a boil for the same length of time. This washing step is then repeated a third time, at which point the wet carbon is transferred to a clean 400-cc. beaker quantitatively by washing out with distilled water and finally drying roughly by the use of the filter stick. It then is placed on the hot plate on "low" heat and left there for about 4 hours, until moisture just ceases to condense on a cold watch glass.

After the drying operation the dry carbon is replaced in the original beaker, and about half a liter of concentrated hydrochloric acid is added, and the mixture allowed to stand about 2 hours. It then is brought to a boil, and the process of filtering and washing described above is repeated. After this the drying operation described above is performed again.

The sample then is placed in a clean, weighed, dry bottle with a screw cap, carefully labeled, and weighed.

7. The final step in the preparation of the sample for measurement consists of grinding in an agate mortar and pestle to a consistency approaching that of powdered sugar, returning the sample to the bottle and mixing it by shaking, after which about 0.5 gram are removed, carefully weighed, and the percentage ash in the sample determined by combustion. Care is taken during this operation to expose the sample to the air for the minimum length of time, to keep cigarette ashes and other room dust out of it, and not to breathe into it excessively. The percentage ash is necessary as a correction on the count rate observed, for, of course, the ash reduces the observed specific radioactivity.

A number of precautions are taken throughout this process. Probably the most important of these is to purchase all the chemicals in large quantities so that a single successful run with coal in which no radiocarbon is obtained will validate the purity of considerable quantities of chemicals. One can then feel free to seek sources other than the chemicals for any contamination that may appear in the sample. We have been singularly fortunate in that to date we have observed no chemical contamination of any sort. We are careful to use the same glassware that has been used in previous runs with coal samples and to be extremely cautious that the carbon is exposed to the air a minimum time while cool and dry. In fact, care is taken to bottle the carbon or to cover it with acid solution quickly after the drying period. The carbon produced in this reaction possesses an extremely high specific surface area so that its power to absorb vapors is large. Rough measurements have indicated that it possesses something over 200 square meters of surface per gram on the average. This means that any considerable exposure to room air is likely to lead to radon absorption and contamination. Of course it

is almost unnecessary to say that the laboratory in which the chemical processing and the sample mounting to be described later are performed should not contain any radioactivity that is not tightly sealed and protected from access to the air. It is good practice to keep the laboratory clean of all radioactivities.

There is a considerable mystery remaining about the origin of the ash in the sample. We ordinarily find it to be less than 10 per cent, but occasionally for some unknown reason it will approach 20 per cent. We do find that unless the material is dried as described above and then re-extracted with acid, the ash usually is above 20 per cent. It is further found that a recalcitrant sample with a high ash can be successfully reduced in ash content by heating to a dull red heat in a quartz or heavy Pyrex test tube which is closed from the air with a loose glass-wool plug. The heat is continued for several hours, and acid extraction as described above is used afterward. This almost invariably reduces the ash below 10 per cent. A source of worry of some importance exists in the chemical composition of the impurities which constitute the ash. The corrections as ordinarily made assume that it is magnesium oxide—in other words, that it has the same chemical composition while in the sample as it does after ignition. Experience has shown that this method gives results which are acceptable in that the same value for the specific activity of a given original sample is obtained from two or more portions which have been burned, reduced, extracted, and measured and in which the final carbon samples obtained from the several portions have different ash contents. We would therefore suggest that the impurity is indeed in the form of magnesium oxide which is tightly covered with carbon and that the drying and heating operations described, which are observed to reduce the ash, essentially crack loose the carbon covering from the small magnesium oxide particles. It has been shown that the ash does indeed consist of magnesium oxide rather than of other materials.

A special equipment and chemicals list for the operations described in this chapter is given in Appendix A.

CHAPTER V

MEASUREMENT OF THE SAMPLE

THE problem of detection and measurement of weakly radioactive substances is an ancient one around which a considerable lore and artistry have been built. In the case of radiocarbon at the levels existing in nature one needs to use the most sensitive techniques known. On the other hand, it is essential that the procedure be as simple and as reliable as possible. There are two obvious ways in which to proceed with the problem. One is to measure the material in the gaseous state as either carbon dioxide or methane, in which the sample being measured constitutes part of the gas phase of the detection instrument. It would seem wisest to use a proportional type counter operating at as high a pressure of methane or carbon dioxide as feasible in which the pulses due to the radiocarbon beta radiation were segregated to a certain extent from pulses of different size due to extraneous effects such as cosmic radiation and wall contamination in the apparatus. This type of attack was not pursued in this research, for calculations indicated that the second obvious approach would be somewhat more sensitive and reliable, though it would require somewhat larger samples. This consists of measuring elementary carbon itself in the solid state.

The construction of the instrument must be such as to insure the maximum ratio of count rate due to the sample to count rate due to background, that is, the cosmic radiation and apparatus and laboratory contamination. In the first place, one immediately chooses a Geiger counter as the detection instrument, since it is the only instrument which will detect a single thermal energy electron with apparently 100 per cent efficiency. This establishes it as the most sensitive of all instruments for detection of ionization. Having selected a Geiger counter, which consists in essence of a cylinder with a wire down the axis, one seeks to mount the carbon sample in the position which will insure the maximum sample effect to background ratio. It is clear from the geometry of the Geiger counter that there is only

one place to do this, and that is on the wall. It is further clear that one must not interpose between the counter gas and the sample any more solid material than is necessary. Therefore, one builds the Geiger counter essentially with the elementary carbon as the wall of the counter. It is fortunate that elementary carbon is an electrical conductor.

The next problem one faces in instrument design in this problem is that of measuring the background without changing the counter gas and other critical characteristics of the instrument. In other words, one wants to change the wall of the Geiger counter from one material to another without changing the Geiger counter in essence. All these things are accomplished by the instrument known as the screen-wall counter,[1] an artist's sketch of which is shown in Figure 7.

The essential principle on which this instrument operates is that the most important part of the counting act takes place near the counter wire, and therefore the only essential requirement is that the field near the wire be undisturbed by changing the counter wall from the carbon sample to bare metal for the background measurement. This is accomplished by interposing gridwork about halfway between the counter wire and the sample cylinder which constitutes the counter wall. One then controls the potential on the screen wall. It then operates essentially as the wall of an ordinary Geiger counter with respect to the wire except that it is extremely porous to radiation. Radiations which miss the screen gridwork structure itself can be recorded, providing they enter the gas at all by the interposition of a small "drag-in" potential which serves to accelerate electrons toward the screen counter structure if they are formed in the space between the screen and sample cylinder. Conversely, if one wants to restrict the counter volume just to the screen structure, this can be done by using a "drag-out" potential. These potentials are small, of the order of 50–100 volts. Figure 8 shows the behavior of the count rate for a typical screen-wall counter of the dimensions and construction used in this research, as a function of the potential between the sample cylinder and the screen. We normally operate with 90 volts drag in potential in the radiocarbon dating work. It is obvious from Figure 8 that there is nothing critical about this number.

1. W. F. Libby, *Phys. Rev.*, **46**, 196 (1934); W. F. Libby and D. D. Lee, *Phys. Rev.*, **55**, 245 (1939).

KEY

1. Lucite tube
2. Screen grid
3. Carbon sample
4. Background
5. Lucite disk
6. Center wire
7. Sample cylinder
8. Center-wire lead
9. End-cap detail
10. Screen-grid lead
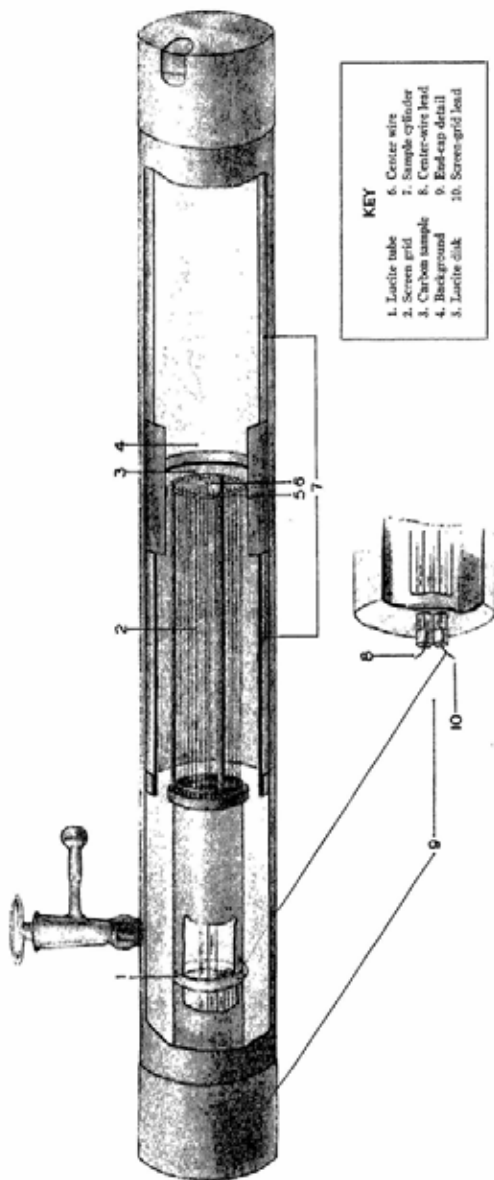
Fig. 7.—Screen-wall counter

In the instrument as described, one has a cylindrical vacuum-type space filled with counter gas, along the middle third of the length of which Geiger counter registration of ionizing events take place, and inside of which a sample cylinder two-thirds as long as the instrument itself is placed. One half of the sample cylinder has the sample mounted on it; in this case elementary carbon. With these dimensions
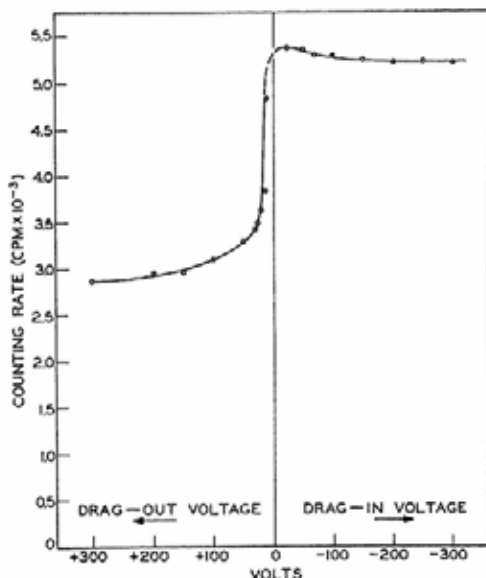
Fig. 8.—Variation of counter sensitivity with potential between screen and case

there are two positions, one in which the sample itself constitutes the wall of the counter, and the other in which the bare metal of the sample cylinder constitutes the wall of the counter. One changes from one position to the other simply by lifting the instrument in one's hands and gently shaking until the sample cylinder slides to the other end. It is purposely machined to have freedom of motion without having excessive radial play. The procedure of measurement

then consists simply in observing the rate in the two positions with appropriate frequency of alteration and recording the data.

The sensitivity of the instrument to radiocarbon radiation is best established by the use of a sample assayed in an absolute manner such as that described in chapter iii. A sample of radioactive carbon dioxide of accurately known specific activity used in the half-life determination[2] was taken, accurately diluted with ordinary carbon dioxide, and then reduced and converted to a standard carbon sample in the way described in the preceding chapter. This material then was mounted and the observed count rate taken under various conditions in order to determine the absolute efficiency of the instrument for radiocarbon radiation when observed from elementary carbon samples. Several such standard radiocarbon samples were devised, and tests were carried out in four different screen-wall counters. One of the tests was made by using a sample only 1 inch in length. The standard sample cylinder is 8 inches in length, so the 1-inch sample was placed in the eight different positions, numbering from the end farthest removed from the counter volume when the sample cylinder is in the "background" position. The reasons for undertaking this test were primarily to reveal the fraction of the radiation which entered the counting volume from the background position and the variation of sensitivity at the very end of the sample cylinder. The data are given in Table 6.

These data show that the efficiency rises rather rapidly as one moves in from the end of the sample, so that only the first 1 inch is appreciably lower in efficiency than the 6 inches of sample in the central portion. It is also clear from these data that some 3–4 per cent of the net sample count that would be observed, were not the background changed by virtue of the radioactivity of the sample, acts to increase the background. Therefore, in deducing the figure by which we are to multiply the observed difference between sample and background positions to obtain the absolute specific activity of the sample, we must take the efficiency calculated from the actual difference between background and sample averaged over the various positions. This is calculated to be 5.35 ± 0.10 per cent for these data. One gram of carbon mounted on the 1-inch-long section of the

2. A. G. Engelkemeir, W. H. Hamill, M. G. Inghram, and W. F. Libby, *Phys. Rev.*, 75, 1825 (1949).

sample cylinder had an absolute disintegration rate of 1860 disintegrations per minute.

Table 7 presents data in which a standard sample of the full 8 grams weight and mounted over the full 8 inches of length of the cylinder was placed in four different counters. The absolute efficiency calculated on the basis of the observed difference between sample

TABLE 6

EFFICIENCY OF SCREEN-WALL COUNTER ALONG ITS LENGTH
(Counter No. 6; standard 10 cm. A + 0.5 cm. C_2H_6)

Position	Background (cpm)	Sample (cpm)	Net Sample from Average Background Positions 1–5	Per Cent Absolute Efficiency	Increase in Background (Per Cent Net Sample Count)
1	147.4±1.3	241.7±1.6	95.0±1.8	5.11	....
2	146.4±1.6	257.1±1.6	110.4±1.8	5.94	....
3	145.8±1.7	253.5±1.5	106.8±1.8	5.74	....
4	149.2±1.9	255.9±1.5	109.2±1.8	5.88	....
5	144.9±1.5	252.5±1.5	105.8±1.8	5.69	....
6					
7	152.4±1.5	257.8±1.6	111.1±1.8	5.98	5.2
8	169.4±1.8	228.4±1.4	81.7±1.8	4.39	20.9
Average*	....	....	....	5.35±0.10	3.5

* Taken with actual backgrounds and not the average of positions 1–5.

TABLE 7

EFFICIENCY OF SCREEN-WALL COUNTERS

Counter	Absolute Efficiency (Per Cent of Absolute Rate)
4	5.56±0.05
5	5.59±0.07
6	5.36±0.07
T	5.37±0.07
Ring (Table 6)	5.35±0.10
Average (weighted)	5.46±0.03

and background is given. This number is used to convert the observed count rates to absolute disintegration rates.

The radiocarbon radiation has a range of some 28 mg/cm²; that is, a foil weighing 28 mg/cm² will just stop the radiation. The absorption is nearly exponential; the half-thickness, or thickness necessary to absorb half of the radiation, is about 2.3 mg/cm². It is

clear, therefore, that for our sample cylinder of 400 cm.² surface area
(the diameter some 2.7 inches) a layer 2.3 mg/cm² thick or a total
sample of 0.92 gram of carbon would give half of the effect that an
infinitely thick layer would give. The formula for this is[3]

$$\frac{I}{I_\infty} = 1 - e^{-8.7x}, \tag{25}$$

where I_∞ is the count rate that would have been obtained from a
sample of infinite thickness (of thickness at least equal to the range),
I is the intensity observed for the sample of given thickness, and x is
the ratio of the actual thickness used to the range of the radiation.
The validity of this formula has been experimentally established on
a number of occasions by carefully mounting radiocarbon samples
of known thicknesses less than the range and plotting the count rate
observed as a function of thickness. It is apparent, however, that
the formula will be valid only if the sample has uniform thickness
over its entire area. Since this is a difficult condition to obtain, we
have chosen to make x so large that the count rate is essentially
equal to the rate for the infinitely thick layer and so to avoid worries
about roughness of the sample. One can show that, if the sample ap-
pears reasonably smooth to the eye, errors due to the existence of
rough spots will be very small. In general, the thickness selected has
been 20 mg/cm², or a total sample weight of 8 grams for the 400 cm.²
area of the sample cylinder. From time to time samples have been
used which did not amount to 8 grams, the smallest being about
5 grams. These were mounted with considerable care to insure uni-
formity, and then the count rate was corrected by the small factor
given by Equation (25). It seems possible that one might measure
samples much smaller than 5 grams by developing a technique of
painting the carbon on the brass cylinder in a very reproducible
and smooth fashion.

The carbon sample is mounted on one half of the sample cylinder
(the sample cylinder is split so that the counting operation can be
conducted with convenience and the cylinder reassembled later).
The other half of the sample cylinder remains bare. Figure 9 shows
the equipment used, together with the two halves of the brass sample
cylinder. As described earlier, the carbon sample in the screw-capped

3. W. F. Libby, *Anal. Chem.*, 19, 2 (1947).
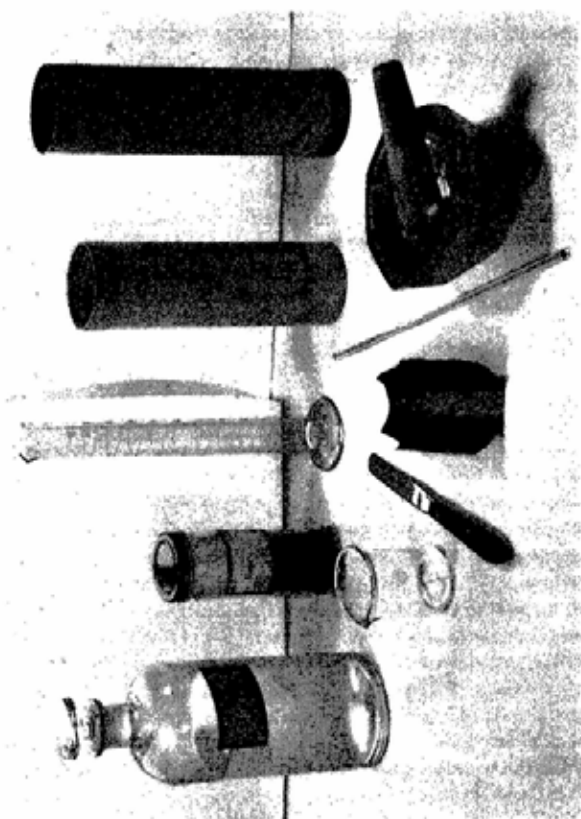
Fig. 9.—Sample mounting display

glass bottle is ground carefully in a mortar and pestle, about 8.5 grams weighed out in a beaker, and some 50-55 cc. of distilled water added. The mixture then is stirred and water added until a consistency like a very thin mush is obtained. One then places a clean white glove on his left hand (if he is right-handed) and, holding the beaker and the sample cylinder in his left hand in such a way that the contents can run from the beaker into the sample cylinder, elevates it toward a light such as an open window so that he can observe the sample flow from the beaker into the cylinder and also scrape out the remnants with a long glass rod. He then replaces the beaker on the table and with the glass rod smooths the sample while rotating the cylinder with his left hand. He then takes the spatula and scrapes out the residual carbon left in the beaker (usually something around 0.5 gram of carbon is left either in the beaker or on the rod) and smooths this onto the surface also. In the early work we used about 20 cc. of 0.15 per cent agar solution to increase the adherence of the sample to the wall. It was found, however, that this was unnecessary providing one was careful not to bump or bang the instrument, and this potential source of contamination was thereby avoided. After the wet carbon sample is smoothed on the cylinder, it is placed on a clean piece of cheesecloth on the table and an ordinary hair-dryer used to blow hot air through it for about 10 minutes. This removes sufficient water to set the sample on the cylinder and yet does not dry the sample completely. It is important that the sample not be dried too long with the hot-air stream for two reasons. The first is that air contains radon, and the sample, if dried, will be extremely susceptible to contamination by absorption of the radon and other possible radioactivities in the air. The carbon samples have large surface areas per gram (of the order of 200 square meters). The second reason is that the warm air has an oxidative action on the brass when the metal gets warm and causes leaching of the zinc out of the brass into the absorbent-carbon sample, so that the ash rises to unreasonable values.

After the drying to the setting stage, the two halves of the sample cylinder are placed together, sometimes fastened with a small piece of Scotch tape if they do not fit snugly, and the sample cylinder placed in the counter proper. The counter cap is then placed on and the counter sealed closed with deKhotinsky wax. The counter then

is placed on a standard vacuum line with two liquid nitrogen traps in series, the first of which has had the internal tube removed so blocking by the ice condensed does not occur readily, and the system allowed to pump for about 24 hours, the nitrogen in the traps being renewed from time to time. At the end of this pumping period the pressure in the line as registered by a Pirani gauge placed between the counter and the first trap will read in the micron range. It is important to remove water to this degree, for, if it is not done, the water absorbed on the sample will slowly evolve and change the operating voltage of the counter during the measurement period. After pumping, 0.5 cm. of ethylene is added. The ethylene is purified by repeated condensation in a liquid nitrogen trap, pumping on the solid, re-evaporation, recondensation, etc., until the vacuum obtained while pumping on the frozen ethylene rapidly approaches a few microns. After the ethylene is introduced, 10 cm. of argon from a standard commercial cylinder of pure argon is added. The counter then is allowed to stand for 2 or 3 hours for mixing, and the voltage measured at which pulses of 6 volts height are obtained. One can run the plateau at this stage, but it is soon found that the plateau characteristics are very reproducible, and this step usually is not taken. The appearance of the pulses on an oscilloscope is observed with care. The oscilloscope is connected so the true pulse shape is shown rather than the first time derivative. This is accomplished by connecting the wall of the counter to ground through a resistor, the potential drop across which is fed to the oscilloscope. Choice of the proper resistor insures that the time constant of the oscilloscope circuit is short enough to afford faithful pulse reproduction. It is particularly important to examine the pulses for multiplicity. The occurrence of multiple pulses is undesirable not only because it is evidence of improper gas composition but primarily because the cancellation of meson counts by the anticoincidence shielding counters will not occur for multiple pulses. The first component of the multiple pulses is canceled, but the following pulses occur later and are not canceled. This means, of course, that the background rate is observed to rise when impurities such as air or water vapor are introduced into the counter gas. The instrument at this stage is ready for placing in the shield and the beginning of the measurement run.

The counter construction is shown in Figure 7. Standard blue-prints can be obtained from the author on request. The materials used in the construction of the counter, and also the shield described later, are given in Appendix B, together with the suppliers we have used. The gridwork is constructed by stringing wires between lucite header disks and the whole assembly is supported on a post, silver-soldered to one of the two end caps. Lead-free brass tubing is used both for the material of the cylinder case and the other brass parts and for the sample cylinder. This precaution is taken to avoid radio-active contamination. The cylinder wall is made as thin as con-venient in order to improve the efficiency of the anticoincidence shielding described later. A glass stopcock is fastened by deKhotin-sky wax to the outlet shown, and this wax is used for all the other closures also. We have constructed one or two instruments with rubber gasket seals at the ends, but in most of the counters we have used wax seals.

The deKhotinsky wax used is made by cooking together approxi-mately equal parts of Georgia pine tar and orange shellac. The mix-ture is melted, heated, and stirred continuously for about 30 minutes, care being taken not to char. This wax is particularly strong and has proved eminently satisfactory. It is applied with an air-gas torch. One should not use an oxygen torch because charring of the wax will be likely. It is difficult to obtain vacuum-tight seals when the wax is charred. The parts to be sealed are heated above the softening point of the wax and the wax applied by touching to the hot metal or glass. One can also heat the wax stick briefly (the wax is poured from the cooking pot onto metal foils which are then rolled to make sticks about 6 inches long and $\frac{1}{2}$ inch in diameter) directly and let it drip onto the hot metal. The counter is then rotated so that a smooth and uniform layer of wax is obtained, and the seal is cooled by blowing air on it. Our experience has been that vacuum-tight seals can be obtained easily in this manner, and the only difficulty en-countered in the use of the instrument so far as vacuum is con-cerned is that one occasionally breaks the wax seal by bumping the sample cylinder too vigorously against the end caps. This, however, is undesirable from the point of view of dislodging the sample itself and should be avoided.

The principal task in the measurement of extremely small

amounts of radioactivity remaining after one has supplied a suffi-
ciently sensitive counter is the reduction of the extraneous back-
ground count rate due to cosmic radiation and the ubiquitous radio-
active products of uranium and thorium which exist in all labora-
tories in such amounts as to give very appreciable count rates. The
latter component of the background is best removed by selecting
solid material which is free of uranium and thorium and of its dis-
integration products such as radon. Consideration of this problem,
together with the problem of cost, has led us to believe that steel
should be an excellent material for a low-level counter shield. It is
reasonably inexpensive and from the metallurgical processing in-
volved in its manufacture should be relatively free of the highly
electropositive elements which constitute the most serious radio-
active contaminates. It is reasoned that elements such as uranium,
thorium, and radium will be removed by the slagging operation. We
do not believe that lead is particularly desirable from either the cost
or the cleanliness point of view, and tests have confirmed the suspi-
cion of radioactive contamination in lead as ordinarily purchased.
We have constructed the shield as shown in Figure 10, of hot rolled
steel plate, 8 inches thick. Two types have been built, in one of
which the door is closed by the hydraulic jack shown, and another
in which the door is bisected and opened with a cantilever arrange-
ment by hand.

The background rate for the unshielded screen-wall counter is in
the vicinity of 500 counts per minute. Placing the instrument in the
shield with 8 inches of iron in all directions reduces this to 100
counts per minute. If instead of the 8-inch shield one uses a shield
with 4-inch walls outside of which 2 inches of lead are placed, the
background is 120 counts per minute. This residual background is
very large due to the cosmic-ray mesons whose penetrating power
is very great. It would be removed only by very great thick-
nesses of shield material. The device used to eliminate this com-
ponent of the background consists of surrounding the screen-wall
counter with a complete layer of Geiger counters 18 inches in
length, 2 inches in diameter, which are in tangential contact and are
placed as shown in Figure 11. This is an end-on view of the assembly
in place with the door of the shield open. When the shielding coun-
ters fire, the central screen-wall counter is inactivated for a small

fraction of a second. This means that the meson radiation is thereby eliminated from the record. The aggregate count rate of the eleven shield counters is about 800 per minute, and the cancellation time is of the order of 10^{-3} seconds, so the screen-wall counter is inactivated for about 1 per cent of the time. This is so small as to be negligible, and we can conclude therefore that the sensitivity of the
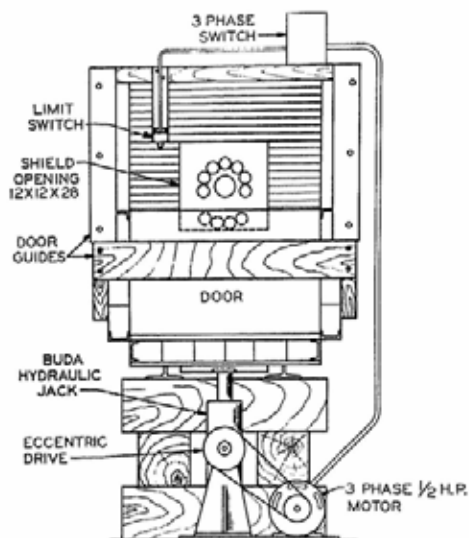
FIG. 10.—Schematic of counters and shield

apparatus to the radiocarbon radiation from the sample is not appreciably reduced by the use of the shielding counter area. The use of the shielding counters reduces the background to 5 counts per minute. The smaller shield mentioned above with 4-inch thick iron and 2-inch lead exterior gives 7 counts per minute. With these rates it is now possible to measure the radiocarbon radiation to about 2 per cent error in 48 hours. Modern wood gives 6.7 counts above the background, so that one observes a rate of 11.7 with the carbon sample in

place and a rate of 5 counts per minute with the bare cylinder in place. The anticoincidence shielding counters are 18 inches long, thereby considerably overhanging the sensitive volume of the screen wall, which is 8 inches in length. We therefore have not placed a layer of shielding counters at either end of the assembly. It is clear, of course, that this would reduce the background further, but the
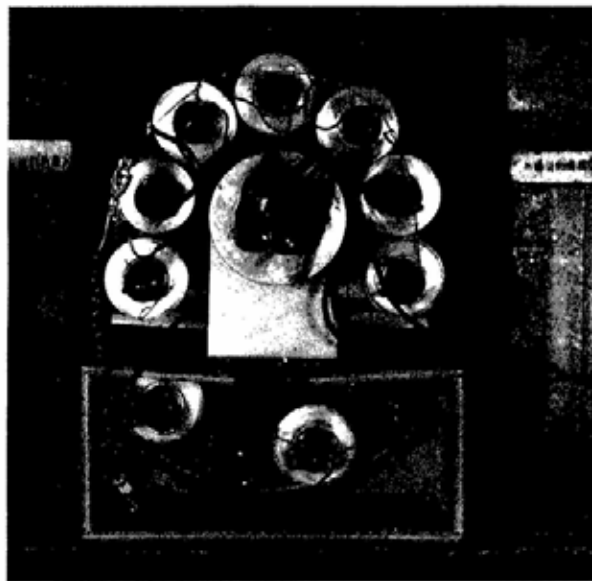
Fig. 11.—Counters in shield (door open)

extra mechanical difficulties involved in changing the sample cylinder and the small advantages to be gained by further lowering of the background have prevented our doing so. The shielding counters used are standard brass-wall cosmic-ray counters sold by commercial suppliers.

The operation of the screen-wall counter in the manner described for the measurement of radiocarbon in the age-measurement pro-

gram involves several sorts of difficulties, one of which is major and which deserves special mention. Counters which have accidentally been connected incorrectly so that the leads from the screen wall and the counter wire are interchanged, and have been maintained in this condition for some time, have a tendency to show spurious counts for some time thereafter. It seems that the only way in which this can be cured, other than by allowing the instrument to stand for weeks, is to replace the lucite insulators. This point, however, is not completely settled; it is merely known that this accomplishes the results. A similar effect may be produced by erroneous application of excessive potentials so that the counter goes into essentially continuous discharge. One should take care to have a connector plug connecting the counter leads to the amplifier and recording apparatus such that this error is not possible.

Any good quenching vapor is satisfactory for the screen-wall counter as far as counting characteristics are concerned, but a consideration of some subtlety is involved which leads one to select ethylene. In our case, where the sample of carbon is very finely divided and possesses a very high absorptive power for condensible vapors such as ethanol, the amount of quenching gas absorbed may be such as appreciably to affect the fraction of the radiation which escapes the sample and reaches the counter gas volume. In the case of ethyl alcohol our experience has been that as much as 1 gram was absorbed on our standard 8-gram sample. This, of course, in addition to absorbing the radiation, may introduce radiation itself, depending on whether the ethanol is grain alcohol or synthetic. The early measurements were made with ethyl alcohol, and the corrections for the specific activity of the ethyl alcohol and its absorptive action on the radiations from the carbon sample computed. The results were acceptable, but an additional error was introduced. For these reasons a quenching gas of lower boiling point was sought, and ethylene[4] has proved to be completely satisfactory in all respects. As mentioned above, the standard filling is 0.5 cm. of mercury pressure of ethylene and 10 cm. of mercury pressure of argon.

We have not found it necessary to purify the commercial argon but have taken the precaution of buying large 200-cubic-foot cylinders so that satisfactory operation is guaranteed for an extended

4. K. H. Morgenstern, C. L. Cowan, and E. L. Hughes, *Phys. Rev.*, **74**, 499 (1948).

period if a good cylinder is obtained. It has been our experience that the argon available on the commercial market is sufficiently pure.

Interesting effects arise if the counter happens to develop a leak. The introduction of air to the counter gas adds to the normal single sharp pulses a group of smaller pulses following the original one after a delay of several hundred microseconds. This may be sufficiently long to extend beyond the cancellation period given by the anti-coincidence shielding counters, so that a pulse which would normally have been canceled from the record registers. One therefore observes a rise in background count together with a rise in the counter voltage and, at appreciable air contaminations, a decrease in the difference between the sample and background counts. This decrease is apparently due to inefficiency in the counter action caused by the presence of the air; presumably the oxygen in the air is the active agent. The decrease probably arises in the volume between the screen and wall, where the collecting field is lowest.

A further effect of some importance to routine operation exists in the temperature dependence of the operating voltage of the counter. It is found that a temperature variation of $10°$ F. will cause 10 or 20 volts change in the counter voltage. This may be due to the temperature dependence of the absorption of ethylene on the highly absorptive carbon sample. It means that one should take care to insure that the room temperature does not vary by more than $5°$ F. during long operating periods when the rate is not being recorded.

It has been our practice to change the sample cylinder from one position to the other every few hours during the day and to allow it to run during an 8- or 10-hour period overnight, arranging the schedule so that the total time spent counting the sample and the background will be proportional to the square roots of the rates in the two positions. This, for example, means that for a measurement of modern wood, where the background rate is about half the rate in the sample position, 60 per cent of the time is spent measuring the sample and 40 per cent measuring the background. In addition, of course, the background count from run to run should check nearly within the statistical error of the counts. One is tempted to cross-average the background counts and thereby to reduce the time necessary to measure. We have never done so, however, for it has been ob-

served that changes in the operating characteristics of the shielding counters may occur which will affect both the background and the sample rate in the same way and not invalidate the difference, though it might cause as much as a half-count per minute change in both rates.

The final cleaning of the sample cylinder before use in the first instance consists in washing in 50 per cent nitric acid, rinsing carefully with distilled water, and drying. We have observed that cylinders prepared in this way of lead-free brass tubing have never given a negative count rate beyond the statistical error when used on carbon derived from coal or oil. They would be expected to register negatively if the sample cylinders were contaminated, the point being that the inert carbon would absorb radiation from the brass. In addition, we have found Armco iron and pure copper sample cylinders to give the same count rate as the cleaned brass cylinders. We therefore believe that not over 0.1 or 0.2 count per minute of contamination exists on our set of sample cylinders and that it is possible to use Armco iron and pure copper as well as lead-free brass.

The statistical error of the count is taken as the square root of the total number of counts divided by the number of minutes during which they occurred. This gives the standard deviation a measure of error 1.5 times the probable error, and all of our results are quoted with this standard error derived solely from the count rate indicated. It has been interesting to observe that the scatter of repeated runs on different portions of a given sample and on recounts of a single portion of a given sample seems not to exceed the error due to the counting alone by any considerable factor. We therefore are inclined to believe that the use of longer counting periods would result in errors almost inversely proportional to the square root of the factor by which the counting time is increased. For example, if our present 48-hour counting interval, which gives us an error of ± 200 years for a sample of a certain age, should be increased by a factor of 4, we might be justified in assigning a ± 100-year error. Only further careful investigation can test this point and fully establish it. It does, however, seem likely that counting for periods even as long as a month with the consequent smaller errors might be worth while.

CHAPTER VI

RADIOCARBON DATES

THE dates obtained prior to the fall of 1951 by the radio-carbon technique are listed below. The number of runs is indicated by the number of dates listed. These runs were completely independent, involving separate portions of the original sample from which the carbon had been extracted independently, unless the dates are linked together with a brace. In this case, the results are those obtained by remeasurement of a given sample, usually in a different counter, and frequently involving re-extraction of the sample with acid. The standard counting time for a given run has been limited to 48 hours in order to accommodate the number of samples necessary to the over-all check of the method, which was the main purpose of this research. The errors given are standard deviations, consisting solely of the error of counting random events.

The archeological and geological significance of these results have been or will be discussed by the donors of the samples, collaborators, and the advisory committee in articles in appropriate journals.[1] We wish to express our gratitude to Frederick Johnson, Donald Collier, Richard Foster Flint, and Froelich Rainey, the members of the Committee on Carbon 14 of the American Anthropological Association and the Geological Society of America, for their indispensable direction and assistance throughout this research.

The numbering of the samples and the names we have used (which appear in parentheses when two names are given) are entirely our own and not those of the donors or collaborators. In many instances more appropriate names assigned by Mr. Johnson are given before the parentheses. The records on the samples are so extensive and so intimately tied to the sample names as well as to the numbers that we feel obliged to include our name as well as the number, though it may be misleading in many cases. The carbon for each of the samples listed is on file and available for check measurements, together in many instances with portions of the original materials.

[1] See, e.g., *Radiocarbon Dating*, assembled by Frederick Johnson ("Society for American Archaeology Memoir," No. 8 [July, 1951]).

I. MESOPOTAMIA AND WESTERN ASIA

(*Principal collaborators:* R. J. BRAIDWOOD, T. JACOBSEN
RICHARD A. PARKER, AND SAUL WEINBERG)

A. EGYPT

Our No.	Sample	Age (Years)
1	*Zoser:* Acacia wood beam in excellent state of preservation from tomb of Zoser at Sakkara. Known age 4650 ± 75 years according to John Wilson. Submitted by Ambrose Lansing, Metropolitan Museum.	3699 ± 770 4234 ± 600 3991 ± 500 *Av. 3979 ± 350*
12	*Sneferu:* Cypress beam from tomb of Sneferu at Meydum. Known age 4575 ± 75 according to John Wilson. Submitted by Froelich Rainey, University of Pennsylvania Museum.	4721 ± 500 4186 ± 500 5548 ± 500 4817 ± 240 *Av. 4802 ± 210*
81	*Sesostris:* Wood from deck of funerary ship from tomb of Sesostris III. Known age 3750 according to John Wilson. Submitted by Colonel C. C. Gregg, Chicago Natural History Museum.	3845 ± 400 3407 ± 350 3642 ± 310 *Av. 3621 ± 180*
62	*Ptolemy:* Wood from mummiform coffin from Egyptian Ptolemaic period. Known age 2280 according to John Wilson. Submitted by John Wilson and Watson Boyes, Oriental Institute, University of Chicago.	2190 ± 450
267	*Hemaka:* Slab of wood from roof beam of tomb of Vizier Hemaka, contemporaneous with King Udimu, First Dynasty, at Sakkara. Accepted age 4700–5100 according to R. J. Braidwood. Sample submitted by W. B. Emery, ℅ British Embassy, Cairo.	{ 4803 ± 260 { 4961 ± 240 *Av. 4883 ± 200*
463	*Middle Predynastic (Predynastic):* Charcoal from point "A-15" of the house floors (*fonds de cabanes*) at El Omari near Cairo, Egypt. A typological assessment of the position of El Omari would be *ca.* midway between the time of the Upper K pits of the Fayum (Nos. 457, 550, and 551) and Hemaka (No. 267). Submitted by Fernand de Bono, Service des Antiquités de l'Égypte, Cairo.	5256 ± 230
457	*Fayum A (Upper K):* Wheat and barley grain uncarbonized with no preservatives added, from Upper K Pit 13 of the Fayum A material as described in *The Desert Fayum* by Gertrude Caton-Thompson. Submitted by Miss Caton-Thompson of Cambridge and Mrs. Elise Baumgartel of the Museum of the University of Manchester.	{ 6054 ± 330 { 6136 ± 320 *Av. 6095 ± 250*
550 and 551	*Fayum A (Upper K):* Wheat and barley grain from Upper K Pit 59, Jar 3, and another of the Upper K pits (number lost) of the Fayum A material as described	6391 ± 180

Our No.	Sample	Age (Years)

in *The Desert Fayum.* Submitted by Miss Caton-Thompson and Mrs. Elise Baumgartel of the Museum of the University of Manchester.

B. TURKEY

115   *Alishar III (Alishar):* Wood from the foundation cribbing for a fortification wall in Square 0–10 in levels assigned to Period III, "Early Bronze Age," in the mound at Alishar Huyuh by the excavator, H. H. von der Osten. Reference: "Oriental Institute Publications," XXVIII, 209–10; Figure 207. Submitted by R. J. Braidwood, Oriental Institute, University of Chicago   3650 ± 350   2823 ± 350   *Av. 3212 ± 250*

183   *Alishar Chalcolithic:* Wood from Level 14 in the central depth cut Square L–14, Alishar Huyuh. The excavators counted Levels 19 through 13 as "Chalcolithic." Reference: "Oriental Institute Publications," Vol. XXVIII. Submitted by R. J. Braidwood, Oriental Institute, University of Chicago.   4519 ± 250

C. IRAQ

113   *Jarmo:* Land-snail shells fairly well preserved from the basal Levels 7 and 8 at Jarmo. Earliest village material in western Asia. The basal levels are preceramic. Excavated and submitted by R. J. Braidwood, Oriental Institute, University of Chicago.   6707 ± 320

D. SYRIA

72   *Tayinat:* Wood from the floor of a central room (I–J—1st) in a large Hilani ("palace") of the "Syro-Hittite" period in the city of Tayinat in northwest Syria. Known age 2625 ± 50 years according to R. J. Braidwood. Submitted by R. J. Braidwood, Oriental Institute, University of Chicago.   2696 ± 270   2648 ± 270   2239 ± 270   *Av. 2531 ± 150*

E. IRAN

492 *Belt Cave (Ghar-i-Kamarband):* Five miles west of Beh-
547 shahr at the southeast corner of the Caspian Sea;
525 stratified cultural deposit 4.05 meters thick contain-
574 ing from, bottom to top, Mesolithic, Late Mesolithic,
524 Neolithic, Late Neolithic, and Bronze Age materials.
494 The samples were burned bone which were treated by
495 dissolving in hydrochloric acid to separate the charred
523 carbon, which was measured. This material was collected and submitted by Carleton S. Coon, University of Pennsylvania Museum. Five samples were measured:

Our No.	Sample	Age (Years)
492 and 547	Lowest gray soil with Mesolithic artifacts 3.00 to 4.05 meters (Levels 21–28).	8004 ± 415
525	Supposedly from the same levels as No. 574. Comment: looks intrusive or altered.	$\begin{cases} 1130 \pm 300 \\ 1260 \pm 430 \end{cases}$
574	Zone containing upper Mesolithic artifacts,1 .25 to 2.15 meters deep (Layers 15 and 16).	8545 ± 500
524	Mesolithic-Neolithic transition at 1.25–1.40 meters (Layer 10).	10,560 ± 610
494, 495, and 523	Zone containing flint blades and pottery sherds of Neolithic type.	8085 ± 720

F. PALESTINE

576 *Bible:* Dead Sea scrolls. Book of Isaiah. Linen wrappings used. Found in cave near Ain Fashkha in Palestine by Père de Vaux (OP) under supervision by G. Lankester Harding, curator of Department of Antiquities of the Jordan Government. Thought to be first or second century B.C. Brought for test by James L. Kelso at suggestion of Ovid R. Sellers and with permission of Mr. Harding. Submitted directly by C. H. Kraeling, Oriental Institute, University of Chicago. — 1917 ± 200

II. WESTERN EUROPE

(*Principal collaborators:* H. L. MOVIUS, E. S. DEEVEY, JR., AND R. F. FLINT)

A. FRANCE

406 *Lascaux:* Charcoal from the Lascaux cave near Montignac northeast of Les Eyzies in the Dordogne. This cave has the remarkable paintings. The charcoal was taken from the occupation level in the northwestern portion of the cave by Abbé H. Breuil and M. Séverin Blanc in 1949. Submitted by H. L. Movius, Harvard University. — 15,516 ± 900

577 *France:* Material from a late Upper Paleolithic (Magdalenian) occupation layer overlain by 1.5–2.0 meters of rock fall. Collected in and around a hearth which measured 60 cm. in diameter and 10 cm. in thickness at the center. Found at La Garenne, St.-Marcel (Indre), France. This sample consisted of 1500 grams of burned bone from which sufficient organic material was obtained by acid dissolution of the bone. Sub- — 11,109 ± 480

Our No.	Sample	Age (Years)

mitted by Dr. J. Allain, 34, Avenue Thabaud-Boislareine, Neuvy-St.-Sépulchre (Indre), France, through H. L. Movius, Harvard University.

578   *France II:* Same as No. 577, except that it consisted of an ashy material with sand, charcoal, and burned bones.   15,847 ± 1200

579   *France III:* Same as Nos. 577 and 578, except found outside the hearth but in same horizon. Burned bone.   12,986 ± 560

588   *Lake Bourget:* Lake Bourget wood and peat samples taken along road between Chambéry and Grenoble in southeastern France. Should be interglacial or interstadial. This sample was wood from 2 inches above base of Level 3d, the lowest lignite bed in the exposure between La Flachère and La Brussère (Isère). Donor's Sample 1. Submitted by H. L. Movius, Harvard University.   At least 21,000

595   *Geneva:* Wood from peat bed in Dranse Valley east of Geneva and south of Lake Geneva in France rather than Switzerland. Submitted by H. L. Movius, Harvard University.   At least 19,000

B. GERMANY

337   *German Alleröd:* Peat with birch remains from Pollen Zone IIb, the younger Alleröd, from Wallensen im Hils, northwestern Germany. Submitted by F. Firbas, Göttingen.   11,044 ± 500

450   *Grenz Horizont Peat (Overbeck Peat):* Peat (Grenz Horizant) from an accurately dated (2500–2700 years) dry period extending throughout northern Europe and associated with archeological remains. This sample was taken carefully from 0 to 2 cm. below the dry horizon at Melhack, Germany. Submitted by F. Overbeck, University of Bonn.   { 1446 ± 250 { 1452 ± 290 *Av. 1449 ± 200*

449   *Grenz Horizant Peat (Overbeck Top):* Peat from 0 to 2 cm. above the dry horizon described in No. 450. Submitted by F. Overbeck, University of Bonn.   1129 ± 115

C. DENMARK

432   *Danish Boreal (Danish Boreal II):* Pine cones from Denmark (Seeland, Aamosen; Ogaarde-K, PØ 1949). They are from Pollen Zone V thought to be 8500 years old. Submitted by J. Troels-Smith, National Museum, Copenhagen.   7583 ± 380

433   *Danish Boreal (Boreal IV):* Hazelnuts from Denmark (Seeland, Aamosen; Kildegaard-K, Ul. Ø, House 1). The nuts are from one single summer dwelling, be-   { 9935 ± 440 { 9927 ± 830 *Av. 9931 ± 350*

Our No.	Sample	Age (Years)

longing to the late boreal age, Pollen Zone VI, thought to be about 8000 years old. Submitted by J. Troels-Smith, National Museum, Copenhagen.

434 *Danish Boreal* (*Danish Boreal III*): Charcoal from the same summer house as No. 433. Expected age about 8000 years. Submitted by J. Troels-Smith, National Museum, Copenhagen. — 8631 ± 540

435 *Danish Boreal* (*Danish House*): Birchwood from the same area as Nos. 433 and 434. From House 2. Probably a few years younger than House 1. Submitted by J. Troels-Smith. Comment: Seems to agree with No. 433 and possibly No. 434, giving a general mean of 9479 ± 280 years. — 9425 ± 470

D. IRELAND

358 *Irish Boreal* (*Boreal II*): Peat from Clonsast, County Offaly, Ireland. Late Boreal Zone VIc. Should be later than Danish No. 432 and earlier than English No. 343. Donor's Sample I-D. Submitted by G. F. Mitchell, Trinity College, Dublin. — 5824 ± 300

355 *Irish Mud:* Lake mud from Knocknacran, County Monaghan, Ireland. Late Glacial, Pollen Zone II. Donor's Sample I-A. Submitted by G. F. Mitchell, Trinity College, Dublin. — 11,310 ± 720

356 *Irish Postglacial:* Lake mud, Lagore, County Meath. Early Postglacial, Zone IV. Donor's Sample I-B. Submitted by G. F. Mitchell, Trinity College, Dublin. — 11,787 ± 700

E. ENGLAND

461 *Beeswax:* Lump of beeswax associated with a smith's hoard of late Bronze Age objects of estimated 2500–3000 years age. Question is whether it is part of hoard or not. Submitted by J. W. Brailsford, British Museum. Comment: Is not part of hoard; it is younger. — { 712 ± 200 / 926 ± 230 / Av. *819 ± 160*

347 *Shapwick* (*Shapwick Peat*): Modified humified peat (Sphagnum-Calluna) from mid-Iron Age to Romano-British period from Shapwick Heath, Somerset. Pollen Zone VIII. Upper Oligotrophic layer; decay pool wood; cf. S.H.6. Submitted by H. Godwin, Cambridge, England. — { 3099 ± 250 / 3520 ± 300 / Av. *3310 ± 200*

343 *Shapwick* (*Shapwick Atlantic*): Humified Sphagnum-Calluna peat of Neolithic Age, early Pollen Zone VII, taken from 6 feet 8 inches to 7 feet at base of old peat at Dewar's track excavation. Submitted by H. Godwin, Cambridge, England. — 6044 ± 380

Our No.	Sample	Age (Years)
462	*English Neolithic (Mesolithic):* Piece of charred wood from the lakeside settlement at Ehenside Tarn, Cumberland. Neolithic "A" material. Conventional dating is 4000 years (cf. *Archaeologia,* XLIV, 280). One of rare cases in England where organic material has been preserved in association with characteristic Neolithic material. Submitted by J. W. Brailsford, British Museum.	4964 ± 300
353	*Starr Carr:* Wooden platform from Mesolithic site at Lake Pickering, Starr Carr, Yorkshire. Pollen Zone IV. Submitted by H. Godwin, Cambridge, England.	10,167 ± 560 8808 ± 490 *Av. 9488 ± 350*
340	*Postglacial (Postglacial I):* Peat from Hawks Tor, Cornwall. Pollen Zone IV, Early Postglacial. Collected from 7 feet to 7 feet 4 inches at Site 1 at base of upper peat. Submitted by H. Godwin, Cambridge, England.	{8011 ± 400 {8540 ± 780 *Av. 8275 ± 350*
349	*Hockham Mere, England (English Allerod):* Calcareous silty nekron mud from 790 to 825 cm. at D.B. 5, Hockham Mere, Norfolk. Late Glacial, Pollen Zones II and III. Submitted by H. Godwin, Cambridge, England.	{6619 ± 380 {6491 ± 420 *Av. 6555 ± 280*
444	*Neasham, England (Godwin):* Lake mud from Neasham near Darlington in the extreme north of England. Pollen Zone II, correlated directly with last glacial stage. Submitted by H. Godwin, Cambridge, England.	10,851 ± 630
341	*Hawks Tor, England (Allerod I):* Peat from Hawks Tor, Cornwall, Late Glacial, Pollen Zone II, 9 feet to 9 feet 4 inches at Site 1, middle of lower peat. Submitted by H. Godwin, Cambridge, England.	9861 ± 500
479	*Ponders End:* Plant debris from Lea Valley Arctic Bed north of London at Ponders End. Glacial stage associated with mammoth, lemming, and arctic plants. Submitted by H. Godwin, Cambridge, England.	Older than 20,000
480	*Cambridge, England (Cambridge Interglacial):* Oak wood debris from Histon Road, Cambridge. Middle of last interglacial, time of maximum extension of the Eem Sea. Submitted by H. Godwin, Cambridge, England.	At least 17,000
602	*Stonehenge:* Charcoal sample from Stonehenge, Wiltshire, England. Taken from Hole 32 of a series of holes that are believed to have been used for some sort of ritual. These holes belong to the first phase of the monument and are considered to be Late Neolithic. Submitted by Professor Stuart Piggott, University of Edinburgh.	3798 ± 275

III. UNITED STATES

(Principal collaborators: E. S. Deevey, Jr., R. F. Flint, J. B. Griffin
R. F. Heizer, F. Johnson, F. H. H. Roberts, and W. S. Webb)

A. New England

Our No.	Sample	Age (Years)
417	*Boylston Street Fishweir (Fishweir I):* Peat from Boylston Street Fishweir site. Lower peat underlying the fishweir. Presumably the fishweir should be younger (cf. *The Boylston Street Fishweir II* ["Papers of the Peabody Foundation," Vol. IV, No. 1], pp. 60, 65, 68). Submitted by E. S. Barghoorn, Biological Laboratories, Harvard University.	5717 ± 500
418	*Boylston Street Fishweir (Fishweir II):* Fragment of coniferous wood from marine silt overlying the lower peat and the fishweir (cf. No. 417). Submitted by E. S. Barghoorn, Biological Laboratories, Harvard University.	3851 ± 390
36–39	*Upper Linsley Pond (Deevey Series):* Pond mud samples from Upper Linsley Pond, Connecticut, as described in E. S. Deevey, Jr., *Am. Jour. Sci.,* **241**, 717–52 (1943). Samples were taken by boring through ice in center of pond. Collected and submitted by E. S. Deevey, Jr., Osborne Zoological Laboratory, Yale University.	

Sample	Depth (Meters)	Pollen Zone	
36	5.5	C3	876 ± 250
37	8.05	C2	1800 ± 500
38	9.15	C1–C2	5159 ± 350
39	11.65	C1–B	8323 ± 400

119–22   *Upper Linsley Pond (Linsley Series):* Pond mud samples from Upper Linsley Pond, Connecticut. These taken from the edge of the pond, compare with Nos. 36–39. Collected and submitted by E. S. Deevey, Jr., Yale University.

Sample	Depth (Meters)	Pollen Zone	
119	4.65	C2	2141 ± 250
120	6.65	C1–C2	5305 ± 250
121	8.65	C1	Heterogeneous: 6911 and 4088 ± 250
122	10.15	B	6668 ± 250

Comment: Appears mixing is involved.

478	*Upper Linsley Pond (Linsley V):* Peat from Upper Linsley Pond, Connecticut. Taken at 10.55 meters with	8794 ± 550

Our No.	Sample	Age (Years)

large sampler. Pollen date is early to middle C-1. Pine zone is at 11.90 meters. Collected and submitted by E. S. Deevey, Jr., Yale University.

335   *Maine Boreal (Boreal I)*: Peat from 6.0 meters in Plissey Pond, Maine. Very top of Pine Zone B. Submitted by E. S. Deevey, Jr., Yale University. 5962 ± 320

B. NEW YORK STATE

191   *Frontenac Island (Frontenac)*: Charcoal from hearth in deepest refuse levels (Trench 4, Section 4), Frontenac Island site. Collected in 1939, Lamoka Focus, Archaic Period (revised terminology 1950) (cf. Ritchie, 1945). From collections of Rochester Museum of Arts and Sciences. Submitted through W. A. Ritchie, New York State Museum. 4930 ± 260

192   *Oberlander 2 (Point Peninsula)*: Charcoal from cremation (Burial 6) on the Oberlander component No. 2 at Brewerton, Oswego County, New York. Collected, 1938. This is early Point Peninsula Focus (cf. W. A. Ritchie, Rochester Museum of Arts and Sciences, *Memoir 1* [1944], pp. 152–60). Submitted by W. A. Ritchie, New York State Museum. $\begin{cases} 2817 \pm 270 \\ 3080 \pm 200 \end{cases}$ Av. 2948 ± 170

288   *Lamoka*: Charcoal from hearth in subsoil under 5 feet of undisturbed refuse at Lamoka Lake Site, Schuyler County, New York. Some rootlets were present in this sample. They were segregated under a low-power magnifying glass. This sample was less carefully collected than No. 367. Collected by A. Frank Barratt. Submitted by W. A. Ritchie, New York State Museum. Comment: Doubt that all rootlets were removed. In view of rootlets, perhaps the 5383 date for No. 367 should be taken. 4395 ± 350 4344 ± 300 Av. 4369 ± 200

367   *Lamoka (Lamoka III)*: Charcoal from Lamoka Lake Site, Schuyler County, New York. From earliest occupation level 5 feet below midden surface. Probably this sample was more suitable than No. 288. Submitted by W. A. Ritchie, New York State Museum. 5383 ± 250

C. ILLINOIS, INDIANA, IOWA, KENTUCKY, OHIO AND PENNSYLVANIA

116   *Annis Mound, Kentucky (Webb I)*: Annis Mound, Kentucky. Archaic period, shell from the 6.5-foot level. Shells powdery on surface but shiny and apparently untouched underneath. Submitted by W. S. Webb, University of Kentucky. 5149 ± 300

Our No.	Sample	Age (Years)
180	*Annis Mound, Kentucky (Webb IV)*: Annis Mound shell from the 3.0-foot level. Submitted by W. S. Webb, University of Kentucky.	7374 ± 500
251	*Annis Mound, Kentucky (Deer Antler)*: Annis Mound deer antler from Archaic 6.5-foot level. Submitted by W. S. Webb, University of Kentucky.	4900 ± 250
254	*Indian Knoll, Kentucky (Indian Knoll)*: Antler from Indian Knoll Oh2 mound at 1.0-foot level. Submitted by W. S. Webb, University of Kentucky.	$\begin{cases} 5709 \pm 350 \\ 4894 \pm 560 \end{cases}$ Av. 5302 ± 300
126	*Adena, Kentucky (Adena I)*: Adena material from Drake Mound, Fayette County, Kentucky, Site 11. Fragments of bark preserved by contact with copper reel-shaped breastplate in association with Burial 7, lying on bottom of pit, the central feature of this site. Submitted by W. S. Webb, University of Kentucky.	1168 ± 150
214	*Adena, Ohio (Ohio Adena)*: Adena material from Cowan Creek Mound, Ohio. Charcoal from subfloor fireplace just outside house structure. Submitted by R. S. Baby, Ohio State Museum.	1509 ± 250
126	*Hopewell, Ohio (Hopewell III)*: Charcoal from Altar 1, Section 3, Mound 25. Hopewell Mound Group, Ross County, Ohio. Excavated in 1891. Specimen 56424, Chicago Natural History Museum. Submitted by G. Quimby, Chicago Natural History Museum.	1951 ± 200
137	*Hopewell, Ohio (Hopewell Shell)*: Conch shells associated with Skeletons 260 and 261, Section 3, almost certainly from Mound 25, Hopewell Mound Group, Ross County, Ohio. Specimens 56358 and 56606, Chicago Natural History Museum. Submitted by G. Quimby, Chicago Natural History Museum.	2285 ± 210
139	*Hopewell, Ohio (Hopewell I)*: Bark associated with Skeleton 248, Section 2, Mound 25, Hopewell Mound Group, Ross County, Ohio. Specimen 56094, Chicago Natural History Museum. Submitted by G. Quimby, Chicago Natural History Museum.	2044 ± 250
152	*Hopewell, Illinois (Hopewell II)*: Wood from wood and bark capping, lower edge of primary mound, Mound 9, Havana Group, Havana, Illinois. Submitted by Thorne Deuel, Illinois State Museum.	2336 ± 250
465	*Oxford, Ohio (Goldthwait)*: Large log from the Tazewell or Cary drift near Oxford, Ohio; Hamilton, Ohio, Quadrangle, Oxford Township, Section 26, just north of the creek. Submitted by R. P. Goldthwait, Ohio State University.	At least 15,000

Our No.	Sample	Age (Years)
364	*Tolleston, Illinois (Tolleston):* Wood from Tolleston level, Lake Chicago (may be Algonquin instead). Log found at base of lake sand overlying till in clay pit at Dalton, Illinois. Submitted by J Harlen Bretz, University of Chicago.	3469 ± 230
466	*Till, Illinois (Illinoian):* Wood found in till directly below Illinoian gumbotil in Vermillion County, Illinois. Submitted by G. W. White, Department of Geology, University of Illinois.	Older than 17,000
535	*Wedron, Illinois (Tazewell):* Early Tazewell Shelbyville wood from Lake Kickapoo, Wedron, La Salle County, Illinois. This is supposed to be our only truly authentic Tazewell sample. Submitted by L. Horberg and J Harlen Bretz, University of Chicago. (Cf. No. 575.)	13,842 ± 780
575	*Wedron, Illinois (Wedron):* Wood from Lake Kickapoo deposits at Wedron, Illinois. From dark peaty silt occurring in a bedrock valley in St. Peter sandstone in the same quarry and position as Sample 535. The wood horizon is overlain by periglacially deformed sand and dark silt, which in turn underlie laminated clay (Lake Kickapoo deposits). These lie under a series of tills which have been regionally correlated by L. Horberg and others. The lowest of these is Bloomington, so the sediments must be early Tazewell (either Bloomington or Shelbyville). This sample was collected by J Harlen Bretz and transmitted by Jerry Olson, University of Chicago. It was taken as a check on No. 535.	Older than 17,000
510	*Farm Creek, Illinois (Farmdale):* Wood from Farm Creek, Illinois, representing the earliest stages of the Wisconsin glaciation. Found 3-4 feet below the surface of the Farmdale loess. Submitted by Guy D. Smith, Bureau of Plant Industry, Beltsville, Maryland.	Older than 20,000
481	*Skunk Creek, Iowa (Skunk Creek):* Wood found beneath a presumably Mankato till on north bank of Skunk Creek, NE. ¼, Sec. 15, T. 80 N., R. 22 W., Polk County, Iowa. Submitted by W. H. Scholtes, Iowa State College, Ames, Iowa.	Older than 17,000
528	*Clear Creek, Iowa:* Glacial wood collected in glacial till in Story County, Iowa. Location south side of Clear Creek in an exposed cut; NE. ¼; SW. ¼; Sec. 5, T. 83 N., R. 24 W. Till thought to be Mankato. The wood was excavated by digging and found in loess which	16,367 ± 1000

Our No.	Sample	Age (Years)

underlies a recent till. Submitted by W. H. Scholtes, Iowa State College, Ames, Iowa.

438 *Bridgeville, Pennsylvania (Bridgeville):* Peat found beneath 17 feet of alluvial deposit just west of Bridgeville, Pennsylvania. Thought to be Taxewell or Cary. Submitted by E. R. Eller, Carnegie Museum, Pittsburgh.
Older than 16,000

526 *Bellevue, Ohio (Lake Lundy):* Wood from Bellevue, Ohio, ¾ mile northwest of Castalia on the 620 contour. This falls within the higher limit of Lake Lundy (Grassmere) but above the Elkston limit. Lake Warren beaches are 50–60 feet higher. Submitted by R. P. Goldthwait, Ohio State University.
8513 ± 500

508 *Camden Moraine, Ohio (Camden):* Wood from Camden moraine, south of Dayton, Ohio. No. 465 was from the outer limit of the drift of which the Camden moraine is a recessional moraine. This may be Cary. Submitted by R. P. Goldthwait, Ohio State University.
Older than 17,000

509 *Farmdale, Illinois (Farmdale II):* Wood found 0 to 1 foot below surface of the Farmdale loess at Farm Creek, Illinois. Same site as No. 510. Submitted by Guy D. Smith, Bureau of Plant Industry, Beltsville, Maryland.
Older than 19,000

500 *Lake Cicott:* Peat from Lake Cicott bog, Indiana. Collected from 22- to 23-foot depth, combined Samples B, G, H, I, L, M. Thought to be Zone C-1, Zone B boundary. Collected by J. E. Potzger, Butler University, Indianapolis, Indiana. Submitted by E. S. Deevey, Jr., Yale University.
5625 ± 310

D. NORTH CAROLINA, SOUTH CAROLINA, AND WEST VIRGINIA

336 *West Virginia Boreal:* Peat of Pollen Zone B (pine) from 12 feet 3 inches to 12 feet 9 inches in Cranberry Glades, West Virginia. Submitted by H. C. Darlington.
9434 ± 840

474 *Singletary Lake, North Carolina (Singletary Optimum):* Peat from highest of the three organic horizons at Singletary Lake, North Carolina. Same site as No. 475. Submitted by David G. Frey, University of North Carolina.
10,224 ± 510

475 *Singletary Lake, North Carolina (Singletary Mankato):* Peat and lake sediments from Singletary Lake, North Carolina. The lake has three organic horizons. This
Older than 20,000

Our No.	Sample	Age (Years)

sample is the second which has been tentatively identified from pollen as lying between the Mankato and Cary substages. Submitted by David G. Frey, University of North Carolina.

476   *Singletary Lake, North Carolina (Singletary Cary)*: Lowest of three layers in Singletary Lake (cf. No. 475). Submitted by David G. Frey, University of North Carolina.   Older than 20,000

363   *Santee, South Carolina (Santee)*: Cypress wood from a large stump buried under 30 feet of sand deposited by the Santee River in South Carolina. Stump was 11 feet in diameter, larger than any now growing in the region. Submitted by Stephen Taber, University of South Carolina.   Older than 17,000

105   *Myrtle Beach, South Carolina (Myrtle Beach)*: Cypress wood from the Myrtle Beach area under the Pamlico Terrace. Submitted by Stephen Taber.   Older than 20,000

E. LOUISIANA, MISSISSIPPI, MISSOURI, NEBRASKA, AND TEXAS

143   *Crooks Site, Louisiana (Quimby IV)*: Charcoal from secondary mantle near junction with primary mantle of east slope Mound A, Crooks Site, La–3, La Salle Parish, Marksville period in Louisiana. Submitted by G. Quimby, Chicago Natural History Museum. 1158 ± 250

150   *Tchefuncte, Louisiana (Quimby II)*: Charcoal from top 6 inches, Tchefuncte Site ST 2, Midden A, in Louisiana. Submitted by G. Quimby, Chicago Natural History Museum. 633 ± 150

151   *Tchefuncte, Louisiana (Quimby III)*: Shell from top 6 inches of same Tchefuncte site as No. 150. Submitted by G. Quimby, Chicago Natural History Museum. 1233 ± 250

154   *Bynum Site, Mississippi (Bynum II)*: Bynum vegetal material from Site MCs–16, in Mississippi, base of Mound B. Submitted by John Cotter, National Park Service. 1276 ± 150

385   *Bonfils, Missouri (Bonfils I)*: Wood from the Bonfils sand terrace near the mouth of the Missouri River. This terrace is a remnant of the Festus Terrace, and the date therefore should apply to the Festus Terrace. Sample taken from 2 feet above top of the gravel. Submitted by Louis C. Peltier, Washington University at St. Louis. $12,148 \pm 700$

65   *Medicine Creek, Nebraska (Schultz I)*: Charcoal from Medicine Creek Site Ft–50 in Nebraska. It is a mix- 5256 ± 350

Our No.	Sample	Age (Years)

ture of soil bands A and B, which are 2 feet apart. Submitted by C. B. Schultz, University of Nebraska.

108a   *Medicine Creek, Nebraska (Schultz III)*: Charcoal from Soil B at Ft-50 in Nebraska. Submitted by C. B. Schultz, University of Nebraska.   8274 ± 500

470   *Medicine Creek, Nebraska (Schultz II)*: Charcoal from Soil B at Ft-50, lower occupation Zone Feature 18, N. 155/E. 45. Collected later and more carefully, otherwise duplicate of No. 108a. Submitted by C. B. Schultz, University of Nebraska.   10,493 ± 1500

471   *Lime Creek*: Lime Creek site charcoal, Ft-41, Frontier County, Nebraska. Reference: *Lime Creek Bulletin*, page 34 (cf. Schultz, 1948, p. 34). Submitted by C. B. Schultz, University of Nebraska. $\left\{ \begin{array}{l} 9880 \pm 670 \\ 9167 \pm 600 \end{array} \right.$ Av. 9524 ± 450

558   *Folsom Bone*: Burned bison bone from Lubbock, Texas, from the Folsom horizon. Submitted by E. H. Sellards, Texas Memorial Museum, Austin, Texas. Mr. Sellards' description· "This burned bone has been collected by Glen Evans and Grayson Meade of our staff. We are entirely satisfied that the horizon is Folsom. This conclusion that it is Folsom is based on two principal observations. We have, as you know, a thoroughly proven section at Clovis, New Mexico, the succession being a gray sand containing elephant, other fossils, and artifacts as the basal stratum of the section, followed by a deposit containing a large percentage of diatomaceous earth as the second stratum. The elephant is absent from this second stratum and instead we have an abundance of bison. At the Lubbock locality exactly these conditions are repeated, gray sand as the basal stratum with elephant as the most common fossil, followed by the diatomaceous material with the extinct bison as the abundant fossil. Later units are present at both localities. At the Clovis locality the Folsom culture is contained in and confined to this second horizon. At the Lubbock locality Folsom culture is present as shown by the fact that we have found Folsom points thrown out in the course of dredging. We have not yet found them in place in the diatomaceous deposit, but are fully convinced that they will be found in place as excavating proceeds."   9883 ± 350

377   *Secondary Channel, Folsom Site, New Mexico ("Folsom")*: Charcoal from a hearth in fill of secondary channel which had cut through the original deposit of bison bone and artifacts at the original Folsom site. Col- $\begin{array}{l} 4575 \pm 300 \\ 3923 \pm 400 \end{array}$ Av. 4283 ± 250

Our No.	Sample	Age (Years)
	lected July, 1933. Submitted by H. J. Cook, Agate, Nebraska.	
469	*Cedar Canyon:* Charcoal from Cedar Canyon, Nebraska, locality Sx–101. Found in buried hearth as described in Figure 8, page 359, Volume LXX, *American Naturalist.* Submitted by C. B. Schultz, University of Nebraska.	1993 ± 190
		2379 ± 430
		Av. 2147 ± 150
153	*Davis:* Corncobs from Davis site, in eastern Texas. No. 5888, Jones 3497. Submitted by Alex Krieger, University of Texas, through James Griffin, University of of Michigan.	1553 ± 175

F. ARIZONA, CALIFORNIA, AND NEW MEXICO

162–74 *Bat Cave:* Corncobs and wood fragments from the debris in Bat Cave, New Mexico. The depth below the top correlates with the development of corn from a primitive form at the lowest layer of 6 feet to essentially modern corn at the top. Excavated by Herbert Dick. Submitted by P. C. Mangelsdorf, Harvard University.

Sample	Layer (Depth in Feet)	
165 (cobs)	0–1	1752 ± 250
173 (wood)	1–2	1907 ± 250
172 (wood)	2–3	2239 ± 250
164 and 171 (corn and wood)	3–4	2249 ± 250
170 (wood)	4–5	2862 ± 250

567–73 *Bat Cave:* Charcoal all from one area in Bat Cave. From levels from which there has been no vandalism and little opportunity for mixture by rodent activity. The development of the corn culture is presumably correlatable with the charcoal dates. Submitted by Paul C. Mangelsdorf, Harvard University.

Sample	Location	
567	Area III, Section Ic, Front, 11–15-inches depth	1610 ± 200
569	Area III, Section Ic, Rear, 24–36-inches depth	2816 ± 200
570	Area III, Section Ic, Front, 36–48-inches depth	2048 ± 170
571	Area III, Section Ic, Front, 48–60-inches depth	5605 ± 290
572	Area III, Section Ic, Front, 54–66-inches depth	5000–7500 (poor run)
573	Area III, Section Ic, Front, 60–66-inches depth	5931 ± 310

Our No.	Sample	Age (Years)

584 *Tularosa Cave I:* Corncobs from Tularosa Cave, New Mexico. This sample of cobs was from Square 2R2, Level 14, the lowest preceramic occupation level resting on sandstone bedrock 9 feet 4 inches from the surface of the dry midden. Submitted by Paul S. Martin, Chicago Natural History Museum. — 2223 ± 200

585 *Tularosa Cave II:* Cobs and tree bark from Tularosa Cave, New Mexico. This sample was taken from Square 2R2, Level 10, 6 feet 8 inches below the surface. This layer is the Pine Lawn phase, the first pottery-making period of the area. Submitted by Paul S. Martin, Chicago Natural History Museum, through Donald Collier. — $\begin{cases} 2112 \pm 230 \\ 2177 \pm 225 \end{cases}$ Av. 2145 ± 160

612 *Tularosa Cave III:* Corn and vegetable material from Tularosa Cave (cf. Nos. 584 and 585), Square 2R2, Level 13. Pre-pottery and associated with Chiricahua type implements. Submitted by Paul S. Martin, Chicago Natural History Museum. — 2300 ± 200

186 *San Francisco Bay Mound, California (California Archaic):* Charcoal from a San Francisco Bay shell mound, Site 4–Mrn–115. Submitted by R. F. Heizer, University of California, Berkeley. — $\begin{cases} 633 \pm 200 \\ 911 \pm 180 \end{cases}$ Av. 720 ± 130

440 and 522 *California Early Horizon:* Charcoal from near Sacramento, Site SJo–68, culture Early Central California Horizon as described in Robert F. Heizer, *The Archaeology of Central California. I. Early Horizon* ("Anthropological Records," Vol. XII, No. 1 [University of California Press, 1949]). — 4052 ± 160

216 *Cochise, Arizona (Cochise):* Charcoal-bearing dirt from l^2 and l^3 beds shown in Figure 13, page 47, *The Cochise Culture* ("Medallion Papers," No. XXIX). This is the Sulphur Springs stage of the culture. Submitted by E. B. Sayles, Arizona State Museum, Tucson, Arizona. — 7756 ± 370

511 *Cochise, Arizona (Sulphur Springs):* Charcoal from Cochise Site 6 North, Sulphur Springs stage. Submitted by E. B. Sayles, Arizona State Museum. — 6210 ± 450

515 *Cochise, Arizona (Chiricahua):* Charcoal from Cochise Site 12, Chiricahua Stage. Submitted by E. B. Sayles, Arizona State Museum. — 4006 ± 270

518 *Cochise, Arizona (San Pedro II):* Charcoal from Site 3, San Pedro stage. Sulphur Springs Valley, Arizona (cf. Pearce 8:9, Fig. 4). Submitted by E. B. Sayles, Arizona State Museum. — 1762 ± 430

Our No.	Sample	Age (Years)
556	*Wet Leggett, New Mexico (Antevs I)*: Cochise charcoal collected by E. Antevs on the Wet Leggett, New Mexico, August 17, 1950. Found in wall of an arroyo tributary to main Wet Leggett arroyo at a depth 9 feet 8 inches below the ground level in beds which may be either Chiricahua or San Pedro. Submitted by E. Antevs through G. Quimby, Chicago Natural History Museum.	4508 ± 680
519	*Cochise, Arizona (San Pedro)*: Charcoal from Cochise Site, San Pedro stage (Benson 5:10), Figure 8, Bed b. Submitted by E. B. Sayles, Arizona State Museum.	2463 ± 310
615	*Searles Lake:* Searles Lake, California, organic matter from mud seam separating upper and lower salt deposits of Searles Lake, believed to have been deposited by flood waters during last glaciation. Organic matter was extracted with acetone, evaporated to a thick syrup and the resinous material precipitated by adding water. Donor's Sample 2. Submitted by W. A. Gale, American Potash and Chemical Corporation, Trona, California.	At least 16,000
628	*Big Sur:* Charcoal from shell midden on California coast at mouth of Willow Creek about 30 miles south of Big Sur on coast of Monetery County. Midden overlain by 10 feet of gravels. Present beach gravels submerge 4.5 feet of midden, indicating shore subsidence. Submitted by R. F. Heizer, University of California, Berkeley.	1879 ± 250

G. NEVADA, OREGON, AND UTAH

221	*Gypsum Cave:* Dung of giant sloth from Gypsum Cave, Las Vegas, Nevada. Collected by M. R. Harrington in 1931 from Room 1, dung layer 6 feet 4 inches from surface. Submitted by M. R. Harrington through Ruth Simpson, Southwest Museum, Los Angeles.	$10,902 \pm 440$ $10,075 \pm 550$ *Av. 10,455 $\pm$ 340*
222	*Gypsum Cave:* Same from small room southwest of Room 1. Taken 2 feet 6 inches from surface.	8692 ± 500 8051 ± 450 8838 ± 430 *Av. 8527 $\pm$ 250*
281	*Leonard Rock Shelter, Nevada (Leonard Rock)*: Unburned guano from layer containing wooden artifacts in Leonard Rock Shelter, Nevada (LRS2). Submitted by R. F. Heizer, University of California, Berkeley.	8443 ± 510 8820 ± 400 *Av. 8660 $\pm$ 300*
298	*Leonard Rock Shelter, Nevada (Leonard Rock II)*: Atlatl foreshafts of hardwood (*Sarcobatus*, greasewood) from layer described in No. 281. Submitted by R. F. Heizer, University of California, Berkeley.	7038 ± 350

Our No.	Sample	Age (Years)
554	*Leonard Rock Shelter, Nevada (Leonard Rock III)*: Carbonized basketry from upper guano layer, Area C. Associated with infant burial. Submitted by R. F. Heizer, University of California, Berkeley.	2736 ± 500
554	*Leonard Rock Shelter, Nevada (Leonard Rock Baskets)*: Another portion of the carbonized basketry found in Leonard Rock Shelter cave and represented by No. 554, "Leonard Rock III," which gave 2736 ± 500. Submitted by R. F. Heizer, University of California, Berkeley. Comment: Earlier measurement must have been in error.	5779 ± 400 5694 ± 325 *Av.* 5737 ± 250
599	*Leonard Rock Guano*: Bat guano taken from immediately above the Pleistocene gravels in the Leonard Rock Shelter, Nevada. Submitted by R. F. Heizer, University of California, Berkeley.	11,199 ± 570
277	*Lovelock Cave, Nevada (Lovelock I)*: Burned guano from preoccupation level, Lovelock Cave, Nevada (LC4A). Submitted by R. F. Heizer, University of California, Berkeley.	4448 ± 250
278	*Lovelock Cave, Nevada (Lovelock II)*: Unburned guano, preoccupation level, Lovelock Cave (LC4B). Submitted by R. F. Heizer, University of California, Berkeley.	{6046 ± 300 {5961 ± 400 *Av.* 6004 ± 250
276	*Lovelock Cave, Nevada (Lovelock III)*: Vegetal material, earliest occupation level, Lovelock Cave (LCB). Submitted by R. F. Heizer, University of California, Berkeley.	2452 ± 280 2517 ± 320 *Av.* 2482 ± 260
587	*Humboldt Cave, Nevada (Humboldt)*: Basketry from Humboldt Cave in Nevada, excavated in 1936. This cave is some 10 or 12 miles west of Lovelock Cave. Submitted by R. F. Heizer, University of California, Berkeley.	1953 ± 175
247	*Mazama*: Charcoal from a tree burned by the glowing pumice thrown out by the explosion of Mount Mazama (this formed Crater Lake). This tree was found in a road cut above the Rogue River on Oregon Highway 230, about 10.5 miles toward Diamond Lake from the junction of Oregon Highways 230 and 62. The pumice is about 75 feet deep at this point, and about 40 feet of pumice overlies the portion of the tree from which these samples came. The impression was that the tree was still in very nearly an upright position. Collected and submitted by L. S. Cressman, University of Oregon.	6389 ± 320 7318 ± 350 5938 ± 400 6327 ± 400 *Av.* 6453 ± 250
609	*Danger Cave, Utah (Danger Cave I)*: Charcoal, wood, and sheep dung from Danger Cave, near Wend-	11,453 ± 600

Our No.	Sample	Age (Years)
	over, Utah. Found on old beach of Lake Stansbury, consisting of 2 feet of sand deposited on cemented gravels. Both sheep dung and wood were found in the sand layer. Above this several feet of later deposits lie. This sample was sheep dung from donor's Sample F 18 FS 535. Submitted by Jesse D. Jennings, University of Utah.	
610	*Danger Cave, Utah (Danger Cave II)*: Wood only from same location as No. 609.	$11,151 \pm 570$
428	*Fort Rock Cave, Oregon (Sandals)*: Several pairs of woven rope sandals found in Fort Rock cave, which was buried beneath the pumice from the Newberry eruption in Oregon. Though Mr. Cressman himself did not dig the sandals, he feels certain that the person who did gave the correct information. They are exactly like ones Cressman had dug but unfortunately had varnished, so that they could not be used for radiocarbon measurement. Submitted by L. S. Cressman, University of Oregon.	9188 ± 480 8916 ± 540 *Av. 9053 ± 350*
430	*Catlow Cave, Oregon:* Organic debris from Catlow Cave No. 1 in Oregon. Taken from 2.88-foot depth (No. 1-3025). Submitted by L. S. Cressman, University of Oregon.	$\{$ 1118 ± 190 798 ± 230 *Av. 959 ± 150*

H. MINNESOTA, WISCONSIN, AND WYOMING

Our No.	Sample	Age (Years)
496	*Bronson, Minnesota (Bronson Interglacial)*: Wood from a well, Bronson Station 1, 88 feet below surface in association with a wealth of plant material in a Preglacial spruce-tamarack forest. Collected by C. O. Rosendahl, Department of Botany, University of Minnesota (cf. *Ecology*, **29**, 291–96 [1948]). Submitted by W. S. Cooper, University of Minnesota.	Older than 19,000
497	*Moorhead, Minnesota (Moorhead Interglacial)*: Wood from Moorhead Station 2, Minnesota, late Pleistocene. May be associated with early history of Lake Agassiz (cf. *Ecology*, **29**, 289–90 [1948]). Collected by C. O. Rosendahl and submitted by W. S. Cooper, University of Minnesota.	$11,283 \pm 700$
334	*Minnesota Boreal (Boreal III)*: Peat from Jackson Camp, Minnesota. Taken from 8-foot depth in Pollen Zone B (pine period) by J. E. Potzger, Butler University, Indianapolis, Indiana. Submitted by E. S. Deevey, Jr., Osborne Zoological Laboratory, Yale University.	7586 ± 490 6866 ± 350 *Av. 7128 ± 300*
332	*Minnesota Boreal:* Peat from 8.5-meter depth in Cedar Bog Lake, Minnesota. Pollen Zone B. Collected by	7988 ± 420

Our No.	Sample	Age (Years)

M. Buell. Submitted by E. S. Deevey, Jr., Yale University.

308
365
366
536
537
Two Creeks, Wisconsin: Wood and peat samples from Two Creeks forest bed, Manitowoc County. Forest bed underlies Valder's Drift (Thwaites). Apparently the spruce forest was submerged, pushed over, and buried under glacial drift by the last advancing ice sheet in this region. Thought to be Mankato in age.

Sample	Collection	
308 (spruce wood)	L. R. Wilson, University of Massachusetts	$10,877 \pm 740$
365 (tree root)	J Harlen Bretz, University of Chicago	$11,437 \pm 770$
366 (peat in which root [365] was rooted)	J Harlen Bretz, University of Chicago	$11,097 \pm 600$
536 (spruce wood)	J Harlen Bretz and L. Horberg, University of Chicago. Collected several years later than 308, 365, and 366 in 1950.	$12,168 \pm 1500$
537 (peat)	J Harlen Bretz and L. Horberg, University of Chicago. Collected several years later than 308, 365, and 366 in 1950.	$11,442 \pm 640$
		Av. 11,404 ± 350

504 *Sand Island, Wisconsin:* Peat from Sand Island, Bayfield County. This unique peat dates the one outlet stage of the Nipissing Great Lakes. Submitted by L. R. Wilson, University of Massachusetts. 3656 ± 640

419 *Lake Butte, Wisconsin:* Glacial wood (cf. *Bull. Geol. Soc. Am.,* **54**, 136 [1943]) found between Appleton and Menasha, on the eastern shore of Little Lake Butte des Morts. Log protruded from a sloping bank of varved clay, perhaps reworked but older than the surface till of Valder's Drift. Appears flattened by pressure. Collected and submitted by F. T. Thwaites, University of Wisconsin. 5938 ± 300
6864 ± 300
Av. 6401 ± 230

302 *Sage Creek, Wyoming (Yuma):* Partially burned bison bone with high organic content, from Sage Creek, Wyoming. Yuma site of Eisely and Jepsen. Submitted by G. L. Jepsen, Princeton University. 6619 ± 350
7132 ± 350
Av. 6876 ± 250

I. SOUTH DAKOTA

454 *Angostura, South Dakota:* Charcoal from site in the Angostura Reservoir area. Horizontal zone 3.5 inches 7715 ± 740

Our No.	Sample	Age (Years)

thick mixed with clay (decomposed Pierre Shale). Sample 39FA65-203 from Square N7E4, Area B. Submitted by F. H. H. Roberts, Bureau of American Ethnology, Smithsonian Institution, Washington, D.C.

604   *Long Site, South Dakota:* Charcoal from the Long Site (39FA65) in the Angostura area of southwestern. The charcoal was taken from an oval-shaped unprepared hearth (Feature 14) 2.1 feet long and 1.5 feet wide in the west center of Square N3E3. Part also was taken from a small surrounding area. Donor's Sample 39FA65-417. Collected by Richard P. Wheeler in the summer of 1950 in the field party of Paul L. Cooper, River Basin Surveys, University of Nebraska. Submitted by Paul L. Cooper.   7073 ± 300

J. ALASKA

101   *Yukon, Canada (Johnson I):* Charcoal and charred-   1606 ± 180
102   wood samples from buried soil layer in the Yukon.   1460 ± 180
112   Submitted by F. Johnson, Peabody Foundation,   Av. 1533 ± 150
Phillips Academy, Andover, Massachusetts.

260   *Ipiutak, Alaska (Ipiutak):* Wood from the Ipiutak site   973 ± 170
at Deering, Seward Peninsula, Alaska. Third level in debris. Estimated date A.D. 0–500. Excavated by Helge Larsen, summer of 1949. Submitted by F. Rainey, University of Pennsylvania Museum, Philadelphia.

266   *Iptiuak, Alaska (Ipiutak II):* Wood from Grave 51 at   912 ± 170
Ipiutak. Described in Larsen and Rainey, *Ipiutak and the Arctic Whale Hunting Culture* ("Archeological Papers of the American Museum of Natural History," Vol. XLII). Submitted by Helge Larsen, University of Alaska, College, Alaska.

409   *Pre-Aleut, Aleutian Islands (Aleut I):* Charcoal from an   { 2920 ± 240
Aleut village site near the village of Nikolski on Uniak   { 3407 ± 520
Island. This particular sample was taken from a   Av. 3018 ± 230
depth of 433 cm. and is pre-Aleut in age. Submitted by W. F. Laughlin, University of Oregon.

299   *Fairbanks:* Wood found under 80–100 feet of frozen   Older than
muck in the gold diggings near Eva Creek, Fairbanks,   20,000
Alaska. Submitted by Wendell Oswalt, University of Alaska Museum, College, Alaska.

506   *Norton Bay, Alaska (Alaska II):* Charred wood from   1460 ± 200
middle levels, Iyatayet site, Norton Bay, Alaska. Excavated by Giddings in 1949. Submitted by F.

Our No.	Sample	Age (Years)

Rainey, University of Pennsylvania Museum, Philadelphia.

563   *Denbigh, Alaska (Denbigh Log)*: Base log from Paleo-Eskimo House 7–IYH7; Cape Denbigh, Iyatayet site. Submitted by F. Rainey, University of Pennsylvania Museum, Philadelphia. — 2016 ± 250

505   *St. Lawrence Island, Alaska (Alaska I)*: Spruce wood from Hillside (Okvik House), Gambell, St. Lawrence Island, Alaska. Excavated by Giddings in 1939. Submitted by F. Rainey, University of Pennsylvania Museum, Philadelphia. — 2258 ± 230

560   *Trail Creek*: Willows and charcoal from 80-cm. depth in Cave 9 at Trail Creek, Alaska. Submitted by F. Rainey, University of Pennsylvania Museum, Philadelphia. — 5993 ± 280

301   *Fairbanks Creek*: Wood from 30- to 60-foot depth on Fairbanks Creek, Fairbanks, Alaska. Associated with extinct mammal bones. Submitted by Wendell Oswalt, University of Alaska Museum, College, Alaska. — 12,622 ± 750

IV. MEXICO
(*Principal collaborator:* H. DE TERRA)

199   *Tlaltilco, Mexico (Mexico I)*: Charcoal from various burials at different depths at Tlaltilco. Early to middle Archaic Period. Collected by H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F. — 3407 ± 250

196   *Zacatenco I, Mexico (Mexico II)*: Charcoal from lowest sherd layer, associated with Zacatenco I pottery. Early Archaic Period, refuse heap at Zacatenco, Mexico. Collected by H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F. — 3310 ± 250

203   *Teotihuacán, Mexico (Mexico III)*: Charcoal from core of Pyramid of Sun, Teotihuacán, Mexico. The sample was taken in an excavated tunnel 65–110 meters from entrance below main center staircase. The core of pyramid contains late Archaic type pottery. Collected by H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F. — 2434 ± 500 / 1519 ± 200 / *Av. heterogeneous*

198   *Tlaltilco, Mexico (Mexico IV)*: Charcoal from preceramic level including "Chalco culture" artifacts in Rio Hondo terrace gravels at Tlaltilco. Collected by H. de Terra. Submitted by D. F. R. de la Borbolla. Museo Nacional de Antropología, Mexico, D.F. — 6904 ± 450 / 6017 ± 320 / *Av. 6390 ± 300*

Our No.	Sample	Age (Years)
200	*Cuicuilco:* Charcoal from pottery level below Pedregal lava near pyramid of Cuicuilco. Associated with pottery and figurines of late Archaic (Qicoman Phase type). Collected by H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F.	2422 ± 250
202	*Loma del Tepalcate, Mexico (Loma):* Charcoal from floor of stone structure, Loma del Tepalcate, late Archaic Period. Collected by H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F.	2565 ± 200
207	*Tamaulipas, Mexico (Pueblito):* Charcoal from top level of Site T174, state of Tamaulipas. Excavated from Square N25, La Perra or Pueblito Culture. Collected by R. S. MacNeish. Submitted by D. F. R. de la Borbolla. Museo Nacional de Antropología, Mexico, D.F., through H. de Terra.	505 ± 165 990 ± 220 *Av. 651 ± 150*
204	*Becerra Wood, Mexico:* Wood from Ciudad de los Deportes near Mexico City, Armenta Horizon associated with mammoth, horse, etc. Younger Becerra formation. Collected in 1944 by Arellano and H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F.	Older than 16,000
205	*Becerra Peat, Mexico:* Peat from same station as No. 204 but 500 meters east. Also from the Armenta Horizon. Collected in 1944 by Arellano and H. de Terra. Submitted by D. F. R. de la Borbolla, Museo Nacional de Antropología, Mexico, D.F.	11,003 ± 500
421	*Marl at Tepexpán, Mexico (Tepexpán I):* Stems and roots of aquatic plants extending from 48 to 70 inches from surface of marl into and through caliche layer beneath which fossil Tepexpán man was found. Collected and submitted by H. de Terra, Wenner-Gren Foundation, New York.	3800 ± 450 4430 ± 350 *Av. 4118 ± 300*
422	*Atetelco, Mexico (Sun Temple):* Charcoal from debris in south chamber of "painted patio," 1.40 meters above floor of patio. In association with Teotihuacán II style pottery. Submitted by H. de Terra, Wenner-Gren Foundation, New York.	{1878 ± 200 2611 ± 330 *Av. 2244 ± 180*
423	*Teotihuacán, Mexico (Sun Temple):* Wood from large pillar on exhibit at Teotihuacán. Excavated 1921 in "Ciudadela" at Teotihuacán, probably part of support for younger temple of Quetzalcoatl superimposed on older structure. Submitted by H. de Terra, Wenner-Gren Foundation, New York.	3424 ± 230

Our No.	Sample	Age (Years)
424	*Monte Negro, Mexico (Alban I)*: Charcoal from Temple X at Tilantongo, Oaxaca. Sample of collapsed roof beams of temple excavated with rubble from temple floor, Monte Alban I level. Submitted by Alfonso Caso, Instituto Nacional Indigenista, Mexico, D.F.	$\{ 2518 \pm 250$ $\{ 2680 \pm 200$ *Av. 2600 ± 170*
426	*Chachoapan, Mexico (Alban III)*: Wood from roof beams in tomb at Chacoapan, District of Nochixtlán, Oaxaca. "Corresponds with pottery of Monte Alban III-A type." Submitted by Alfonso Caso, Instituto Nacional Indigenista, Mexico, D.F.	1652 ± 185
425	*Monte Alban, Mexico (Monte Alban II)*: Charcoal from Well of Offering No. 3, Mound II (Temporada XII), Monte Alban, Monte Alban II level. Submitted by Alfonso Caso, Instituto Nacional Indigenista, Mexico, D.F.	2223 ± 145

V. SOUTH AMERICA

(*Principal collaborator:* J. B. Bird)

321 318 316 315 313	*Huaca Prieta, Peru (Chicama)*: A series of samples from Huaca Prieta Mound 3, which is preceramic. Collected and submitted by J. B. Bird, American Museum of Natural History, New York.	

Sample	Level (Depth in Feet from Top)	
321 (12) (plant material)	HP-D; 6	2966 ± 300
318a (9) (wood)	HP3-J2; 22	1989 ± 196
318b (9) (wood)		3550 ± 600
316 (7) (wood)	HP3-M; 30	4380 ± 270
315 (6) (shell)	HP3-M; 30	3572 ± 220
313 (4) (wood)	HP3-Q1; 36	4257 ± 250

Comment: First sample (No. 318a) looks incorrect.

362	*Huaca Prieta, Peru (Chicama VII)*: Sample of cattail roots from Layer K-2 of Huaca Prieta Mound 3. Should be between Nos. 316 and 318. Submitted by J. B. Bird through H. C. Cutler, Chicago Natural History Museum.	4044 ± 300
598	*Huaca Prieta:* Charcoal from the lowest occupation level of Huaca Prieta Mound 2, found directly on bedrock by Constante Larco, under the direction of J. B. Bird. Submitted by J. B. Bird, American Museum of Natural History, New York.	4298 ± 230
75	*Huaca Prieta, Peru (Peruvian)*: Algaroba wood from roof beam section of subterranean house found in Huaca Prieta Mound 5 at the level of first appearance of maize and Cupisnique pottery, Chicama Valley,	2665 ± 200

Our No.	Sample	Age (Years)
	Peru. Collected and submitted by J. B. Bird, American Museum of Natural History, New York.	
322	*Huaca Prieta, Peru (Chicama IV)*: Wooden digging stick from House No. 2 of Huaca Prieta Mound 5. Should be more than 100 years older than Cupisnique (No. 75). Submitted by J. B. Bird, American Museum of Natural History, New York.	$\{$ 3278 ± 250 $\{$ 3333 ± 340 Av. 3310 ± 200
323	*Huaca Prieta, Peru (Peruvian Rope)*: Rope in excellent condition from cache in lowest layer (D) of Huaca Prieta Mound 1. Associated with early Negative (Gallinazo) pottery. Submitted by J. B. Bird, American Museum of Natural History, New York.	2632 ± 300
382	*Moche*: Ash mixed with bone from Moche site at Huaca del Sol, northern Peru. Taken from habitation site, ground level, beneath pyramid on north face in center. Associated with Mochica sherds. Collected and submitted by G. Kubler, Yale University.	2823 ± 500
619	*Virú Valley, Peru (Mochica Rope)*: Rope from a late Mochica burial at Huaca de la Cruz in the Virú Valley. Associated pottery indicates it dates from the latter part of the Mochica period as recorded in the Virú, the first valley south of Moche. Submitted by W. D. Strong, Department of Anthropology, Columbia University, through J. B. Bird, American Museum of Natural History, New York.	1838 ± 190
271	*Paracas Necropolis, Peru (Paracas)*: Cotton cloth from the mummy brought to New York in 1949 by Dr. Rebecca Carrion, National Museum of Anthropology and Archaeology, Peru. From Paracas Necropolis. Submitted by J. B. Bird, American Museum of Natural History, New York.	2190 ± 350 2336 ± 300 Av. 2257 ± 200
460	*Nazca Valley, Peru (Nazca I)*: Sections of four darts, distal ends painted black, three hard and whipping at end. Cahuachi, Nazca Valley, Section Aj, Location A, Grave 10, Nazca A Period. Excavated by A. L. Kroeber. Specimen 171210, Chicago Natural History Museum. Submitted by D. Collier, Chicago Natural History Museum.	1314 ± 250
521	*Nazca Valley, Peru (Nazca II)*: Wood fragments of Atlatl shaft from Grave 12, Location A, Section Aj, Cahuachi, Nazca Valley. Nazca A Period. Catalogue Nos. 171245 and 171246. Should be contemporaneous with Paracas mummy. Collected by A. L. Kroeber and submitted by D. Collier, Chicago Natural History Museum.	$\{$ 1681 ± 250 $\{$ 2477 ± 200 Av. 2211 ± 200 Av. including No. 460 1988 ± 200

Our No.	Sample	Age (Years)

378 *Chincha, Peru (Chincha)*: Guano from North Chincha Island found beneath 3 feet 6 inches of wind-borne sand at Quebrada del Panteon by G. Kubler, Department of History of Art, Yale University. Submitted by G. Kubler.

Older than 19,000

484 *Mylodon Cave, Chile (Chilean Sloth)*: Dung of giant sloth from Mylodon Cave, Ultima Esperanza, Chile (51°35′ S.). Not associated with human artifacts, though sloth and man found together in three caves 125 miles distant (cf. No. 485). There is an as yet undetermined correlation with the last ice advance in Patagonia. Submitted by J. B. Bird, American Museum of Natural History, New York.

$\{$ 10,800 ± 570
$\{$ 10,864 ± 720
Av. 10,832 ± 400

485 *Palli Aike Cave, Chile (Chilean Bone)*: Burned bone of sloth, horse, and guanaco, associated with human bones and artifacts. Valuable in determining time of arrival of man at tip of South America. Material found in Palli Aike Cave, 125 miles east of Mylodon. Submitted by J. B. Bird, American Museum of Natural History, New York.

8639 ± 450

VI. TREE-RING SAMPLES

103 *Broken Flute Cave, New Mexico (Tree Ring)*: Douglas Fir wood excavated by Morris in 1931 from Red Rock Valley, Room 6, Broken Flute Cave. Inner ring A.D. 530; outer ring A.D. 623. Submitted by T. L. Smiley, Laboratory of Tree Ring Research, University of Arizona, Tucson.

973 ± 200
1070 ± 100
Av. 1042 ± 80

159 *Sequoia*: Wood from the heart of the giant redwood known as the "Centennial Stump" felled in 1874, with 2905 rings between the innermost (and 2802 rings between the outermost) portion of the sample and the outside of the tree. Therefore known mean age was 2928 ± 51 years. Submitted by E. Schulman, Laboratory of Tree Ring Research, University of Arizona, Tucson.

3045 ± 210
2817 ± 240
2404 ± 210
Av. 2710 ± 130

VII. OTHER AREAS

548 *Ubayama Shell Mound, Japan (Japanese)*: Charcoal from Ubayama shell mound, about 10 miles west of Tokyo, Japan. Charcoal was part of structural remains in a house area in the bottom levels of the mound. Found in fall of 1948. Thought to be oldest house site in Japan. Submitted by Ralph D. Brown, 26 West Rustic Lodge Avenue, Minneapolis, Minnesota. Similar sample submitted by Lieutenant Colonel H. G. Schenck. This sample was not measured.

4850 ± 270
3938 ± 500
Av. 4546 ± 220

Our No.	Sample	Age (Years)
603	*Ubayama Shell Mound, Japan (Late Jomon)*: Charcoal collected by Father Groot from the early Late Jomon (Horinouchi Stage) horizon at the Ubayama shell mound (cf. No. 548) in Japan. Submitted through H. L. Movius, Harvard University.	4513 ± 300
580	*West Africa:* Carbonized wood from a late Upper Pleistocene deposit at Mufo, Angola, Portuguese West Africa, associated with a Lupembian stone blade (late Stone Age). Found on the eastern bank of the Luembe River (7°38′ S.; 21°24′ E.). Stratigraphy was gray-white sand at surface 2.50 meters thick. At the base of this the Lupembian (late Stone Age) backed blade was found in mint condition, unworn and associated with the carbonized wood measured. Next below the sand was a gravel layer 65 cm. thick; next a ferritized gravel layer 5 cm. thick; then a gravel layer identical with the second layer from the surface. This was 10 cm. thick and rested on the bedrock of mica schist. Submitted by J. Janmart, Museo do Dundo, Comparrhia de Diamantes de Angola, Dundo-Lunda, Angola, through H. L. Movius, Harvard University.	11,189 ± 490
581	*West Africa:* Carbonized wood found 15 cm. down in the gravel layer underlying No. 580. Submitted by J. Janmart through H. L. Movius, Harvard University.	14,503 ± 560
540	*Hawaii:* Charcoal from earliest Polynesian culture in Hawaii. Found in Kiliouou Bluff Shelter, Kuliauaw, Oahu Island, by Kenneth P. Emory, Bernice P. Bishop Museum, Honolulu 17, Hawaii. Submitted by K. P. Emory.	946 ± 180
600	*Australia A:* Aboriginal kitchen midden charcoal from Australia, taken from Goose Lagoon, western Victoria, on property called "Leura" east of Goose Lagoon. The midden was on the north side of the acolianite region and toward its east end, about 15 feet above the alluvium flat. Collected by Edmund D. Gill, National Museum of Victoria, Melbourne. Submitted by H. L. Movius, Harvard University.	1177 ± 175
601	*Australia B:* Aboriginal kitchen midden charcoal from Australia, taken from Koroit Beach at Armstrong's Bay, northwest of Warrnambool, Victoria. Collected by Edmund D. Gill, National Museum of Victoria, Melbourne. Submitted by H. L. Movius, Harvard University.	538 ± 200

Our No.	Sample	Age (Years)
606	*Waterton, Canada:* Western Alberta, Canada, glacial forest bed in northwest quarter, Sec. 8, T. 2 R. 29 at Waterton (cf. Waterton Lakes topographic map). Stratigraphy: Top soil 1 foot; gravel 12 feet; lacustrine clay ½ foot; gravel 2 feet; sandy silt with invertebrate fossils 2 feet; forest bed 2 feet; dark-brown Kewatin drift 9 feet. This sample was wood. L. R. Wilson, University of Massachusetts, says it is black and white spruce. The ecology is similar to that at edge of tundra now. Submitted by Leland Horberg, University of Chicago.	3261 ± 250
607	*Waterton Peat:* Same as No. 606, except peat instead of spruce wood.	3327 ± 320
629	*Manchuria (Seeds):* Ancient Manchurian lotus seeds, still fertile. Collected by Ichiro Ohga in the Pulantien Basin of southern Manchuria in a peat layer presumably of Pleistocene age; uplift and erosion had exposed the layer on the walls of the Pulantien River Valley. Ohga germinated several hundred seeds, either filing the thick outer shell or soaking in concentrated sulphuric acid for 1–5 hours. Genus *Nelumbo*, similar to the Indian lotus *N. nucifera*. Submitted by R. W. Chaney, University of California, Berkeley.	1040 ± 210

CHAPTER VII

THE SIGNIFICANCE OF THE DATES FOR ARCHEOLOGY AND GEOLOGY

By FREDERICK JOHNSON

ARCHEOLOGISTS, geologists, and palynologists are continually searching for the means of improving methods of counting time. The commonly available relative chronologies lack precision and direct correlation with the calendar, except when they may be checked with old written records or with a few more definite systems, for example, the calendar based on tree-ring counts. The latter kinds of methods, however, have definite regional and temporal limitations. Despite such difficulties, dates of varying reliability can be assigned to all major events and a large proportion of minor ones included in the subject matter of the several fields. The error in these dates varies from ± 150 years or less, as those of the Near and Middle Eastern civilizations where written records supplement archeological data, to geological estimates of Pleistocene events the errors of which are often ± 30 per cent or more. The possibility that the radiocarbon method might increase our knowledge of chronology was heartening, but this was tempered by the realization that the archeologically and geologically dated materials used in developing the method were not precise and that some were actually subject to question. The results were surprisingly consistent, and our early qualms were unjustified. In general, series of dates having reliability which can be supported by archeological or other investigations have been, with puzzling exceptions, substantiated by the radiocarbon method. The agreement between radiocarbon and other methods on dates which are not so well documented is quite erratic. However, on the whole the results are very satisfactory, and the "failures" simply present problems requiring attention.

Libby and his associates asked archeologists and geologists for materials of a nature which no one dreamed would ever be useful. Furthermore, precautions preventing contamination of samples by

extraneous radiocarbon had rarely been taken. The kind of sample needed is relatively rare in many archeological collections, for formerly the bulk of this sort of material, once its presence had been recorded, was often discarded in the field. Furthermore, all too frequently an otherwise acceptable sample might be an ancient tool, an example of some product of industry or a work of art. The excavator retained and preserved with various preparations such artifacts for a definite purpose. In large measure these conditions are responsible for the lack of adequate series of samples from important regions. However this may be, sufficient material has become available through the interest and generosity of a large group of people and institutions, and it is satisfactory for preliminary discussion. Its importance in relation to the method itself has been amply described by Dr. Libby. Here we will offer a brief discussion of the results in relation to archeology, geology, and palynology.

In making initial plans, the Committee on Radioactive Carbon 14 decided that the collection of such a wide range of samples could best be controlled if they were collected in groups. The committee, rather arbitrarily, selected particular but broad problems which had been under investigation. The primary purpose was to aid in the development of the method. However, it was hoped that significant chronological data, useful in many ways, would be produced. An archeologist was requested to take charge of each problem, collect through his colleagues appropriate samples for Libby, and in the end prepare a report on the results. Geological problems were assigned in a single group which was expanded to include palynological samples. The series of archeological reports have been published under the auspices of the committee in *Radiocarbon Dating*, assembled by Frederick Johnson ("Society for American Archaeology Memoir," No. 8 [July, 1951]). The discussion of the geological and palynological data appears in Richard Foster Flint and Edward S. Deevey, Jr., "Radiocarbon Dating of Late-Pleistocene Events," *American Journal of Science*, **249**, 257–300 (1951). The following remarks are brief discussions of a few representative series of dates selected from the above publications. These series have been chosen for the purpose of indicating the character of the results, particularly from the point of view of a particular field or problem.

Judgment concerning the accuracy of a date depends upon a num-

ber of factors. Considering the radiocarbon method alone, a date is satisfactory if it is in agreement with calculated values. On the other hand, the age of many samples submitted by archeologists and others is known within certain limits, having been determined by other means. Disregarding contamination, undetected laboratory errors, and other extraneous factors, it may be observed that, when a valid radiocarbon date disagrees radically with an archeological date, we are faced, temporarily we hope, with a dilemma. There are a number of these in the list, and the reasons for the discrepancies cannot be explained. Because of the nature of the results, there is an understandable tendency to give greater credence to values obtained by the method rather than to ages determined by methods available to archeologists, geologists, and palynologists. It must be emphasized, however, that, in spite of the lack of precision in all cases, many archeological and other dates are based upon evidence the validity of which is at present impossible to refute. A very brief summary review of some salient points will provide some background for such a statement.

The time scales used by geologists, palynologists, and archeologists are, with rare exceptions, based upon stratigraphic sequences. Dates given in numbers of years for levels in a stratification are often misunderstood, and they can be misleading. With some exceptions such dates are but convenient ways to indicate the estimated age, and a relatively large probable error is implied if not stated. Actually a date from one level indicates only its relationship to those above and below. The location of samples in a series of levels in the ground or distributed over historically identifiable surfaces of the earth establishes chronological relationships between the samples. Knowledge of the extent of this relationship varies with the character of subsidiary information which may be derived from a study of the characteristics of the several levels. As has been said so often, materials from the lowest strata are older than materials from higher ones, provided of course that the whole deposit has not been overturned or otherwise disturbed. It may be added that, where superimposition is not directly observable, it may often be accurately deduced, so placing in sequence nonoverlapping strata which may even be located in areas widely separated horizontally. Although general principles governing such deductions are commonly known, there

are instances, often due to lack of fact, where chronologies based upon series of strata vary in degree of accuracy.

An adequately documented relative chronology of a sequence of geological or archeological events can be relied upon at the very least to indicate the order of events. Frequently reliable inferences concerning relative time intervals between events may also be made. However, when it is necessary to correlate events in one such sequence with those in another, inferences of contemporaneity or succession must be made with care. Such are not dependable unless supporting evidence indicates strong probability. In the earth sciences, archeology, etc., such inferences are frequently made, and at times they are highly useful when properly considered. Regardless of these difficulties with relative chronologies, provable and, in large measure, inferred sequences supply a background for the determination of chronology even though the results are not precise in terms of a limited number of years in the Christian calendar.

Perhaps because archeology, a relatively young science, is only approaching a stage permitting the definition of basic principles governing the determination of the chronology of human existence, investigators may be said to be experimenting with methods. During the last 20 or 30 years, in America at least, various ways of counting time during the past 5000 years or so have been invented, discarded, or reorganized and improved. This inevitably confuses nonarcheologists, especially in instances where discussions of sequences of events refer to specific materials and their provenience and fail to mention clearly differences of opinion concerning the derivation of chronological factors.

There are two general kinds of problems. One involves especially the older remains of man where archeological materials can be assigned relative dates of varying degrees of reliability through collaboration with geology, palynology, and other overlapping fields. The second is more frequently concerned with later cultural material found in situations having physical characteristics which are almost wholly due to the fact of human occupation. In such locations stratification is present, but it is frequently impossible to identify it. Consequently, archeologists augment scarce definite stratigraphic data with inferences from internal evidence, such as the evolution of styles of pottery, changes in the form of tools, the shape of houses, etc.

The resulting chronological framework is of course very insecure and is recognized as such by any reputable archeologist. The use of such must strain the credulity of investigators in allied fields, especially those in possession of more precise data. Be all this as it may, certain points in the relative time scale for recent human development in North America have become rather firmly established, not perhaps by logical proof, as in exact science, but rather by the sheer weight of confirmatory evidence. In other words, the probability of their accuracy is so strong that the possibility of error is slight indeed. Unfortunately, no suitable statistical expression of this can be made. Other dates, "guess dates" they are called in archeological jargon, are subject to controversies. These cannot be resolved at the present time, but they may be reduced by a process of elimination so that either ranges of error of these dates or hypothetical and sometimes multiple locations upon a time scale may be suggested. It is inevitable that further archeological research will bring to light evidence which will remove much of the uncertainty from these estimates.

Above all, the radiocarbon method gives promise that it will be a, a tool useful in shortening the process of establishing the time when many events in human prehistory took place. However, if present conclusions are correct, the ordering of these events cannot be accomplished by the radiocarbon method alone, at least until such time as a number of uncertainties can be clarified. The results must be checked and revised in the light of unassailable stratigraphic fact. This need for careful cross-checking leads to a collaboration between the several fields which, as it is carried out, will inevitably result in further development of the radiocarbon method and vast improvement in the recording and interpretation of the provenience of the samples.

The group of samples having "known" dates came from archeological sites in the Near and Middle Eastern regions. The accuracy of these archeological dates ranges from about ± 50 to ± 150 years, such errors being due largely to lacunae in the existing records. It is also true that the beginning of recorded history of the several areas in the region varies over a range of some 900 years. However, comparative archeology, using in large measure records and sequences of events in Egypt and Mesopotamia, makes it possible to establish a

rather reliable regional chronology extending backward in time for some 5000 years.

Four of these dates have been plotted on Figure 1. The date "Zoser" (No. 1) is the only one of these which in the range of 1σ is unacceptable to archeologists, for it is much too late. While statistical probability indicates general consistency of this date with the others in the series, the range of 2σ is too large to permit useful comparison with archeologically derived figures. Of the seven remaining dates from the same region, one (No. 115) is about 800 years too late. However, the sample is suspect because of doubts concerning the status of the period it is assigned to. Also there is a possibility that its provenience on the sloping side of a mound has been misinterpreted. Because of these uncertainties, this sample probably should not have been submitted at this time. The date of another sample (No. 183) is too late, but the archeological date could well be in error. A third date (No. 113) is comparable only to an archeological date, the error of which is as yet undetermined. Excepting the Zoser sample, dates on other samples, referable to dynastic Egyptian sequences and records, are in good agreement with archeological opinions. Comparing archeological and radiocarbon dates without regard for statistical factors, especially the counting error, imposes rather strict limitations. Even so, the agreement between the two systems is remarkable, especially for such a small series.

The determination of the chronology of rise and fall of civilizations in the Near and Middle Eastern regions is complicated by many factors not the least of which is the size of the cities which flourished over long periods of time. Changes in town planning and repair and rebuilding of houses and palaces increase the difficulty of determining stratigraphy. In general, however, the good agreement of the dates implies confirmation of a number of present archeological opinions concerning chronology. Where questions do arise, it is notable that the archeological data are uncertain. There is little doubt that, as a whole, the results of radiocarbon measurement are quite satisfactory.

It was not until 1927, when a type of fluted arrowpoint called Folsom was found in association with an extinct animal, that it became generally admitted that the human occupation of North America was at all ancient. Since that time the study of "Early

Man" has greatly expanded the horizon. It has been discovered that the culture of which the Folsom arrowpoints were a part is widely distributed in the continent. In addition, evidence of old human occupations other than Folsom has come to light. Many of the levels in which evidence of these occupations is found can be associated with geological events and hence may be referred to a geochronological time scale of the Pleistocene and Late Pleistocene. The difficulty has been that, in spite of general agreement concerning sequences of strata, estimates of age by several authorities for various features have not always agreed, sometimes by as much as 15,000 years. Another problem involves the correlation of deposits in the north, where glacial phenomena are present, with deposits south of the range of glacial ice which are identifiable through the effects of climatic and other factors. Similarly there is the problem of correlation of deposits on either side of the Rocky Mountains.

The radiocarbon dates from these early American sites on reliable samples are actually too few to justify conclusions. However, the consistency of them, as a whole, may well indicate what the future has in store. In general, the oldest known remains, especially Folsom, appear to be about 10,000 years old (e.g., No. 558, 9883 ± 350 years). The age of another group of artifacts, Yuma arrowpoints, has been subject to some controversy. Dates determined from locations in Wyoming (No. 302, 6876 ± 250), South Dakota (No. 454, 7715 ± 740), and elsewhere may well constitute proof, otherwise lacking clarity, that Yuma is younger than Folsom. In any case, the suggested sequence is in good agreement with facts available even though these lack precision.

The age of the Cochise culture which was distributed over the Southwest (Nos. 511, 515, 518, 519, 556) is acceptable even though it requires revision of some not-too-well-documented contentions that Cochise is older than Folsom. In Nevada the age of layers in the Leonard Rock Shelter, ranging from 8660 ± 300 years (No. 281) to 5737 ± 250 years (No. 554) (cf. also No. 298), does no violence to present estimates, except that the accepted date for No. 554 (5737 ± 350) may indicate that the Altithermal period in this region began closer to 4000 B.C. than to 5000 B.C., as formerly estimated. The eruption of Mount Mazama in Oregon was an event of major importance, and the ash layer it produced has become a chronological landmark

used by a number of fields. Previous estimates, including revisions by several investigators in as many fields, of the time when this took place have ranged from 4000 to 15,000 years. If the radiocarbon date, 6453 ± 250 (No. 247), is substantiated by additional measurements, chronologies for the region can be corrected and correlated.

The age of a recent discovery, Tepexpán Man, in the valley of Mexico is presumed to be about 11,003 ± 500 years by the excavator. His conclusion is based on the determination of the age of the peat deposit associated with the skeleton (No. 205). However, the available archeological and geological information, although sufficient to justify attempts at dating, is not definitive in all details. To some extent this is borne out by comparing Nos. 205 and 204. The latter, a piece of wood from the same deposit, is "older than 16,000 years." Undoubtedly Tepexpán Man is an "Early Man," but, before his exact place in the scheme of things can be accepted with confidence, additional dates and more definite data must be secured.

Lack of opportunity has prevented extensive search for older occupations in South America. However, samples from caves in Chile in the neighborhood of the Straits of Magellan were measured. Here suggestion of possible human occupation some 9000 years ago may be made. Of even greater significance is the tenuous support of a hypothesis that similar geological and climatic developments were synchronous with those of Europe and North America.

A detailed discussion of the items listed above and the inclusion of a number of dates which have been omitted here would pose questions concerning some of the radiocarbon results. A few dates are obviously in error, but in almost every case there are possibilities of contamination or uncertainties concerning identification. For example, the record of the material from Medicine Creek, Nebraska (Nos. 65, 108a, 470), is equivocal. Of greater interest are questions concerning lapses of time. For example, the dates indicate the somewhat startling possibility that a type of Yuma point may have been made and used over a period of some 3000 years. Similarly, the Cochise culture appears to have flourished without great change for some 4000 years. These are simple hunting and gathering cultures of a type which does not change rapidly. However, in shortening the whole time span of human occupation in North America, as the radiocarbon method has done, and indicating that some cultures did

not become modified over such lengths of time, it becomes necessary to assume that in later times the rate of cultural development speeded up more rapidly than is generally believed. Nothing prevents such an assumption, of course, but many more chronological data documenting the earlier and later periods are necessary before the process may be fully understood.

The consistency in the archeological and geological dates is of considerable interest and significance. In one way or another and with varying degrees of reliability, the chronology of Early Man in North America is tied to the Mankato glaciation. The advance of the ice occurred about 11,000 years ago, a date which is derived from measurements on five samples taken from the Two Creeks forest bed in Wisconsin (Nos. 308, 365, 366, 536, 537). Previously this maximum advance had been assumed to date from about 25,000 years ago. The occupation we have been discussing took place subsequent to the advance, and the new dates indicate a shorter span of time between the occupation by Early Man and the later peoples. This revising upward of these dates may indicate that geological developments were speedier than formerly supposed. Also this increases the possibility that some migration routes in North America were located very near the ice front. This revision partially closes a gap between the older and younger cultures which has sorely puzzled archeologists for some fifteen years. An additional idea finds its origin in the dates. The materials from Oregon, Nevada, California, New Mexico, Texas, and perhaps Mexico and South America appear to have existed during a broad period now some 10,000 years old. Even at that time, different culture patterns were present. If the Indians of North America had a single origin, we can postulate that it was earlier, that is, during the Interstadial period or before. If not, the implication that culture change was slow leads to a number of somewhat tenuous working hypotheses such as: a single migration route into the continent was crowded with people bearing a curious mixture of culture traits; early diversion of peoples from a single source, say, the Bering Strait region, into several subsidiary routes led to the rise of different cultures; the possibility of several major routes of migration into the continent in what is believed to be very early times.

It is recognized that, barring undetected laboratory errors, satis-

factory measurement of an uncontaminated sample poses no problem
as far as the method itself is concerned. The interpretation of the re-
sults is a different matter; it involves questions of judgment, espe-
cially at the present stage. It has not yet been possible to devise a
means of fully determining the validity of a sample, that is, whether
or not the materials are what they are believed to be and whether
they may be used for dating or for any other purpose. When a few
dates correlate satisfactorily with other estimates of age, the con-
clusion that they are valid naturally is quickly formed, and con-
sideration of possibilities of error is neglected. When one or two
dates in an otherwise satisfactory series are out of line with present
ideas, there is pause for thought. Of even greater concern are con-
tradictory dates. There is no way at the moment to prove whether
the valid dates, the "invalid ones," or the "present ideas" are in
error. Under other circumstances more rigorous statistical tests
would help select the more accurate groups. However, the two sys-
tems of dating are based on rather different principles, and so it
seems that confidence in the final results can depend only upon a
much more extensive correlation of additional series of measure-
ments. Until the number of measurements can be increased to a
point permitting some explanation of contradictions with other ap-
parently trustworthy data, it is necessary to continue to form judg-
ments concerning validity by a combination of all available informa-
tion.

Dr. Libby has been able to remove from some samples much radio-
active carbon 14 which was not contemporaneous with the samples.
It is certainly gratuitous to suggest here that more investigation of
the whole complicated problem of contamination will probably aid
materially in the development of the method. There are other fac-
tors in connection with the samples; for example, the manner of col-
lection is of prime importance. It is necessary to attend to slightly
different details than has been customary in archeology and, pre-
sumably, in geological work. Observations on specimens in excava-
tions have varied, and always will vary, with the circumstances.
However, samples intended for radiocarbon measurement must often
be recorded more accurately than has been necessary heretofore.
Unless this is done, the results of measurements are confusing, some-

times in the extreme. One example of such confusion arose during the present research through initial lack of knowledge or understanding by archeologists of the many insidious sources of contamination and of the effect poorly recorded samples would have upon the results. The committee hoped that some cross-checking of dates and other information would add weight to important hypotheses concerning the age and distribution of the Adena and Hopewell cultures, which are spread throughout the Mississippi Valley and east along parts of the Atlantic Coast.

The Hopewell-Adena problem has not been satisfactorily solved by archeologists. However, there is general agreement among workers that available evidence proves beyond reasonable doubt that Adena preceded Hopewell. Dates on nine samples (Nos. 126, 136, 137, 139, 143, 150, 151, 214) directly contradict this evidence. Furthermore, the dates suggest distributions of these cultures over periods of time and in a manner which, if true, requires an almost complete revision of archeological concepts of recent human developments in eastern North America. It is entirely possible that a new and accurate method of measuring time can very well do this. However, it cannot be done to the extent of reversing a number of well-substantiated stratifications. At the moment, the Hopewell and Adena dates appear to do this. As we look at these dates, however, it seems possible that one or two may be valid archeologically. That is, Hopewell may well be older or Adena younger than inferences from relative archeological sequences suggest. However, it seems certain that both these possibilities cannot be true.

An inspection of the record reveals much of the cause of the present trouble. Three of the samples were collected in 1891; their history since then is not known. There is some question concerning the provenience of three other samples and their history since collection in the early 1930's. The remaining three samples appear to be dependable, but, unfortunately, even these contradict the idea that Adena is older than Hopewell. On the basis of these three dates, one may postulate an overlap in the period of occupation of the sites from which these three samples came, but this requires that the places were coexistent during a period of about 1000 years. Available data do not support such an assumption. At present there is no clue

to the source of these disagreements. The discordant note caused by the measurement of these samples is indeed unfortunate, particularly at this stage. Actually the unsuitable nature of most of these samples renders valid judgment of the results impossible.

The rise and fall of civilizations in Peru have long been of major interest to Americanists, who have revised or amended ideas concerning chronology as rapidly as excavations produced appropriate data. A long sequence beginning with rather well-advanced hunting cultures, and ending in the mid-sixteenth century with the climax of the Spanish conquest, is best known from the northern coast of Peru. The earlier, and sections of the later, parts of the sequence were clarified considerably by recent excavations in the Virú Valley. Excavations in ruins of large cities and mounds of debris from human occupations have made it possible to describe periods when the prehistoric people emphasized different interests and abilities during their long history. One way this has been expressed by archeologists is by naming levels in a stratigraphic column beginning with Hunters and continuing upward with Early Farmers, Cultists, Experimenters, Master-Craftsmen, Expansionists, City Builders, and Imperialists. From characteristics of the strata, it has been inferred that these periods lasted different lengths of time. The determination of the actual number of years for each one of these periods is an important but difficult and complicated problem, for points in a time scale have to be inferred from observations upon the size and extent of strata, the origin and development of ideas by the prehistoric peoples, the distribution of cultural features, at least throughout the Andean region, etc. Just previous to the radiocarbon measurement of some twenty samples from South America, a rather new estimated time scale had been generally accepted, even though a number of points on this were, and still are, being actively debated. Some of the radiocarbon measurements agree with these estimates rather well, but others, particularly the later ones, are believed by some to be open to serious question. In spite of these doubts, and in view of the lack of precision of the comparative data, the dates are surprisingly consistent. Regardless of archeological problems, of a series of eight dates, "five out of eight fall within one sigma and the other three within two sigma. Two of these are barely out of the one sigma range.

None falls outside of two sigma. This result is very close to the statistically expectable one."[1]

These dates have been the subject of extensive analysis by Junius Bird,[2] who has compared the dates within the range of 1σ in an attempt to equate the most probable figures with the known stratigraphy. This procedure indicates, if nothing else, that in some cases longer counting periods are essential, and probably additional samples from a single layer in a mound will have to be measured in order to reduce the error appreciably so that the results may be comparable in detail to meticulously recorded information from the stratification. Study of Bird's remarks is recommended. In the meantime, and to illustrate an example of one kind of situation, we may look at two dates, the means of which are not in harmony with the positions of the samples. Number 313 (4257 ± 250 years) lay below No. 316 (4380 ± 270), being separated from it by 1.45 meters of ash and occupational debris. This debris must have accumulated slowly, but there is no way of estimating the time involved except to make what is believed to be a conservative guess that it was built up in something over a century. This figure is partially supported but not at all substantiated by comparisons of other dates. To arrive at possible spans of time, in which the age of the samples may actually be located, comparison with various other samples locates the age of No. 313 between years 4507 and 4210 and No. 316 between 4407 and 4110. Number 598 appears to support the date of No. 313, and so it seems most likely that the date for No. 316 may fall in the upper portion of its range, that is, perhaps between 4157 and 4110. Such a manner of figuring will arouse the ire of the statistically minded. However, if the dangers of such procedure are fully recognized, it becomes possible to adapt the results of radiocarbon measurement to an archeological problem based upon adequate stratigraphic information. In this case, for example, the series is sufficiently large, and it is closely tied to a particularly detailed stratification. The manipulation of the figures provides a better-founded estimate of two dates than was previously possible.

1. *Radiocarbon Dating* ("Society for American Archaeology Memoir," No. 8 [1951]), p. 47.

2. *Ibid.*, pp. 37–49.

Problems similar to those encountered by archeologists were common in geology and palynology. Aside from errors which cannot be explained as yet, the fixing of samples in stratifications is sometimes attended by doubts leading to questions concerning the validity of the dates relative to a geochronological time scale. Nevertheless, the results are consistent in themselves, and, upon justifiable adjustment of previous estimates, they agree with opinions rather generally held.

As a rule, strictly geological dates have a much greater "probable error" than archeological ones. Because of this, only their internal consistency can be used in judging the accuracy of the results. On the other hand, the radiocarbon measurements seem to check and expand upon present geochronological time scales. Through the study of the pollen in numerous levels identified in part by geological and archeological means, a series of postglacial periods or "zones" have been described. Although the dates sometimes assigned to some of these zones are often tenuous inferences, evidence of the validity of the relative chronology is accumulating. This kind of extremely painstaking research began in Europe, and the results in the Old World are more extensive than in the New. However, in recent years much progress has been made, especially in North America, so that definitive, if incomplete, data exist for a number of regions.

As mentioned above, the Mankato maximum in Wisconsin was probably attained about 11,000 years ago. "Four samples from the Allerod horizon in Germany, England and Ireland give an age averaging about 10800 years ago. As this horizon (Zone II of European pollen stratigraphers) underlies solifluction deposits assigned to the Fennoscandian glacial substage, the essential agreement of the dates implies that deglaciation of northern Europe was contemporaneous with that of North America."[3]

Concerning the palynological series, Flint and Deevey make the following cogent comments in an abstract of their report:

The meaning of a number of dates for post-Mankato-maximum events can be assessed only in the light of the pollen chronology. As this chronology is a relative one, based on climatic changes and vegetational responses during deglaciation, its calibration will require samples from many more localities. All of the dates are of the right order of magnitude, with a few exceptions where it seems likely that the stratigraphic position of the sample, and not the radio-

3. Flint and Deevey, "Radiocarbon Dating of Late-Pleistocene Events," *Am. Jour. Sci.*, 249, 257–300 (1951).

carbon age, has been incorrectly given. Most of the available dates, unfortunately, represent isolated determinations that could be either "right" or "wrong" without necessarily affecting confidence in the method itself. The most important and interesting results are these:

The Postglacial spread of forests, and of Mesolithic cultures adapted to forests, took place in England about 9000 years ago. The time of attainment of the Boreal type of climate, i.e. the time of the pine zone, differed appreciably according to the latitude of the locality. The pine zone is about 9000 years old in West Virginia, about 8000 years old in Connecticut, and about 6000 years old in Maine; it is about 8000 years old in southern Minnesota and about 7000 years old in northern Minnesota. The age of the thermal maximum ("climatic optimum") has not been precisely fixed, but several samples from horizons not far from it give ages ranging from about 6000 to about 3000 years ago. In addition to pollen-dated peat and gyttja from Connecticut and the British Isles, samples within this time range date the eruption of Mount Mazama in Oregon and bracket the Boylston Street fishweir in Massachusetts.[4]

This very brief discussion deals with ideas based on a consideration of about half of the measurements which have been made by Dr. Libby and his associates. More complete comment and explanation are available in the two publications to which reference has been made. The salient conclusion which may be reached is that the initial experiment, if that is what it may be called, was successful from the archeological and geological point of view. There is great promise that a valuable tool for the constructing of a chronology has been developed. Its value rests not only upon measurements of dates of events which have been impossible to secure within a given range of accuracy heretofore but also upon the institution of a chronological scale world wide in scope. As inevitable refinements are made, the course of events in all continents may be directly compared. Once this becomes possible, the value and usefulness of interpretations of the significance of the events will be immeasurably enhanced.

Inconsistencies in the results were inevitable, and in specific instances they lead to untenable conclusions. This is to be expected; in fact, it is remarkable that more "erroneous dates" are not listed in the results. Actually the dates in question pose problems not only for workers in radiocarbon laboratories but particularly for collectors of the samples. For a considerable time, improvement of the machine itself will to a considerable degree depend upon the refinement of methods of sample collection and recording and the revision of archeological, geological, and palynological hypotheses involving chronology.

4. *Ibid.*, pp. 257–58.

APPENDIX A

SPECIAL EQUIPMENT AND CHEMICALS FOR THE C^{14} SAMPLE PREPARATION APPARATUS

Item	Source
Vycor combustion tubes; 25 mm. I.D., 31 mm. O.D., 750 mm.	Corning Glass Works
Iron tube; 30 inches, $1\frac{1}{2}$ O.D., 0.035 wall	Central Steel and Wire Company
Copper oxide; wire form	Merck and Company
Hydrochloric acid, CP	Baker and Adamson Company
Ammonia CP	Baker and Adamson Company
Calcium chloride, dihydrate, AR	Mallinckrodt Chemical Company
Magnesium turnings, CP	Merck and Company
Cadmium metal	*See* Dr. Bergman (Institute for the Study of Metals)
Furnace tubes, alumdum; 4 cm. I.D., 9-inch lengths or longer	Norton Company
Nichrome wire, Nos. 20 and 28	Driver-Harris Company
Pyrex fritted disks; medium; No. 39570-10	Sargent Company
Drierite; mesh No. 4	Sargent Company

APPENDIX B

SPECIAL MATERIALS FOR SCREEN-WALL COUNTER

Item	Source	Type
Unleaded brass tubing (direct from mill, $51.70 per 100 lb.)	American Brass, 1327 West Washington Street, Chicago, Illinois (Mr. Baker)	
Stainless Steel	Steel Sales	18-8; Type 304, 302
Copper (Commercial Copper)	Chas. Besley, Chicago	
Polyethylene	Heat Seal Container Company, 323 West Randolph Street, Chicago 6, Illinois, RAndolph 6-0075 (Mr. Crouder)	5×4×500 gusseted; 9 inch×250 (flat)
Spool copper-clad iron-core wire, Nos. 28 (0.012) and 30	Sylvania Electric Company	

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