88

RADIOCARBON DATING

Willard Frank Libby (b. 1908)

The discovery of the transformation of the radioactive elements, into another through the step-by-step disintegration process, soon led information on the half-lives of these unstable substances. The recog- on of the long half-lives of uranium and thorium, of the order respec- ly of one billion and ten billion years, suggested that these elements, ether with some of their disintegration products, might serve as ac- ate clocks yielding the time of their formation and of the earth itself. er the intervening years this hope has been realized. It would seem, v, that our planet originated some 4.5 billion years ago.

Until rather recently no radioactive substance was known whose prop- es and half-life were such that it could be used to date substances in organic, as opposed to the inorganic, world. The dating of ancient nts and civilizations through organic artifacts, refuse, or through ani- or even human remains, could supply much valuable information to historical record if a precise means and the right radioactive element e available. Fortunately, after World War II through the discovery he radioactive isotope, C^{14}, with a half-life of 5,568 years, a highly ful dating technique was developed. The isolation of this isotope, the stigation of its properties, and the refinement of its use in dating are owed to Willard F. Libby and his associates.

Recorded history extends back only some five thousand years; in that rval there are many gaps because of the lack of written records. But 't's culture is older by many thousands of years than his written records. s clock ticks on in the artifacts, refuse, animal remains, and even the ned-out campfires of those ancient times. From radiocarbon, we have ned that the cave drawings in the Lascaux caves of France can be gned to men of skull and skeletal structures similar to modern Euro-

peans and that they flourished about 15,000 years ago. An even earlier dating from the Aurignacian period of some 27,000 years ago indicates that *Homo sapiens* was then already fully differentiated as a species.

The appearance of early man in North America has generally been linked to the maximum advance of the ice sheet in the most recent glaciation. Previously assumed to have occurred about 25,000 years ago, this most southerly advance of the ice sheet has now been placed by radiocarbon analysis of wood samples from the Two Creeks forest bed in Wisconsin in the more recent past of 11,000 years ago. Evidences of early habitation on this continent when analyzed give dates of the order of 10,000 years, corroborating the appearance of man in North America with the maximum of the last glaciation; the time of these events, though, is much more recent than previously supposed. The value of this method to the construction of an accurate archaeology is thus apparent.

The following article, which describes the physical basis of the dating technique, is taken from Libby's monograph "Radiocarbon Dating." [1] Briefly, the method depends upon the fact that C^{14} is being continually formed in the upper atmosphere by the interaction of the incoming primary cosmic radiation with air atoms. This reaction produces neutrons that, entering the nuclei of nitrogen atoms in the air, result in the formation of C^{14} atoms. Such atoms quickly combine with oxygen in the air to form molecules of carbon dioxide, and these molecules soon become homogeneously mixed with molecules of stable CO_2 by the churning of the atmosphere. Thus, all samples of atmospheric carbon dioxide will be found to be radioactive and consequently all plants, since plants grow by incorporating this substance. In the same way, since all animals ultimately subsist on plants, all animals and all humans are radioactive.

Present evidence leads to the conclusion that there has been a constant rate of production of radiocarbon in the atmosphere for at least the past ten thousand years and this production has been in equilibrium with its decay. This balance has been a characteristic over that time of all living carbonaceous material. During the lifetime of any plant or animal, the radiocarbon assimilated from food will be in exact balance with the radiocarbon disintegrating in the tissues. When death occurs, the balance immediately ceases, and the radiocarbon atoms present become fewer and fewer as time goes on. The mean number of disintegrations per minute per gram of carbon atoms from living material is 15.3; from a knowledge of the half-life of C^{14} we know that the same carbon 5,568 years after the death of the material would show an average of 7.65 disintegrations.

Radioactive C^{14} atoms decay by emitting a β particle, that is, an electron. To determine the age of a once-living substance such as wood, the

[1] Willard F. Libby, *Radiocarbon Dating* (Chicago: University of Chicago Press, 1952).

sample must be very carefully reduced to pure carbon, taking care that all other material is excluded. If the activity is determined from the pure carbon itself the material must be so disposed that all β particles released by the disintegrating atoms will be counted. Alternatively, the carbon may be reacted into a gaseous form such as carbon dioxide or acetylene. Whether gas or solid, the carbon is introduced into a sensitive Geiger counter and its activity determined. The measured disintegrations per gram per minute are then substituted for I in equation (5) of the paper from which the desired value of t, the age of the material (in years), is found.

Willard Frank Libby was born at Grand View, Colorado, on December 17, 1908. He completed his undergraduate studies at the University of California at Berkeley in 1931 and received his Ph. D. at the same institution in 1933. He was then appointed instructor in chemistry and in 1938, assistant professor. In 1941 he was awarded a Guggenheim Fellowship which he held at Princeton University. He later transferred to Columbia University, Division of War Research, serving during the period of the war, 1941–1945, on the uranium isotope separation project. After the war he was appointed professor of chemistry at the Institute of Nuclear Studies and the University of Chicago. It was during this time at Chicago that he carried on the C^{14} research and developed the dating techniques that are presented in the selection which follows. In 1954, Libby was appointed a member of the U. S. Atomic Energy Commission; he served for five years, resigning in 1959 to become professor of chemistry at the University of California at Los Angeles, his present position. The recipient of many awards, medals, and prizes for his distinguished contributions to chemistry, he was honored by the Nobel Prize in chemistry for 1960 for his development of the C^{14} dating techniques.

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LIBBY

Radiocarbon Dating [2]

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

[2] Willard F. Libby, *Radiocarbon Dating* (Chicago: University of Chicago Press, 1952), pp. 1–10.

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. 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 neutrons, 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 [3] 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 ± 30 years.

[3] "Cross-section" for the capture of a neutron by a nucleus means the area surrounding a nucleus (like a target area) which a neutron must hit, on the average, if it is to be captured. The larger the cross-section (expressed in square centimeters), the greater is the probability that the neutron will be captured.

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 in 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. 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,

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

has been reported in the laboratory. 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. 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, a search in nature for both radioactivities was instituted. Both have since been found in amounts and concentrations corresponding roughly to those expected.

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, 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.

$$C^{14} = \beta^- + N^{14+}. \qquad (4)$$

Since laboratory measurement of the specific disintegration rate of radiocarbon 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 [a] 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 probably is not in excess of 500 years. This is the so-called "turnover" 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 equatorial and polar regions, the intensity being greater in the polar regions.

As expected, however, on the basis of the probable brevity of the turnover 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 88–1].

TABLE 88–1. *Carbon Inventory*

SOURCE	AMOUNT (gm/cm^2)
Ocean "carbonate"	7.25
Ocean, dissolved organic	0.59
Biosphere	0.33
Atmosphere	0.12
Total	8.3

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 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 88–1] 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. 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. 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 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 88–1], 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.

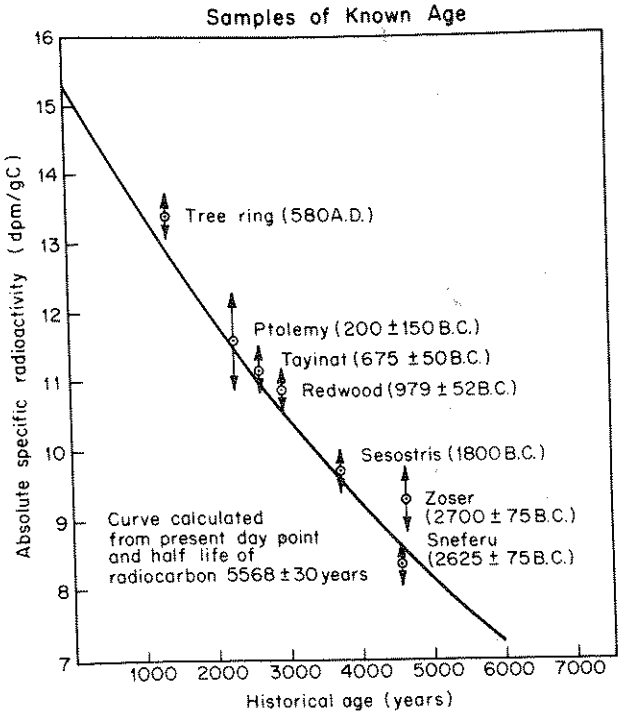

Fig. 88–1. Predicted versus observed radioactivities of samples of known age.

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 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 [Fig. 88–1], 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

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

or

$$I = 15.3 \times 2^{(t/5568)}, \tag{5'}$$

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 [Fig. 88–1] are the observed assays for various samples of known age. . . . 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.