

Chapter 2

Radiocarbon Dating: Development of a Nobel Method

R.E. Taylor

2.1 Discovery of Radiocarbon

In later retrospectives, Willard Frank Libby [1909–1980], the American nuclear chemist responsible for the development of the ^{14}C dating method (Fig. 2.1), noted his indebtedness to his collaborators, James Richard Arnold [1923–2012] and Ernest Carl Anderson [1920–2014]. He expressed the view that “Certainly, nothing would have been done without them” (Libby 1952).

Libby’s later recall of how the ^{14}C dating discovery process unfolded appears not to have been entirely accurate in each and every detail. This is understandable since, as both a review of his publications for this period and more recent discussions with contemporary colleagues and students reveal, during the time that he and the group was engaged in the research that established ^{14}C as a dating isotope, Libby was supervising a large cohort of graduate students and postdoctoral fellows who were pursuing a wide range of research topics, as was his custom throughout most of his scientific career. For a complete and accurate reconstruction of the history of the early development of ^{14}C dating, the only dating method whose development was recognized with a Nobel Prize, the information provided by James Arnold and Ernest Anderson has been absolutely essential.

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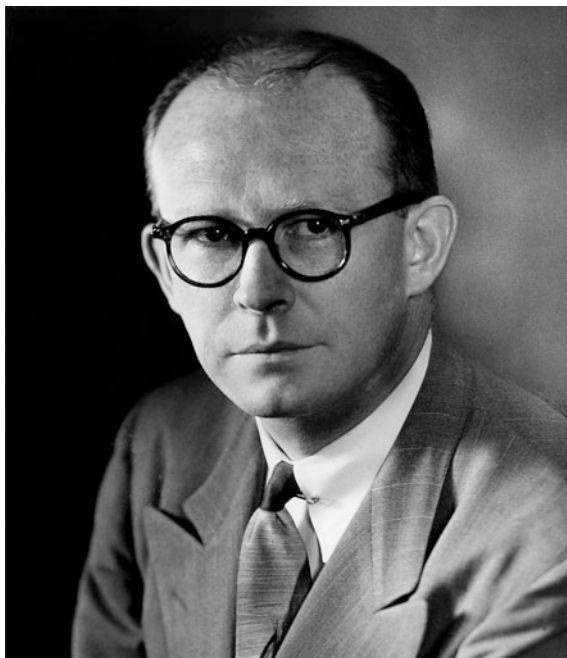
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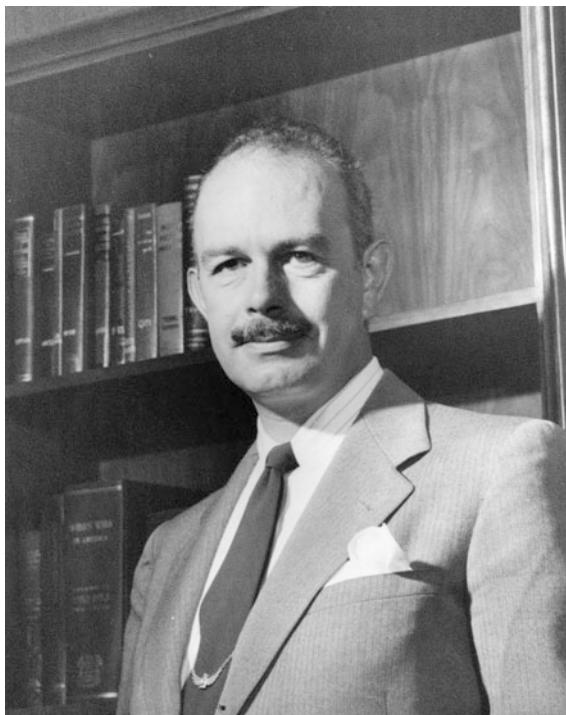
Fig. 2.1 Willard Frank Libby (1909–1980). 1960 Nobel Laureate in chemistry for the development of ^{14}C dating. *Source* US Atomic Energy Commission photograph taken in 1952



As was the case with a number of isotopes, radiocarbon (^{14}C) was produced in a particle accelerator prior to being identified as a naturally occurring radioisotope. Both Libby (1967) and Martin Kamen [1913–2002], a physical chemist who had a research position at the University of California, Berkeley (UCB), Radiation Laboratory in the mid-1930s (Kamen 1963), have noted that the first published suggestion of the possibility of the existence of ^{14}C was reported by UCB physicist Franz Newell Devereux Kurie [1907–1972] in a one-page letter in the June 15, 1934, issue of *Physical Review* (Fig. 2.2). The experiment Kurie carried out photographed particle tracks created when neutrons interacted with supercooled nitrogen and oxygen gases contained in a Wilson cloud chamber. These neutrons—uncharged particles found in atomic nuclei—had been produced when beryllium was bombarded by deuterons in the Berkeley 27-cm (11-in.) cyclotron.

In reporting on this experiment, Kurie listed six possible reactions to account for the observed tracks—three for nitrogen and three for oxygen. For those involving nitrogen, he listed ^{14}C , ^{13}C , and ^{12}C . He noted that ^{14}C was improbable since this isotope does not correspond “to a known isotope of these elements ... Whether or not N ... is made radioactive by neutrons has not been conclusively established.” He argued that either ^{12}C or ^{13}C as stable isotopes would be favored (Kurie 1934).

Fig. 2.2 Franz N.D. Kurie (1907–1972). Research Fellow, University of California, Berkeley, Radiation Laboratory, 1932–1939. While at Berkeley, he conducted experiments which resulted in the first published suggestion of the possible existence of ^{14}C . *Source* University of California, Lawrence Berkeley National Laboratory



2.2 “Wild Bill” Libby at Berkeley: 1927–1941

Kurie’s paper appeared the year following Libby’s receipt of his doctoral degree in chemistry at UCB. Libby’s 26-page dissertation was entitled “Radioactivity of Ordinary Elements, especially Samarium and Neodymium: Method of Detection” filed in the Spring of 1933 (Libby 1933). Libby had also been an undergraduate student at Berkeley, completing his baccalaureate degree in chemistry in 1931. He had acquired the sobriquet and perhaps epithet of “Wild Bill Libby” based, at least originally, on his high school football reputation which had followed him to Berkeley. However, his very forceful personality, the manner in which he approached his laboratory experiments, and certain other aspects of both his later personal life and professional career reinforced his lifelong reputation as “Wild Bill,” at least in the eyes of some of his contemporaries and later in the view of both some of his supporters and antagonists. James Arnold would much later comment that those “meeting him for the first time tended to be either attracted or repelled. He made both friends and enemies easily” (Arnold 1992).

While still a UCB undergraduate, Libby had built for his Senior Honors Thesis what almost certainly was the first Geiger–Müller (GM) ionizing radiation detector assembled in the USA (Libby 1964b, 1981, Libby nd, de Messières 2001). The basic features of the GM tube design had been first published in 1928 in a German

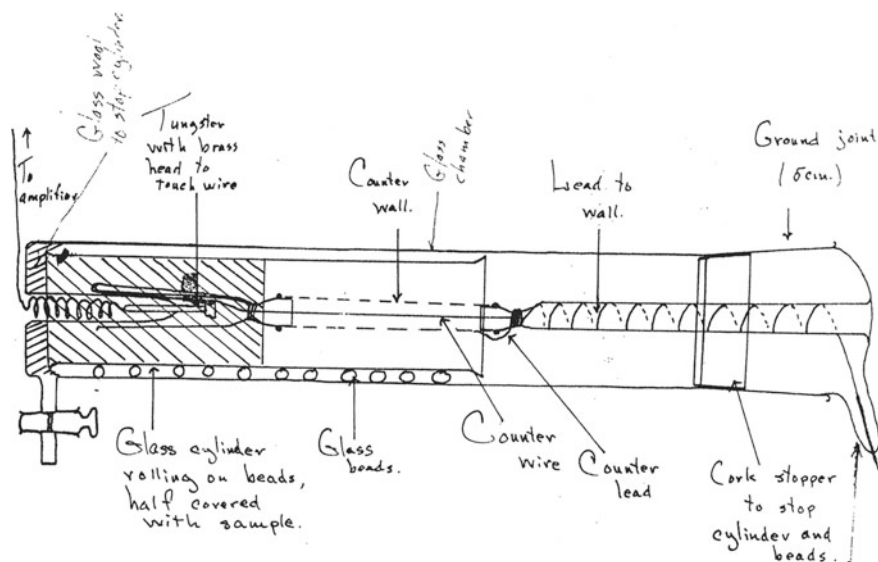


Fig. 2.3 Drawing by Libby of the design of the screen wall counter used in his dissertation research at the University of California, Berkeley, in 1932–1933. *Source* Libby (1933)

scientific periodical by Hans Geiger [1882–1945] and his student, Walther Müller [1905–1979] (Geiger and Müller 1928). The GM detector that Libby constructed consisted of a brass tube down the length of which was stretched an iron wire. It used air at a reduced pressure as the counting gas. A meter that could measure milliampere-level pulses in the detector current was connected to the output of the grid element of a two-stage amplifier circuit. These pulses recorded the effects of a cascade of electrons produced when ionizing radiation was present in the detector. A description of the circuit of this amplifier constituted Libby's first scientific publication (Libby 1932).

In Libby's dissertation research, his GM counter envelope was fabricated from glass rather than metal (Fig. 2.3). A wire grid or "screen wall" was substituted as the cathode of the counter in place of the more typical solid metal wall. His samples of rare earth elements were mounted on the inside surface of a glass sleeve rolling on spherical glass beads acting as ball bearings which allowed the sleeve to be moved in and out of the active region of the counter where the effects of ionizing radiation could be detected. This permitted measurements to be alternated between the sample and the blank or background count levels in the detector without changing the counter gas (Libby 1933; Libby and Lee 1939). The reason for this arrangement was that the count rate of his samples resulting from beta decay was very close to the counter's background rate (i.e., the activity exhibited in the counter with no sample present). With some relatively minor modifications, the general design of the counter used in Libby's dissertation research served as the model of the type of screen wall counters that he would employ more than a decade later in all of his ^{14}C experiments using solid carbon (C) counting at the University of Chicago.

Fig. 2.4 Ernest Orlando Lawrence (1901–1958). 1939 Nobel Laureate in physics for the invention of the cyclotron. Organized Radiation Laboratory (now Lawrence Berkeley Laboratory), University of California, Berkeley. *Source* University of California, Lawrence Berkeley National Laboratory



Ernest Orlando Lawrence [1901–1958], who would receive the physics Nobel prize in 1939 for the invention and development of the cyclotron, had arrived at Berkeley from Yale University in 1928 (Fig. 2.4). He began his research with a 27-cm (11-in.) cyclotron instrument that he constructed in 1931. This was the instrument that had been employed to produce neutrons for Kurie's experiment. Throughout the decade of the 1930s, Lawrence built larger and larger diameter cyclotrons that permitted the production of particles of higher and higher energies.

In an attempt to determine whether ^{14}C was the isotope being produced from nitrogen interaction with neutrons in a cloud chamber, Samuel Ruben [1913–1943], then a Berkeley chemistry graduate student, was set to work by Lawrence to produce ^{14}C by irradiating ammonium nitrate in Lawrence's 68-cm (27-in.) cyclotron. At that time, ^{14}C was assumed to have a half-life of not more than a few months based on the energy of its decay products which were similar to a radioactive isotope of sulfur, ^{35}S . The experiment, undertaken on the assumption of a short half-life, failed to produce any measurable amounts of ^{14}C . No studies focused on ^{14}C were immediately undertaken in view of its presumed short half-life. This was because the work of Lawrence's laboratory between 1937 and 1939 was largely focused on the production of isotopes for biomedical applications. In this pre-US National Science Foundation or National Institutes of Health era,

Lawrence believed that this promised the best chance of more stable, long-term funding to support the operation and expansion of cyclotron research at Berkeley (Kamen 1963; Libby 1967, 1979).

In late 1939, a question was raised concerning the practical worth of radioisotopes in biochemical or biomedical research. For example, ^{11}C , which was used as a tracer in the study of photosynthesis, had a half-life of only 20 min. As a result, Lawrence initiated a maximum effort to determine definitively whether any longer-lived radioactive isotopes existed for any of the biologically important elements, which included hydrogen, nitrogen, oxygen, and C (Kamen 1963). The work on C was undertaken by Ruben and Kamen who began by exposing graphite to deuteron bombardment in a 94-cm (37-in.) cyclotron. Following the bombardment, the graphite was burned to CO_2 , precipitated out as CaCO_3 , and used to coat the inside of a screen wall counter designed by Libby. The counter registered the presence of artificial ^{14}C , and after several months, when there was no decrease in the activity of ^{14}C , the researchers came to realize that the half-life had to be orders of magnitude in excess of that previously assumed.

This initial experiment had been based on the assumption that the reaction of deuterons with ^{13}C rather than neutrons with ^{14}N would be the *most likely* reaction in the formation of ^{14}C . To exclude the possibility of a favored reaction of neutrons with nitrogen, an experiment was devised in which a solution of saturated ammonium nitrate was irradiated with neutrons. The expectation was that no detectable amount of ^{14}C would be produced. Instead, a relatively small amount of precipitate paralyzed the screen wall counter because of the high ^{14}C count rate. Within a few months in early February 1940, despite strong theoretical arguments to the contrary, Kamen and Ruben had experimentally demonstrated that the (“slow”) neutron mode of ^{14}C production was heavily favored and that the half-life had to be somewhere in the range of 10^3 – 10^5 (1000–100,000) years (Ruben and Kamen 1941; Kamen 1985).

Libby later reported that sometime in the mid-1930s, he had become aware of the work of Serge A. Korff [1906–1983] who was then a cosmic ray physicist at the Bartol Research Foundation. Korff had been measuring the increase of cosmic rays with increasing altitude in the atmosphere by sending GM counters aloft in balloons (Heusser 1990). As we have noted, neutrons had been produced in the laboratory, but it was not known whether they existed in natural radiation received by the earth. Korff set to work to build a counter that would be sensitive only to neutrons.

Sending these counters up in balloons, Korff found an increase of neutrons with altitude up to about 16 km (10 miles) after which there was a rapid decrease (Fig. 2.5). These data were interpreted to indicate that neutrons existed naturally but were secondary radiation, a product of the collision of high-energy cosmic rays with nuclei of the gaseous components of the earth’s atmosphere. The decrease at the top of the atmosphere was attributed to the escape into space of some of the neutrons so formed (Libby 1952). Korff noted that the neutrons that remained would be slowed down by collisions with atmospheric gas nuclei and that these “slow” or thermal neutrons would disappear by being captured by nitrogen to form ^{14}C . This was apparently the first published prediction that ^{14}C should exist *in nature* (Korff and

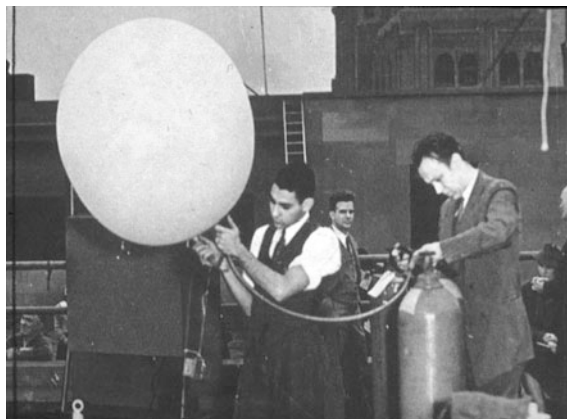


Fig. 2.5 Serge Alexander Korff (1906–1983) New York University [on *right* in photograph], preparing a balloon to lift counter to measure neutrons at various altitudes. *Source* Bartol Research Foundation, Franklin Institute

Danforth 1939; Montgomery and Montgomery 1939; Korff 1940; Libby n.d.). Four decades later, Libby stated that the origin of his conceptualization of ^{14}C dating involved his reading of the Korff and Danforth (1939) publication which reported finding neutrons in the atmosphere: “As soon as I read Korff’s paper ... that’s carbon dating” (Libby 1979).

2.3 Libby at the Manhattan Project: 1941–1946

The entrance of the USA into World War II quickly redirected the activities of a large percentage of the US scientific community into a wide variety of applied science and engineering projects directed toward enhancing the pursuit of the war effort. US scientists involved in nuclear physics or nuclear chemistry research were quickly recruited to pursue the development of a nuclear weapon based on fears, which turned out to be correct, that Nazi-ruled Germany had a similar project underway.

In 1941, Libby was at Princeton as a Guggenheim Fellow on his first sabbatical leave from Berkeley. He was one of the first scientists recruited by Nobel chemistry laureate Harold C. Urey [1893–1981] to join the Manhattan Project (officially, the Manhattan Engineer District) at Columbia University in New York, one of more than thirty sites in the USA, Canada, and England which were established to work on the World War II development of a nuclear weapon (Fig. 2.6). Urey’s group had the task of developing a means of undertaking uranium isotope separations on a large scale by gaseous diffusion (Arnold 1981).

Libby’s most important Manhattan Project scientific research involved the development of a material that could withstand the extremely corrosive effects of uranium hexafluoride (UF_6) as part of a technique to accomplish the gaseous

Fig. 2.6 Libby and Harold C. Urey (1893–1981) at an award ceremony for Libby. *Source* University of Chicago Regenstein Library, Special Collections, Photographic archive



thermal diffusion enrichment of ^{235}U in its separation from ^{238}U . Interestingly, he later expressed the view that his research to develop a thermal diffusion barrier was “better than my carbon 14 dating” (Libby 1978).

2.4 Libby at Chicago: 1946–1954

In 1945, at the conclusion of World War II, looking forward to continuing his relationship with Urey, Libby accepted an appointment as a professor in the Department of Chemistry and Institute for Nuclear Studies (later renamed the Enrico Fermi Institute for Nuclear Studies) at the University of Chicago rather than returning to Berkeley. He arrived to take up his position in October 1945 with a number of research projects in mind. Libby later commented that he initially determined to pursue his ^{14}C project “in secret.” In a 1979 interview, when later asked to identify the most difficult and critical part of the development of the technique, Libby responded: “Being smart enough to keep it secret until it was in hand . . . I don’t care who you are. You couldn’t get anybody to support it. It’s obviously too crazy.” Libby stated that only Urey initially knew of the goal of the research (Libby 1979). Neither of his collaborators at the time, James Arnold nor Ernest Anderson, recalled that they were ever informed by Libby, or were cognizant on their own, that the research they were undertaking was being conducted in a secretive manner (James Arnold and Ernest Anderson, personal communications 2001).

The first published hint of the direction in this thinking appeared in a short paper that appeared in *Physical Review* in June 1946. In this paper, he noted that if the half-life of ^{14}C was much greater than 1000 years, then a balance between ^{14}C production and decay would exist in living organics and predicted what the specific ^{14}C activity of modern C would be. Most importantly, however, he predicted that there would be a significant difference in the ^{14}C activity between living biological and fossil C (Libby 1946).

In his autobiography, Emilio Segrè, an Italian physicist resident at the University of Chicago at this time, notes parenthetically that he had “been told that the

suggestion [for ^{14}C dating] came from [Enrico] Fermi in a Chicago seminar” (Segrè 1991). Segrè’s (1970) earlier biography of Fermi made no mention of this rumor. Contemporaries report that the informal exchange of ideas was a constant feature of academic life at both Berkeley and Chicago. If Libby’s later statement that the basic idea was formed in his mind in 1939 is not considered credible, this rumor might reflect the views of some that Libby, like some of his colleagues, was not adverse to taking and rushing quickly to do “quick and dirty” experiments to determine the feasibility of some offhanded comment expressed by a colleague.

What ever was its ultimate source, the kernel of the conception of using ^{14}C as a dating isotope is without question contained in Libby’s 1946 publication. Interestingly, two reviewers of the paper recommended rejection on the grounds of “insufficient general interest” (Arnold 1981). As far as can be determined, this paper contained the earliest use of the term “radiocarbon,” and although no contemporary statement has been found that confirms this, the later oral statements of his contemporary collaborators lead to the conclusion that Libby himself was the first to employ this term for ^{14}C .

At a party (he later thought perhaps a Christmas party) late in 1946, Arnold, now a postdoctoral fellow who, since February 1946, had worked with Libby and two other professors at Chicago and reports that he became cognizant of Libby’s serious intention to use ^{14}C as a means of dating. Arnold had been able to undertake his dissertation research as part of the Manhattan Project efforts, while he had been a Princeton graduate student during the years 1943–1945. For a short period in the Spring of 1946, he was associated with Libby at Chicago working with reactor-produced ^{14}C . Employing his wartime connections, Libby had had a sample of barium carbonate inserted into a reactor at the Oak Ridge National Laboratory in Tennessee that was producing a high flux of neutrons. This bombardment yielded about a millicurie of ^{14}C . This amount of ^{14}C was many orders of magnitude in excess of what had ever been, to that date, produced and was sufficient to undertake the experiment that would produce a more accurate and precise ^{14}C half-life measurement (Marlowe 1980, 1999; Arnold, personal communication 2001).

During the Christmas holidays of that year, Arnold mentioned Libby’s work to his father, who although a corporate attorney by profession, was very knowledgeable in Egyptian archaeology, having served for many years as the American Secretary for the British-based Egypt Exploration Society with responsibility for fund raising (Arnold 1992). The elder Arnold communicated the news of this potential new dating technique to Ambrose Lansing [1891–1959], then a curator in the Egyptology Department at the Metropolitan Museum in New York. As a result of this conversation, Lansing sent a set of ten samples from various Egyptian sites to James Arnold at Chicago (Marlowe 1980, 1999). That package contained what was to become the first sample to be dated by ^{14}C (C-1), cypress wood from the tomb of the Third Dynasty Egyptian king Zoser or Djoser (Netjerikhet). Lansing did not communicate the age of any of the samples, but did indicate the provenience of each. Since James Arnold had grown up in a household where Egyptian archaeology was talked about often and at length, he was knowledgeable enough to be able to deduce the age on his own (Arnold, personal communication 1986). The

arrival of these samples was certainly highly premature for as yet there was no experimental confirmation of any of Libby's assumptions concerning the distribution of natural ^{14}C in nature. However, Arnold later reported that Libby took the package containing the samples and placed it on a shelf behind his desk. Arnold recalls thinking at that time that Libby was really serious about his ^{14}C dating idea (Arnold, personal communication 1986; Arnold 1992).

2.5 The Critical Experiments: 1946–1948

In May 1946, Ernest Anderson joined Libby's group, originally as a laboratory assistant and then as his first graduate student at the University of Chicago (Anderson, personal communication 1986; Marlowe 1999). During the war years, Anderson had worked on the Manhattan Project at the Los Alamos Scientific Laboratory. However, unlike Arnold, he had not been able to utilize these years to obtain his Ph.D. In Libby's group, he was first given the responsibility by Libby to fabricate the counting apparatus (Fig. 2.7). This began a three-year period [1946–1948] during which three critical experiments were undertaken which empirically examined the implications of the predictions Libby had published in his short 1946 *Physical Review* paper.

Fig. 2.7 Libby and Ernest Carl Anderson (1920–2013) taken in 1948 in Libby's laboratory in Jones Hall, University of Chicago. In the background are parts of the instrumentation used in making ^{14}C measurements. *Source* University of Chicago Regenstein Library, Special Collections, Photographic archive



The first experiment was designed to determine whether there was a measurable difference in ^{14}C content between a contemporary or modern C sample and a sample of fossil C of great geological age. A modern sample would establish the equivalent of a “zero ^{14}C age” or 0 BP value on the ^{14}C timescale. A sample of fossil C, in which it would be reasonably expected that its ^{14}C concentration would have decayed below detectable levels, would establish an infinite or “greater than” ^{14}C age. If no difference between the ^{14}C activity in modern and fossil C could be measured, this clearly would constitute a catastrophic flaw in Libby’s original conceptualization of using ^{14}C as a dating isotope.

For the modern sample, biological CH_4 gas (“biomethane”) from a sewage disposal plant in Baltimore, Maryland, was employed. The sample of great geological age was petroleum CH_4 (“petromethane”) obtained from a Sun Oil Company refinery. In the absence at that time of any reliable technology that could directly measure the differences in natural ^{14}C content of these samples to a reasonable level of precision, the two CH_4 gas samples were enriched to the same degree in thermal diffusion columns used to make ^{13}C for tracer biomedical applications. The ^{14}C activity in both of these enriched CH_4 samples was then counted in a conventional GM counter (Libby 1970).

It was determined that whereas the ^{14}C activity of the modern biomethane increased in direct proportion to the measured amount of ^{13}C enrichment, there was no significant increase in the ^{14}C activity of the petromethane. Clearly, the ^{14}C in the CH_4 derived from the fossil source had decayed to a level below detection limits. There was thus no measurable ^{14}C to enrich in the petromethane (Anderson et al. 1947a, b).

The focus of much of the subsequent research on the ^{14}C dating project was to develop a relatively routine method to directly measure natural ^{14}C levels without resorting to time-consuming and energy-intensive and thus costly gaseous enrichment procedures using a thermal diffusion column (Libby 1970). The use of proportional gas counters using CH_4 or CO_2 was briefly considered (Libby 1947; Anderson, personal communication 1987). However, gas counting for ^{14}C was finally rejected by Libby in favor of a modification of his dissertation screen wall counter design using solid or elemental C.

A screen wall counter using solid C rather than a gas system was chosen by Libby on the basis of several considerations. The principal problem was to fabricate a detector that could obtain the maximum and most stable count rates with the minimum physical size (Anderson 1949, 1953). The physical size of the counters was crucial since, if all other factors remain constant, the background count rate—in this case, the counting rate of a detector absent a ^{14}C -containing carbonaceous sample—is proportional to its size. It was also extremely important to employ a detector that yielded stable count rates over relatively long periods since attempts would be made to measure ^{14}C at natural concentrations close to the background levels of the counters.

A detailed comparison of gas and screen wall detector technologies available at that time determined that the counting sensitivities of the two alternative approaches were not significantly different for counter volumes and pressures that were then

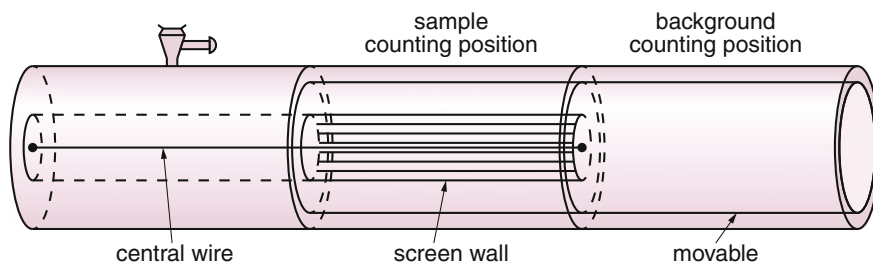


Fig. 2.8 Chicago solid C counting instrumentation. Simplified diagram of major features of the screen wall counter showing the sample counting position of sleeve containing solid sample and the background counting position of sleeve when the screen wall would be moved to the right side of the counter. Figure modified from Taylor (1987: Fig. 6.2)

considered practical. The use of larger counters and higher pressures together with more reliable electronics and stable power supplies would later shift the balance in favor of gas counters. The relatively low efficiency of a screen wall counter, e.g., the percentage of the decay events that occurred within the counter that was actually detected, which in this case was about 5 %, was offset by the fact that it could contain about 20 times more C than a gas counter of similar size (Anderson 1953; Anderson, personal communication 1987, 2002).

The major design features of the counter assembly used at the Chicago laboratory are shown in Fig. 2.8. The effective or active volume of the detector represented about one-third of the total length of the cylinder as defined by the wire grid (Libby 1952, 1955). A highly significant outcome of this arrangement, as with the original Berkeley design, was to permit the background of the detector and radioactivity emanating from the sample to be measured repeatedly without changing the counting gas filling (Libby 1967). This characteristic was a critically important consideration in the decision to use the screen wall counter design since it increased the chances of obtaining reproducible counting rates (Anderson, personal communication 1986). Counting background and ^{14}C activity in the sample were accomplished in the same manner as in Libby's pre-World War II instrument by having a sleeve that could be moved in and out of the sensitive volume of the counter.

Samples intended for solid C counting after chemical pretreatment were converted first to CO_2 by combustion or acidification. Following chemical steps to eliminate trace impurities in the sample gas, the CO_2 was reduced by reaction with magnesium at high temperature. One of the reaction products was elemental C or "lamp black." The magnesium oxide was separated from the C by treating the reaction product with concentrated hydrochloric acid. Unfortunately, not all of the magnesium oxide—termed "ash" in Libby's publications—could be removed even with repeated acid treatments. The amount of ash remaining in the sample had to be determined very carefully, since it would reduce the measured ^{14}C specific activity (Libby 1955).

The inside surface of the sample sleeve, which was constructed of metal rather than glass as was the case in Libby's Berkeley instrument, was coated with the C

powder to which had been added, at various times, water, ethyl alcohol, and/or agar to form a paste. Spreading the paste containing the C powder on the inside surface of the metal sleeves was reported by those who were involved in solid C counting to be a very challenging task which required a great detail of dexterity and perseverance. Once the liquid was evaporated and the coating thoroughly dried, considerable care had to be exercised to avoid dislodging the coating from the walls of the cylinder. Arnold later reported that this feature of the solid C counting instrument caused him to regard the technology as being “developed in Hell” due to the frequency with which the coating became dislodged. Interestingly, Anderson was one of the few individuals involved in early ^{14}C studies who did not have highly negative memories of having to work with solid C counting technology.

The air used for evaporating off the water or alcohol contained traces of radon, an isotope in the uranium decay chain, which resulted in unwanted radioactivity being picked up in the C sample. Fortunately, radon has a half-life of a few days. By waiting a few weeks to pass allowed the radon to decay below the level where the beta daughters of the alpha radiation from the radon could be detected. This step became a major problem as fallout from atmospheric nuclear testing rapidly increased in the early 1950s, causing solid C counting to become an obsolete technology. For counting, the C-coated sleeve was fitted into the screen wall counter assembly. The cylinder was sealed, originally using a specially prepared black wax compound and later with o-rings, evacuated, and a counting gas was then introduced. Alternate sample and background counts were obtained by sliding the sleeve containing the sample coating in and out of the sensitive volume of the counter as defined by the wire grid.

The most crucial technical element in the development of routine low-level ^{14}C work in decay counting was the application of the anticoincidence principle to reduce background count rates. This involved surrounding the central detector containing the sample with a ring of Geiger counters and connecting their electronic output circuits together. With such an arrangement, pulses coming from the sample counter could be electronically compared as to coincidence or non-coincidence (anticoincidence) with pulses coming from one or more of the “guard” counters. The circuitry in the instrument was arranged so as to count pulses from the central counter *only* if these pulses were *not* accompanied by an essentially simultaneous pulse from the surrounding guard counters (Fig. 2.9). If a pulse from the sample and guard counters arrived within a very small time window (several milliseconds), it was assumed that the ionization event occurring *inside* the sample counter had been caused by the same event that triggered the guard counter, was thus *not* the result of a ^{14}C -decay event inside the sample counter, and thus would not be counted as a ^{14}C -decay-caused event. Figure 2.10 is the sample counter surrounded by the ring of GM counters used in the Chicago laboratory.

Although Libby was not sure of the source of this idea to reducing background counts (cf. Libby 1970, 1979), the principle of *coincidence* counting had been a standard method employed in cosmic ray studies since the 1930s (Anderson 1953). Arnold expressed his view that the concept was “borrowed by Libby from the cosmic ray physicists and put together in the first crude form by Anderson” (Arnold

Fig. 2.9 Principle of anticoincidence counting used to reduce background counts in Libby's solid C counters.

Source Taylor (1987: Fig. 4.7)

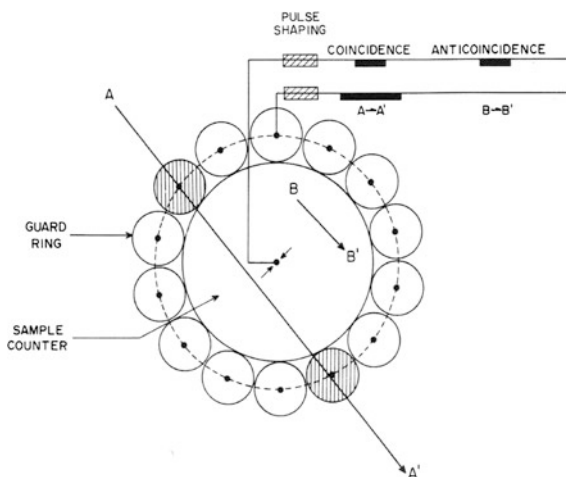
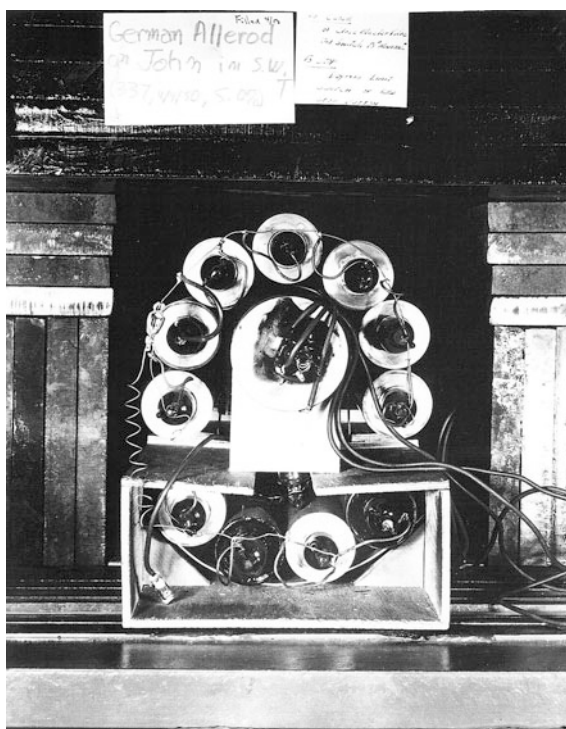


Fig. 2.10 Chicago solid C counting instrumentation. Screen wall counter used for ^{14}C measurements (center counter) surrounded by a ring of GM tubes. Source R. Berger and L.M. Libby, University of California, Los Angeles (USA), and Isotope Foundation, Santa Monica, California



1992). Several others questioned by the author had the impression that Anderson was the source of the idea. When queried about this much later, Anderson did not take credit for it, stating that the idea was “kind of in the air.” Anderson later discovered that Danish scientists in the 1930s had employed the anticoincidence

principle for low-level counting applications. This technology was not known to Libby or his coresearchers when ^{14}C dating was being developed at Chicago because it had been published in a Dutch language journal (Libby nd, Anderson, personal communication 1987, 2001).

Throughout the first part of 1948, problems with the counting instrumentation were slowly and painstakingly solved by Anderson and Arnold to the point that reasonably reliable counting data could be obtained (Anderson 1949). At first, only two or three days of acceptable counting runs in an entire month could be obtained (Marlowe 1999, information confirmed by Arnold 2006). By the early Spring of 1948, Anderson's and Arnold's painstaking work permitted estimates of the specific ^{14}C activity in a sample to a precision of about $\pm 10\%$. This was sufficient to undertake the second and third critical experiments resulting in the establishment of the use of ^{14}C as a dating isotope.

The second critical experiment constituted the dissertation research of Anderson. His task was to determine whether the natural ^{14}C activity in *living* organics varied as a function of the geographic location on Earth. Since ^{14}C production in the atmosphere at the geomagnetic poles was about five times that at the equator, the worldwide comparability of ^{14}C -inferred age values would require the relatively rapid and complete mixing of cosmogenic ^{14}C into air masses near the Earth's surface on a worldwide basis. This would result in ^{14}C concentrations in living organics to be approximately equal no matter their geographical locality. If this turned out not to be the case, it would seriously violate one of the prime assumptions on which the ^{14}C dating model rested.

To test this assumption, Anderson measured the ^{14}C specific activity expressed in terms of counts (or disintegrations) per minute per gram of C (cpm g^{-1} or dpm g^{-1}) in a series of mostly wood samples from locations situated from 65° north (Sweden) to 45° south (Australia and Tierra del Fuego). In several cases, the specific ^{14}C activity of samples from high altitudes (2750–3000 m) was also obtained. The result of these experiments revealed that the values of widely geographically separated modern organics ranged from 11.81 ± 0.60 to $13.33 \pm 0.43 \text{ cpm g}^{-1}$ of C. Anderson summarized his results by stating that the “average of three equatorial samples is $12.32 \pm 0.35 [\text{cpm g}^{-1}]$ and that of the six samples from magnetic latitudes greater than 40° [North or South] is $12.54 \pm 0.20 [\text{cpm g}^{-1}]$. The difference is 0.22 ± 0.40 , which is not statistically significant” (Anderson 1949).

The average terrestrial biospheric specific activity of ^{14}C reported in Anderson's dissertation was $12.50 \pm 0.2 \text{ cpm g}^{-1}$ of C. This same average value was also reported in Libby et al. (1949) although there is some variation in the values cited for individual samples. A higher value of $15.3 \pm 0.1 \text{ cpm g}^{-1}$ of C reported in Anderson and Libby (1951) and incorporated in Libby's *Radiocarbon Dating* volume (Libby 1952, 1955) was a result of the later recalibration of the counter data of Anderson to account for the effect of differences in ash content in samples and counter efficiency (Libby 1952; confirmed by Anderson, personal communication 1987). Interestingly enough, however, even this first set of results revealed

variations in ^{14}C activity of marine shell and in samples from the higher latitude regions. Both of these problems have continued to be studied down to the present day.

The third critical set of ^{14}C measurements was obtained on a suite of presumed known-age samples. The first reported ^{14}C age determination (C-1) was on the piece of cypress wood sent by Ambrose Lansing to Libby in January 1947 from the tomb of Djoser (Zoser), whose reign is thought to have occurred from about 2665 to 2650 BC (Shaw 2000). The age on this sample was calculated in Libby's laboratory by Arnold on July 12, 1948 (Arnold and Anderson, personal communication), and published in March 1949 (Libby et al. 1949). If one wanted to identify a specific day as the single "birthday" of radiocarbon dating, then this date might be used. In publishing this result, the age of a wood of assumed similar age from the tomb of Snofru (Sneferu), the first king of the Egyptian Fourth Dynasty who was considered the father of Khufu (Cheops to the Greeks), the builder of the first or great Giza pyramid, was also measured. In combining the ages obtained by a weighted average expressed as specific activity in counts per second per gram of C from multiple measurements on both samples, the final result was reported as agreeing "with the expected value within 1 standard deviation unit" (Libby et al. 1949).

The second measured sample was expected to have a known age about one-half that of the Zoser–Sneferu samples. However, the result of this measurement was never reported in print until 1967 (Libby 1967). This is because its count rate was essentially the same as that of the modern or contemporary samples measured by Anderson. What had transpired was that John Wilson, then the director of the University of Chicago Oriental Institute and a highly respected Egyptologist, had been asked to supply a piece of wood dating from the Hellenistic period (323 BC–14 AD). Unfortunately, the sample he selected had been obtained from a "reputable Cairo antiquities dealer" a phrase well known to be oxymoron among Egyptologists. When measured, its ^{14}C activity was statistically indistinguishable from that obtained on biomethane. It was a modern piece of wood and therefore obviously a fake (James Arnold in Marlowe 1980).

Since Arnold reports that this affair ruined his Christmas (December 1948), one wonders what would have happened if the wood supplied by John Wilson would have been the first "known-age" sample to be measured or if the sample supplied by Lansing would have been a modern fake. Libby later commented that fortunately their early studies encountered few fakes "as otherwise faith in radiocarbon dating would have been rapidly shaken and the research abandoned ..." He later publicly mused that much of his ^{14}C research benefited from what he called "good fortune," which he suggested bordered on the "miraculous" (Libby 1970; Deevey 1984).

The capstone to the more than fifteen months of intensive work was "Age Determinations by Radiocarbon Content: Checks with Samples of Known Age," published in the December 23, 1949, issue of *Science* (Arnold and Libby 1949). In this paper, the first "Curve of Knowns" was presented with six data points spanning a period from about AD 600 to 2700 BC (Fig. 2.11). Earlier in that year, Libby had organized a measurement of the ^{14}C half-life by a group at the Argonne National Laboratory located near Chicago (Engelkemeir et al. 1949). Their value of

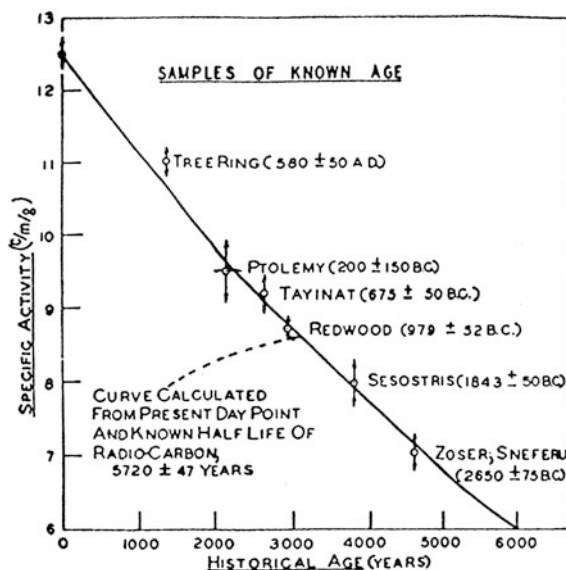


Fig. 2.11 The first of Libby's "Curve of Knowns" (Arnold and Libby 1949: Fig. 1; Libby 1952: Fig. 1). This plot employed the first ^{14}C half-life used by Libby, 5730 ± 40 years, and expressed ^{14}C activity in samples in terms of counts of ^{14}C per minute per gram of C (c/m/g). Libby's second "Curve of Knowns" substituted 5568 ± 30 years, the so-called Libby half-life and expressed ^{14}C activity in samples in terms of percentage of modern ^{14}C activity. *Source* Rainer Berger, University of California, Los Angeles (USA)

5720 ± 47 year was used to convert the sample count rate of each sample to its ^{14}C age. For Libby, the reasonably close ($\pm 10\%$) correspondence between the "known-age" and " ^{14}C age" of these seven samples indicated that the major assumptions on which the dating model rested were valid for at least the last 5000 years to a first-order approximation based on the then typical counting precision of $\pm 10\%$.

2.6 Dating Unknown-Age Samples: 1949–1954

By early 1949, Libby had been confident enough to move into what he called the "great unknown periods of prehistory." Since there were no fixed chronometric points with which the ^{14}C values could be directly compared, it was anticipated that validation would be accomplished by the degree of "internal consistency from a wide variety of samples and in a wide variety of problems" (Arnold and Libby 1949).

During the period of the Chicago laboratory's routine dating operation from about March 1949 until early 1954, ^{14}C values on more than 500 samples were obtained. About two-thirds of these determinations were on samples of archaeological

significance, most of which had been submitted by or through the collaborators. The first listing of “provisional” ^{14}C dates was prepared in mimeograph form on January 1, 1950, with a supplement dated in April. Both lists were sent principally to the collaborators. A number of these values were subsequently modified, and these revised values appeared in a booklet published by the Institute of Nuclear Studies and dated September 1, 1950. This booklet contained 148 ^{14}C values and carried a notation in the preface that the “list itself is not for publication in its present form, though the dates themselves may be quoted freely” (Arnold and Libby 1950; Johnson 1951).

The text of the booklet with some modifications constituted the first Chicago list of dates, which appeared in the journal *Science* in February 1951 (Arnold and Libby 1951). This inaugurated the custom of laboratories publishing their ^{14}C values in the form of “date lists.” For US laboratories, the earliest date lists continued to appear in the journal *Science*. The half-life chosen by Libby to calculate the ^{14}C age determinations beginning with the Chicago date list booklet in 1950 was 5568 ± 30 year. This value replaced the earlier 5720 ± 47 year that had been used to calculate the first “Curve of Knowns” (Arnold and Libby 1949). The 5568 ± 30 year value was a weighted average of three published measurements, 5580 ± 45 , 5589 ± 75 , and 5513 ± 165 year that had been obtained by Libby and his collaborators and two other groups (Engelkemeir et al. 1949). The 5568 years value became known as the “Libby half-life” and has continued to be used to calculate “conventional” ^{14}C age values, as later explicitly defined by Stuiver and Polach (1977), even though it now is clear that the half-life Libby originally used (5720 ± 47 year) was closer to the correct value. With only a few exceptions, e.g., some French laboratories, the “Libby half-life” has been used to calculate all conventional ^{14}C values published in the journal *Radiocarbon*.

The Chicago laboratory ceased operation with the departure of Libby in October 1954 to accept an appointment by President Eisenhower to become a commissioner of the US Atomic Energy Commission (AEC) [now the US Department of Energy]. He held this position until June 1959 when he joined the faculty of the University of California, Los Angeles. At the AEC, Libby was a major supporter of the growth of the electric nuclear power industry as well as the development of nuclear weapons. He also directed “Project Sunshine,” a study of worldwide stratospheric mixing using radioactive fallout from the testing of nuclear weapons (Buck 1983; de Messières 2001). This project continued the work he had begun during the Manhattan Project and he had maintained direct involvement in US atomic energy development at the AEC while at the University of Chicago from the time the AEC had been established, serving as a member of its General Advisory Committee. It was his access to classified information concerning the magnitude of the fallout from “bomb” ^{14}C that alerted him to the problem that this fallout would create for solid C counting. Together with his colleague at Chicago, physicist Edward Teller, Libby was an outspoken advocate of the development of nuclear weapons. As the result, both were considered controversial figures in the public discourse concerning the uses of atomic energy.

2.7 Radiocarbon Dating Comes of Age: 1954–1960

The acceptance by the vast majority of scientists from a number of disciplines of the overall, general validity of the ^{14}C method is reflected in the rapid establishment of laboratories to perform ^{14}C analyses. Solid C counting instrumentation was installed at eight institutions in the early 1950s. These pioneering laboratories included the University of Arizona (Wise and Shutler 1958), University of Copenhagen, Denmark (Anderson et al. 1953), Lamont Geological Observatory, Columbia University (Kulp et al. 1951), University of Michigan (Crane 1956), New Zealand Institute of Nuclear Studies (Fergusson and Rafter 1953), University of Pennsylvania (Ralph 1955), University of Saskatchewan (McCallum 1955), and Yale University (Blau et al. 1953). In at least three instances at US universities (Arizona, Michigan, and Pennsylvania), archaeologists were instrumental in establishing the laboratories. Some thought at that moment that they stood “before the threat of the atom in the form of [^{14}C] dating. This may be our last chance for old-fashioned, uncontrolled guessing” (Phillips et al. 1951).

Low-level ^{14}C counting using Libby’s solid C approach required an extraordinary attention to detail in laboratory procedure. Many who attempted to duplicate the technique experienced moderate to severe difficulties in obtaining reproducible values. Most frustrating was the problem of avoiding contamination of the solid C samples with nuclear fission fallout products resulting from the testing of thermonuclear devices in the atmosphere beginning in the middle of the 1950s. As a result of these and other problems, the laboratories previously noted, which had begun operations with solid C counting, converted over to some type of gas counting by the end of the decade. Meanwhile, other early laboratories had commenced operations with gas counting using CO_2 or acetylene or, in one case, with the use of liquid scintillation technology. These included the facilities at the University of Groningen, the Netherlands (de Vries and Barendsen 1954), the University of Heidelberg, Germany (Munnich 1957), and the US Geological Survey in Washington, D.C. (Suess 1954).

By the inauguration of the journal *Radiocarbon* in 1959, more than twenty ^{14}C laboratories were actively pursuing a wide range of research topics utilizing ^{14}C . *Radiocarbon* (initially the *Radiocarbon Supplement* to the *American Journal of Science*) was inaugurated to solve the problem of the increasing number of ^{14}C laboratory date lists which could no longer be accommodated in the journal *Science* as well as to provide an archive of primary data on individual ^{14}C dates (Deevey 1984). This later function was of particular concern at that time since, in some cases, ^{14}C values were being cited without laboratory number or without descriptions of any kind (Deevey and Flint 1959). Rapid development during this period also took place particularly in Europe (Waterbolk 1960) as well with laboratories being built in England (at the British Museum and Cambridge), Sweden (Stockholm and Uppsala), France (Gif and Saclay), Ireland (Dublin), Germany (Cologne and Hanover), Belgium (Louvain), Russia (Moscow), Italy (Pisa and Rome) as well as in Switzerland (Bern) and Norway (Trondheim). In the USA

during this period, the first commercial ^{14}C laboratory was opened and several oil companies briefly supported ^{14}C facilities.

Initial ^{14}C data that yielded age estimates at dramatic variance with the views of individual archaeologists or geologists (e.g., Neustupný 1970; Antevs 1957; Lee 1981) generated discussions that questioned the validity of the ^{14}C method in general (Barker 1958; Johnson, personal communication 1986). However, with the rapidly mounting evidence of the general validity of the ^{14}C model in broad outline, discussions quickly turned to questions of accuracy of ^{14}C values from specific archaeological or geological contexts or geochemical environments (Broecker and Kulp 1956).

2.8 Nobel Prize: 1960

The capstone at the end of the first decade of ^{14}C dating was the award of the 1960 Nobel Prize in chemistry to Libby for the development of the method (Fig. 2.12). Translated from Swedish, the citation reads “At its meeting of November 3, 1960, the Royal Swedish Academy of Science has decided, in conformity with the terms of the November 27, 1895 will of Alfred Nobel, to award the prize to be given this

Fig. 2.12 Text of the 1960 Nobel Prize in chemistry awarded to Willard F. Libby for the development of the ^{14}C dating method. *Source* Image made available for reproduction by L.M. Libby, University of California, Los Angeles (USA)



year for the most important chemical discovery or improvement to Willard F. Libby for his method to use Carbon-14 for age determinations in archeology, geology, geophysics, and other sciences.” Interestingly, when President Eisenhower was informed that Libby had been awarded the Nobel Prize in chemistry, he expressed surprise since he had not been aware that Libby was a scientist. Eisenhower had known him only in his role as a member of the Atomic Energy Commission (Libby 1981).

At the time the Nobel Laureate was awarded, Libby had the year previously arrived at the University of California, Los Angeles (UCLA), to take up a faculty appointment as professor of chemistry and, two years later, as the director of the Institute of Geophysics and Planetary Physics (IGPP). In 1961, Libby brought to UCLA Gordon J. Fergusson [1922–2009], formerly of the New Zealand Institute of Nuclear Studies ^{14}C laboratory, to build an Isotope Laboratory for the IGPP and collaborate in geophysical research. In the 1960s, the author of this chapter served as a graduate research assistant in the UCLA laboratory while a graduate student in the UCLA Department of Anthropology specializing in archaeology and archaeometry/archaeological science (Taylor 1970). In 1968, Rainer Berger [1930–2003] succeeded Fergusson as the director of the UCLA laboratory having faculty appointments in the UCLA departments of anthropology, geography, as well as the IGPP. Libby’s UCLA laboratory, having operated for 34 years, was closed when Rainer Berger retired from UCLA in 1995.

2.9 Afterward

Willard Libby retired from UCLA in 1976 and died in Los Angeles four years later at the age of 71 (Arnold 1981). His wife, Leona Marshall Libby, also a noted chemist, noted that “Until the day of his death, he was carrying on his research at top speed as he always did. One week before [his death], he had completed a seminal paper on the geometrical theory of catalysis of light hydrocarbon reactions, important in oil refineries and on the role of electron tunneling therein” (Libby 1981).

The Analay High School in Sebastopol, California, from where Libby graduated in 1926, named a Willard F. Libby Science Classroom Wing in his honor and a large mural with his likeness, has been painted on an exterior wall of the school. A Sebastopol park was named the Willard Libby Memorial Park, and an 8 km (5 mile) segment of a California State highway between Sebastopol and an adjacent town became the Willard F. Libby Memorial Highway.

During the period of his collaboration with Libby, James Arnold pioneered in the development of liquid scintillation technology for low-level counting (Arnold 1954). After leaving the ^{14}C dating project at Chicago in 1955, he served as the faculty of Princeton University. While at Princeton, he discovered the presence of ^{10}Be in nature (Arnold 1956). In 1958, he was asked to be the founding chairman of the University of California, San Diego (UCSD), Department of Chemistry. He

spent the remainder of his illustrious scientific career at UCSD, a campus located at La Jolla, California, overlooking the Pacific Ocean. Arnold was elected to the US National Academy of Science in 1964 and was appointed as the first holder of UCSD Harold C. Urey Professorship in Chemistry. Arnold retired as professor emeritus from UCSD in 1993 and died at the age of 88 on January 6, 2012.

Upon completion of his Ph.D. at Chicago, Ernest Anderson returned to the University of California, Los Alamos Scientific Laboratory in Los Alamos, New Mexico, where he spent the remainder of his scientifically productive career. He continued to be involved in the development of low-level counting (Anderson and Haynes 1956) and assisted in the development of the ^{14}C laboratory at the University of Copenhagen in the early 1950s (Anderson et al. 1953). While in Denmark, he was surprised to learn that the principle of anticoincidence counting for low-level radioactivity measurement had been developed in the 1930s by Dutch scientists. In 1966, he received the Ernest O. Lawrence Award from the US Department of Energy for his contributions to nuclear technology. He retired from Los Alamos in 1995 and died at the age of 92 on May 20, 2013.

For a more detailed discussion of the scientific background to and initial development of ^{14}C dating with a particular focus on its application in archaeology, interested readers are directed to Chap. 8 in the 2nd edition of *Radiocarbon Dating: An Archaeological Perspective* (Taylor and Bar-Josef 2014).

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Radiocarbon and Climate Change

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