Early History of Carbon-14

Discovery of this supremely important tracer was expected in the physical sense but not in the chemical sense.

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When, how, and why was carbon-14 discovered? As T. S. Kuhn has remarked (*1*), discovery is seldom a single event that can be attributed wholly to a particular individual, time, or place. He notes that some discoveries, such as those of the neutrino, radio waves, and missing isotopes or elements, are predictable and present few problems, as far as establishment of priority is concerned. Others, such as the discoveries of oxygen, x-rays, and the electron, are unpredictable. These put the historian in a "bind" when he tries to decide when, how, who, and where the discovery was made. Much more rarely does he have a basis for an answer to the question "Why?"

I propose in this account of the "prenatal" history of carbon-14 to provide the answers to my leading questions (*2*). These make a story which is a fragment of the whole record. That record must be constructed by future historians who seek to probe the events of a period in which there has been an unparalleled impact of intellectual curiosity and scientific creativity on the structure of society.

The tremendous outburst of technology in the past half century, the result of the rise of nuclear science, has crowned man's quest for the philospher's stone so successfully as to be hardly credible even to the most optimistic alchemist. Tracer methodology, an offspring of nuclear science, has provided essential support for the ever-widening and deepening knowledge of structure and function in biological systems, expressed as the dynamic science of molecular biology.

These developments have profound, but unknown, implications for the future of our social structures. They obviously bring with them an unexampled load of grist for the mills of cultural historians, social scientists, and philosophers. Perhaps the novelists will dig into the record of these exciting times for fresh insights into the age-old drives of mankind.

Carbon-14, the long-lived carbon isotope, is the most important single tool made available by tracer methodology, because carbon occupies the central position in the chemistry of biological systems. Thus it plays, and will continue to play, an essential role in the elucidation of biochemical mechanisms, knowledge of which is essential in the further development of molecular biology. Obviously, the circumstances surrounding its discovery are valid objects of interest for the historian (*3*).

Initial Phases, 1934–36

In the early 1930's, nuclear physics, immersed in the great traditions of the Cambridge school led by Ernest Rutherford, was concerned primarily with observations of processes associated with the scattering of elementary nuclear particles by various atomic nuclei. Reports in those times show painstaking determinations of range-energy relations for the fundamental projectiles (protons, deuterons, alpha particles). The energies used did not exceed approximately 10 Mev, because of the limitations set by the relatively primitive accelerators and by the radiation characteristics of the naturally radioactive materials that were available. The rationale for such work, which often involved tedious attention to detail and much labor, was that if enough precise facts were put together, accurate binding energies for nuclei could be deduced. From these energies, it was reasoned, there could be derived a solid basis for further attack on the problem of the nature of nuclear forces.

By 1933, such data—binding energies, angular distributions in scattering experiments, and so on—had demonstrated that nuclear forces could be described as analogous to saturation exchange forces like those postulated previously for chemical bonding. The so-called "alpha-particle" model of the nucleus already contained the seeds of what was to be the full-fledged modern "shell" theory of nuclei, to be developed later by Maria Mayer, Eugene Feenberg, and others.

As to my part in this, I was a young, eager student and had just begun doctoral research, using the Wilson cloud chamber to study the angular distribution of neutrons scattered in collisions with protons and other nuclei. These researches were part of a general program initiated in the laboratory of W. D. Harkins in the chemistry department at the University of Chicago (*4*). My decision to work in this field was largely a result of the influence of D. M. Gans, Harkins' associate and an assistant professor in the department (*5*).

Most significantly for this history, similar work was also under way at Yale, where F. N. D. Kurie, investigating neutron-induced disintegration of light elements, had obtained certain anomalous results for the angular distributions of protons in collisions with neutrons. In 1934 he proposed a radical interpretation (*6*) of certain events he noted in the cloud chamber. When nitrogen was exposed to fast neutrons, for instance, he noted that in some cases the ejected nucleus produced a very long, thin track. This he ascribed to a proton, rather than to an alpha particle. Thus, he supposed that the usual reaction, $N^{14}(n,He^{4})B^{11}$, was accompanied by a less frequent but readily observable reaction, $N^{14}(n,H^{1})C^{14}$. (As far as I am aware, this is the first suggestion in the literature that C^{14} might exist.) Kurie also suggested, however, that the tracks he was observing might arise from H^{2}, or even H^{3}, and thus that the reactions $N^{14}(n,H^{2})C^{13}$ and $N^{14}(n,H^{3})C^{12}$ were also possibilities. In fact, he felt the reactions with emission of H^{2} and H^{3} were the more likely because they resulted in nuclei of known stability.

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What was radical about Kurie's suggestion was the idea that something other than an alpha particle could emerge in a disintegration of a nucleus such as N^{14}. But the physicists at the time assumed from their everyday experience that the alpha particle was much the most likely nucleon to be formed in such a nuclear reaction. This belief found a ready basis in the relatively great stability of the alpha particle, which was considered to exist as an entity in all nuclei because of its relatively enormous binding energy per nucleon, and because invariably in natural radioactivity it was the only heavy nucleon ejected.

In the meantime, T. W. Bonner and W. M. Brubaker (*7*) published observations on the energies of recoils induced by neutrons in inelastic collisions with nitrogen nuclei. Assuming the usual reaction, $N^{14}(n,He^4)B^{11}$, they calculated from the mass values given by Hans Bethe (*8*) that Q, the heat of reaction, was about 1.5 Mev. Most significantly, however, Bonner and Brubaker (*6, 7*) and W. Chadwick and M. Goldhaber (*9*) independently reported that the distintegration of N^{14} occurred also with *slow* neutrons.

This, it turned out, was the crucial observation in the "prenatal" history of C^{14}, because it prompted a re-evaluation of the assumptions on which analyses of the nitrogen disintegration tracks were based.

Chadwick and Goldhaber had detected disintegrations in an ionization chamber connected to a linear amplifier and oscillograph. From the size of the oscillograph deflections they had deduced that Q was about 0.5 Mev. Bonner and Brubaker had used a cloud chamber and observed a group of tracks with a sharply defined range of 1.06 centimeters (in air, at normal temperature and pressure) which they thought to be alpha particles. On this basis, they had calculated a value for Q of 2.33 Mev. The discrepancy in the two values for Q was far beyond any experimental error. W. E. Burcham and Goldhaber (*10*) then were inspired to suggest that both sets of data were referred to the wrong reaction, and that if the disintegration were assumed to take place with proton emission—that is, $N^{14}(n,H^1)C^{14}$—then the value for Q taken from the range observed by Bonner and Brubaker became 0.58 Mev, in good agreement with the value of Q deduced from the ionization measurements. Bonner and Brubaker not only concurred but advanced further evidence in support of this suggestion by noting that when they measured Q for a related reaction, $B^{11}(H^2,n)C^{12}$, they found a value of 13.5 Mev, which, taken together with Q values known for some other reactions, enabled them to construct a reaction cycle in which the $N^{14}(n,He^4)B^{11}$ reaction turned out to be endergonic ($Q = -0.28$ Mev), rather than exergonic ($Q = 2.33$ Mev). Thus the alpha-particle emission could not have been induced by slow neutrons, at least if one accepted the rather marginal negative value for Q.

Burcham and Goldhaber proceeded to use the visualization technique of nuclear emulsion, by means of which they could distinguish more certainly between protons and alpha particles. They showed conclusively (*10*) that alpha particles were not emitted in the slow-neutron disintegration of N^{14} and proposed that the recoil particles be assigned definitely to the reaction, with C^{14} as a product. They could not exclude experimentally the possibility that H^2 or H^3 particles, rather than protons, might account for the recoil tracks observed. On the other hand, they remarked that reactions that could produce such particles were unlikely on energetic grounds. Thus, Kurie's original intuitive suggestion, based on the appearance of certain unusually thin, long tracks in his cloud-chamber experiments of 1933–34, was raised to the status of a practical certainly by 1936.

I think it is safe to say that in the *physical* sense the discovery of C^{14} had been established by the observations of Burcham and Goldhaber. But the discovery of C^{14} in the *chemical* sense—which I must say has turned out to be the more important—was delayed by many obstacles. If I may refer again to the remarks of Kuhn (*1*), the discovery of C^{14} in a physical sense belongs in the "expected" category but its discovery in the chemical sense does not.

Intermediate Phases, 1936–38

Meanwhile, "back at the ranch," I was plugging away collecting pictures of proton recoils produced by collisions with neutrons from a pathetically weak mesothorium-beryllium source of a few millicuries equivalent. By the end of 1936 I had obtained results from an analysis of 730 tracks, which showed a marked asymmetry in the angular distribution of protons in the energy range from ~ 0.1 to 3 Mev (*11*). This result confirmed results obtained by Kurie a few years earlier (*12*). At the time, Kurie's results had been in contradiction to theoretical expectations. Before his and my anomalous findings could be taken seriously, it was necessary that greater numbers of events be analyzed—an objective quite unrealizable with the feeble neutron sources then available. It had taken 3 years of constant labor to produce and analyze a few hundred proton recoils—in fact, 10 man-hours per track had been required. This statistic shows how slender were the means available for research in nuclear physics in 1936—which, after all, is not so long ago.

It was natural in the mid-1930's to look toward Berkeley, where Ernest O. Lawrence was assembling a group of young physicists drawn by the fact that the cyclotron, a much stronger particle source than any then existing, was in operation.

Thus, in January 1937 I found myself at the Radiation Laboratory, along with Kurie, who had arrived there a short time before. Because of our mutual interest in neutron scattering, we quickly began a collaboration in which we proposed to investigate not only the various apparent anomalies in the neutron-proton interactions but neutron-nuclear interactions in general. The neutron fluxes available with the cyclotron, even in its primitive 1937 form (an accelerator 27 inches in diameter), were already greater by four or five orders of magnitude than any with which we had been familiar.

Unfortunately, the neutron flux obtainable with the new cyclotron was not a well-collimated beam with minimal energy spread. The cyclotron contained innumerable scattering sites from which great numbers of neutrons of undefined energies emerged in a welter of direction. To achieve some measure of order in the neutron beam, Lawrence and his group set to work on a major program, with responsibility vested largely in Arthur Snell. The procedure was to lead the deuteron beam away from the main vacuum accelerating chamber so that it would hit a beryllium target at some distance from the scattering bulk of the cyclotron. The emergent neutrons from the $Be^9(H^2,n)B^{10}$ reaction were to be piped through a hole in the water shield around the cyclotron. It was hoped that, with judicious use of auxiliary absorbers, this effort, called "snouting," would produce a relatively well collimated, intense beam of neutrons with energies only slightly lower than the maximum obtainable in the reaction.

Kurie and I found that when a cloud chamber, filled with hydrogen as target, was placed to either side of the "snout" hole, there were relatively few recoil pictures, whereas the yield was enormous when the chamber was placed directly in front of the hole. A typical single expansion, in front of the snout hole, with an exciting deuteron beam of a few microamperes incident on the beryllium target, exhibited more recoil tracks than either Kurie or I had seen in all our previous experience with the strongest naturally radioactive sources obtainable—for example, hundreds of millicurie equivalents of polonium or radium mixed with beryllium.

In the light of the earlier findings on the production of C^{14}, we decided to investigate the neutron disintegration of N^{14}. The slow-neutron disintegration of N^{14}, with its characteristic recoil product—a proton with a range of 1.06 centimeters in air, as dictated by the Q value of 0.58 Mev—manifested itself on almost every other expansion in the cloud chamber as a short, stubby track with a knob at the starting end. This track was the track of the proton, which, because of its relatively low mass, took up practically all the energy of the reaction as kinetic energy; the knobby stub was the C^{14} recoil product, which, because of its relatively high mass, possessed very little of the kinetic energy released in the reaction. These characteristic short, stubby tracks provided a convenient and accurate internal monitor for calibrating the stopping power of the mixture of nitrogen gas and water vapor in the cloud chamber. In this way we solved a very bothersome technical problem—that of determining just what value for stopping power we should use in calculating recoil energies. Thus, by early 1937 tracks of C^{14} were being used in the calibration of cloud-chamber experiments, and its existence was well established.

However, nothing was known about its physical characteristics. One could attempt to make some predictions. First, it seemed certain that C^{14} was radioactive and that it must emit negative beta rays in the transformation to N^{14}. This conclusion followed from the observation that in no known element of low atomic number were there neighboring isobaric pairs in which more than one member of the pair was stable. Examples of pairs with an unstable member are He^6-Li^6, Be^7-Li^7, Be^{10}-B^{10}, and C^{11}-B^{11}. So, one might expect that for the isobaric pair C^{14}-N^{14} the stability of N^{14} requires that C^{14} be unstable and that it decay to N^{14} by transformation of a neutron into a proton, with emission of a negative beta particle and a neutrino. Second,—and here a great uncertainty arose—one would expect the rate of decay to be fairly high, as it is in one known analogous case (He^6-Li^6) in which a nucleus with two excess neutrons decays to a nucleus with equal numbers of neutrons and protons. For this pair as well as for another similar pair, Be^{10}-B^{10}, the expected decay ratio was in quite good agreement with the ratio actually observed. Thus, He^6, with an upper energy limit for beta rays of 3.5 Mev and a possible spin difference of no more than 1 unit, could be expected to decay with a period of 10^{-1} to 10^1 seconds. Its half-life is, in fact, 0.8 second. The decay of Be^{10} with its enormously long half-life—of the order 10^6 to 10^7 years (*13*)—represented a highly forbidden transition, despite a fairly high beta-ray energy maximum of about 0.5 Mev. In this case, a high degree of forbiddenness could be rationalized on the basis of the shell model available—that is, a large spin difference was a possibility. The C^{14}-N^{14} pair was analogous to He^6-Li^6, with a maximum spin difference of 1. The lower energy limit to be expected depended on the difference in mass between C^{14} and N^{14}. Thus, for the reaction with slow neutrons,

$$(n-H^1) = (C^{14}-N^{14}) + Q.$$

From then-accepted values for the masses and a value for Q of +0.58, the maximum energy for the emergent beta particles was estimated to be about 0.3 Mev. On this basis, a tentative estimate of a few hours or days for the half-life of C^{14} was made by P. Morrison and J. R. Oppenheimer. Thus it appeared that C^{14} was probably quite short-lived. If attempts to isolate it were unsuccessful, it could be assumed that the half-life was too short for the isotope to be isolated, rather than too long—that is, $\tau_{1/2}$ was expected to be on the order of seconds, not centuries.

None of these arguments were wholly convincing, for it was recognized that the state of beta-decay theory was quite unsatisfactory; nevertheless, they were sufficiently impressive to discourage us from making a determined effort to isolate C^{14} at that time. E. M. McMillen had noted the presence of some very long lived activities in old cyclotron targets and bits of metal scraped from various parts of the acceleration chamber. With what now is seen to have been extraordinary intuition he surmised that these activities could represent radioactive species of beryllium and carbon. In an abstract (*13*) submitted to a meeting of the Physical Society in 1936 he described two activities residual in an old beryllium target. The major activity was a very soft component, with a decay rate consistent with a half-life of 10 years or longer. This component, he thought, might be assigned tentatively to Be^{10}. He suggested that the other activity, which was weaker but harder and decayed with a half-life of a few months, was attributable to a radioactive isotope of carbon—in particular, to C^{14}. In later years (*14*) he published a final summary of work done with S. Ruben in the years 1938–40, in which the activity assigned to Be^{10} was reassigned with some certainty to H^3. The other activity obviously could not have been attributable to C^{14}, because, as we know now, the half-life of C^{14} is about 5700 years. In an effort to produce C^{14} by the $N^{14}(n,H^1)C^{14}$ reaction, McMillen exposed solid ammonium nitrate to the intense neutron flux of the 37-inch cyclotron for several months in 1938–39, but this experiment ended when the bottle containing the salt was inadvertently knocked off the magnet coil tank and smashed.

However, a new—and what was to prove decisive—factor entered late in 1937. As we all know, the ancient alchemists ascribed to the "philosopher's stone" two magical powers—the ability to transmute elements and the ability to banish disease. The old alchemical treatises bear constant witness to the state of mind which supported, through centuries, what were tedious, disappointing, and often hazardous—even fatal—searches. Even after chemistry was well established and alchemy was in some disrepute, Robert Boyle could still make his well-known statement (*15*), "There may be some agent found out so subtile and powerful, at least in respect of those particular compounded corpuscles, as to be able to resolve them into those more simple ones, whereof they consist."

With the discoveries of radioactivity by Becquerel and x-rays by Röntgen at the end of the 19th century and the experiments of Rutherford early in this century, the prophecy of Boyle and the hopes of the alchemists had been realized. Lawrence saw even greater potentialities in the exploitation of the immensely more powerful agents available from artificial radioactivity and man-made accelerators and was eager to see them applied. For this reason he had interested his brother, John Lawrence, a physician and worker in medical research, in the possible use of the neutron as a therapeutic agent and had assigned P. C. Aebersold, then a graduate student, to help him establish the physical and radiological procedures involved. A small beginning had already been made in utilization of the radioactive isotopes of phosphorous, sodium, and iodine as tracers in biological research. To facilitate the development of such researches, both at Berkeley and elsewhere, I was asked to assume responsibility as staff chemist to develop procedures whereby target materials could be bombarded, processed, and delivered in forms suitable for direct application in biological systems. The problems involved were so challenging and urgent that from the early months of 1937 until well into 1940 most of my energies were channeled into this activity.

Almost immediately I found it necessary to devise a dependable procedure for rapid preparation of C^{11}, with half-life of 21 minutes, for use by S. Ruben, W. Z. Hassid, and I. L. Chaikoff, who planned to investigate carbohydrate metabolism by means of C^{11}-labeled sugars prepared photosynthetically from $C^{11}O_2$. In a short time it became apparent (*16*) that bombardment of B_2O_3 powder by deuterons in a special external target chamber, designed by Kurie, produced as $C^{11}O$ or $C^{11}O_2$ almost all of the C^{11} made in the $B^{10}(H^2,n)C^{11}$ reaction. The success of this procedure, which eliminated the exposure to hazardous radiation incidental to manipulation of target material, expedited the research to such an extent that Ruben was encouraged to initiate research on photosynthesis itself—an undertaking into which I was soon drawn full time, outside of my duties as radiochemist.

In the meantime, Ruben observed, in May 1938, that a number of graphite targets, which I had been using to make N^{13} by the $C^{12}(H^2,n)$ reaction for some research on nitrogen fixation (*17*), contained no residual long-lived activity isotopic with carbon. He concluded that any C^{14} formed by the $C^{13}(H^2,H^1)$ reaction, if it had a half-life up to 200 years, could have been detected. This finding underscored the probability that C^{14}, if it existed, was a short-lived isotope.

My constant exposure to cyclotron targets kept me in a steady state of radioactive contamination which rendered me *persona non grata* around assay equipment. I recall an experience during collaboration with Philip Abelson in late 1937, when we were attempting to use an apparatus consisting of an ionization chamber connected to an FP–54 Pliotron tube amplifier. We were harassed by the occurrence of an eccentric and irregular background drift of variable magnitude. Finally, Abelson noted that the effect was correlated with my movements toward and away from the apparatus. While I stood in a corner he systematically stripped me and established that the disturbance originated from the front of my pants. Likewise, in my collaboration with Ruben, it was necessary to keep me away from the counting equipment. Eventually, Ruben assumed sole responsibility for assay and I concentrated on the production of tracer isotopes.

Ruben deserves almost all the credit for the growth of interest in tracer methodology which occurred at Berkeley in the years 1937–38. His unique combination of skill, energy, wide-ranging interest, and quick grasp of essentials when confronted with new and unfamiliar areas of science provided a focus for the efforts of an ever-increasing number of able investigators.

By the middle of 1938 the demands for cyclotron time on the part of biologists and clinicians was so great that round-the-clock operation of the cyclotron—by that time a 37-inch accelerator—was mandatory. In addition, the pressure to build bigger accelerators had impelled Lawrence to seek additional subsidies from biologically oriented foundations and other organizations likely to support such projects. As an argument, Lawrence cited preliminary results of neutron therapy and of the use of radioactive isotopes, such as Na^{24}, P^{32}, and Fe^{59}, in medical diagnosis. A 60-inch cyclotron was almost ready for operational tests, and further development depended critically on financial support from private organizations. The demonstration that energies and ion currents far in excess of the limits earlier thought to be reasonable might ultimately be obtainable lent added urgency.

The researches of R. R. Wilson in this period were of considerable importance in pointing the direction for further development of cyclotron design. Wilson showed that very large beam currents at energies somewhat lower than those in the external target area circulated inside the accelerating electrodes (*18*). He realized that if a means could be devised to use these internal beams, bombardments of much greater magnitude than those possible with external targets could be effected. Moreover, he was able to show that a large fraction of the internal circulating ion current could be intercepted by appropriately designed "probes" without appreciable diminution of external beams. However, the problems involved in the achievement of acceptable internal targets were formidable, and no immediate efforts were made to exploit the internal ion currents. For example, the external beams of 7 to 8 Mev and 50 to 100 microamperes required dissipation of 300 to 800 watts—a power input which, even with well-cooled targets of good heat conductance, required sequestration of target material from the cyclotron vacuum by aluminum or other metal foil windows. Internal beams with ion currents of as much as several milliamperes and energies only slightly less than 6 to 7 Mev generated power inputs of an order of magnitude greater than those associated with the external beams.

However, the cyclotron was increasingly unable to meet the demands for radioisotopes, as well as for bombardment time for clinical trials; even the needs for essential nuclear physical research could not be satisfied. This led Wilson and me to try to devise acceptable internal targets for radioisotope production—an enterprise in which we succeeded late in 1938. This research was to prove the turning point in the sequence of events which led to the production of C^{14}. In fact, as we remarked at that time (*19*), "Obviously, the method of internal targets should find its most important application in the preparation of radio-isotopes which are long-lived and difficult of activation, as well as in the demonstration of the existence of many radio-isotopes as yet undiscovered."

Final Phase, 1938–40

The search for funds proceeded with some success through 1938 and into 1939, and thus both cyclotrons were in operation on a full schedule when the discovery of nuclear fission burst on the world in January 1939. In the meantime, Lawrence's hopes of producing an even greater machine had been raised by the successful operation of the 60-inch cyclotron. Citing the expanded collection of clinical data and the enormously developing tracer program made possible by the Berkeley cyclotrons, he pressed for more support from the organizations that had provided it before.

In our own researches on photosynthesis, C^{11} had by this time been exploited to its ultimate limits (*19–21*).

There had been many difficulties. We had found it essential to try to make an ultracentrifugal determination of the molecular weight of the labeled intermediates produced during photosynthesis in the presence of $C^{11}O_2$. The necessary apparatus was at Stanford University, 50 miles away from the Berkeley cyclotrons along a heavily traveled road. We calculated that it would be possible to produce the $C^{11}O_2$, incubate algae with it, extract the resultant intermediates, and drive with these to Stanford. There would be insufficient time, however, to make a proper centrifuge run. We considered a number of possible courses of action, such as arranging a police escort for the motor trip to Stanford or posting one of us at Stanford to have the counting apparatus ready. One night a brilliant solution occurred to Sam Ruben: he woke me by phone at 2 A.M. to suggest carrier pigeons!

Fortunately, this problem was finally solved by the discovery that an apparatus identical with that at Stanford was available at the Shell Oil Company research laboratories, only 10 minutes' drive from the cyclotron. Even so, we found it impossible to obtain the precision needed to establish with certainty the average size of the early intermediates in photosynthesis.

In a gloomy conference late in September 1939, Ruben and I reached the conclusion that without a long-lived isotope of carbon our researches were at an end. I suggested one last desperate try to produce C^{14} by means of the internal-target technique. The difficulty was that, in view of the general pessimism about the probability of isolating a long-lived isotope, we could not arrange to use any of the internal targets, which were being constantly used to produce P^{32} and Fe^{59}.

Table 1. Plan for production reactions for possible long-lived carbon isotope, September 1939. Target chemistry for all but the reaction in the bottom row is as follows: Collect C^*O in gas, burn residue to CO_2, with carrier C. Target chemistry for the reaction in the bottom row: Aspirate CO_2-free air through solution, burn emergent gases, and trap C^*O_2.

Reaction†	Target material
Atmosphere:	*3% CH_4 in O_2*
$Be^9(He^4,n)C^{12*}$	BeO
$B^{10,11}(He^4,H^1)C^{13*,14}$	B_2O_3
$B^{11}(H^1,\gamma)C^{12*}$	B_2O_3
$B^{11}(H^2,n)C^{12*}$	B_2O_3
$C^{12,13}(H^2,H^1)C^{13*,14}$	Graphite
$N^{14,15}(n,H^1)C^{14,15}$	Ammonium nitrate (nitrite)

† Energies available: protons (4–8 Mev), deuterons (8–10 Mev), alphas (16–32 Mev).

It was with some amazement therefore, that I found myself shortly after this conference being told by Lawrence that both cyclotrons must be diverted forthwith to a full-time effort to determine definitely whether long-lived isotopes of hydrogen, carbon, nitrogen, and oxygen did or did not exist. The reason for this was soon evident. During Lawrence's most recent efforts to achieve increased and continued subsidies for cyclotron development, some question had been raised as to the real value of radioactive isotopes in biological research, relative to the rare stable isotopes such as H^2, C^{13}, N^{15}, and O^{18}. Thus, while these very useful stable isotopes existed as tracers for the elements of primary importance in biology, there were no comparable radioactive isotopes with reasonably long lifetimes available; no radioactive hydrogen isotope existed (it was thought that tritium was stable relative to He^3), the carbon isotopes C^{10} and C^{11} had half-lives of 8 seconds and 21 minutes, respectively, and only very short-lived N^{13} and O^{15} were known for nitrogen and oxygen.

Lawrence asked me to organize a complete and systematic campaign to determine whether or not long-lived isotopes existed for any of the elements in the first row of the periodic table—especially hydrogen, carbon, nitrogen, and oxygen. From experience gained in previous years it was a simple matter to draw up a comprehensive plan which included protocols for every nuclear reaction obtainable with the projectiles available, including the choice of target materials and target chemistry. It was natural to concentrate first on carbon. An abridged plan taken from my notebook, as drawn up in September 1939, is shown in Table 1. Similar plans were devised for nitrogen and oxygen activities, based on bombardments of B_2O_3, graphite, BN, and $(NH_4)_2F_2$ targets. Every possibility was assumed—even that there might be long-lived isomers of stable nuclei (for example, C^{12*}, C^{13*}) or of short-lived nuclei (for example, N^{13*}, O^{15*}).

The first trials involved bombardment of B_2O_3 with 16-Mev alpha particles in the 37-inch cyclotron, from 27 to 29 September. A 5 microampere-hour exposure yielded no long-lived activity in the gas space, as assayed by direct introduction of the target gases into an ionization-chamber and pliotron apparatus. The residual powder was burned with a small bit of filter paper as a carbon carrier, but the resultant gases were also inactive. It could be concluded that the 16-Mev alpha particles were inadequate to produce significant quantities of N^{13*}, N^{14*}, or C^{13*} or of the isotope C^{14} by means of the (He^4,n) or (He^4,H^1) reactions. Next, B_2O_3 was bombarded for 34 microampere-hours with 16-Mev deuterons in the 60-inch cyclotron. In this experiment, E. Segré collaborated with me and examined the activities produced in the gas phase, which were introduced again directly into an ionization chamber detector. He found the expected C^{11} in enormous quantities and also an activity with a half-life of 112 minutes. But we traced this to F^{18} produced by the $(H^2,2n)$ reaction with O^{18}. By 16 October 1939 I had reached the conclusion that none of the alpha-particle-induced reactions were feasible: it appeared that at least 5×10^5 microampere-hours of 32-Mev alpha particles would be needed to produce one microcurie of radioactivity with $\tau_{1/2} \sim 1$–3 hours.

On 17 October, I tried exposing methane to 20 microampere-hours of 16-Mev deuterons in the 60-inch cyclotron and obtained the expected N^{13} (several hundreds of millicuries), and about 0.01 microcurie of F^{18} from a small amount of contaminant oxygen, but again no long-lived activity.

In the meantime, I had begun continuous exposure of a graphite probe target introduced through the north port of the 37-inch cyclotron. This probe was allowed to collect stray deuterons in the internal cyclotron beam for nearly a month, throughout January 1940. The probe was inserted so as to intercept practically all deuterons during night operation and was retracted to allow normal operation in the daytime. I undertook the night bombardments, aided occasionally by others, who needed the copious supply of neutrons produced for further studies on the uranium fission reactions. The probe target was not designed to withstand intense bombardment. I had merely smeared colloidal graphite on the water-cooled copper surface and had counted on replacing, during frequent inspections, whatever graphite was found to be blasted off. The weather was unusually violent, even for January, and on most nights there were heavy drenching rains and wind storms. The noise of the rain on the tin roof of the laboratory, accompanied by cannonades from high-voltage discharges from the cyclotron, created an appropriate fanfare for the birth of C^{14}, which was fated to occur during this bombardment.

This experiment had been regarded as the one most likely to produce C^{14}. It was performed in a spirit of mixed desperation and resignation, and it involved a considerable degree of hazard from radiation exposure, as it was necessary to examine the intensely radioactive probe nightly to insure that some graphite still clung to the target surface. Occasionally I found the irradiated graphite almost on the verge of flaking off and had to cement it back on with more graphite.

On 15 February, during a particularly violent storm, I terminated this bombardment, which had involved exposure of the graphite to 5700 microampere-hours of 7- to 8-Mev deuterons. Shortly before dawn I left the graphite, which looked like bits of gravel, in a weighing bottle on Ruben's desk. On the way home to get some sleep for the first time in several days I must have presented a sorry spectacle—unshaven, red-eyed, and dazed—for I was intercepted and questioned by police looking for an escaped convict. Fortunately I failed to pass muster and was released, to continue stumbling onward toward sleep.

On awakening some hours later I phoned Ruben, who had found the sample, burned it to CO_2, precipitated it as $CaCO_3$, and found some activity when he examined the precipitate inside a screen-wall counter of a type designed by W. F. Libby (*20*) to permit assay inside the sensitive volume of a Geiger-Müller tube. (No activity could be detected with the usual thin-walled tubes.) The effect was very small—about four times the counting background—but reproducible. In some excitement I hurried back to the laboratory, prepared a new probe target—this time one made up of graphite solidly bonded to copper—and then joined Ruben to press on with identification of the activity. By Tuesday afternoon, 27 February, we had disposed of the last uncertainty—that the activity might have arisen from S^{35} produced by the (H^2,H^1) reaction on the surface as a possible contaminant of the graphite used—but had only about one-eighth of the original activity left. We wrote a preliminary account for publication as a letter, and later as an abstract, in the *Physical Review* (*21*), and on Wednesday evening we motored to Lawrence's home to acquaint him with the result. Lawrence was resting in an attempt to banish a cold before his appearance the next night, Thursday, 29 February, to receive the Nobel prize in physics. His pleasure was unbounded but it revived nagging doubts in our own minds, about the reality of the activity we were ascribing to C^{14}. After all, it was an activity only half that of the counting background when the sample was counted as solid $CaCO_3$, even though it had persisted through repeated cycles of precipitations with $CaCO_3$ and acidification to CO_2. It was a comfort to realize that, of all the elements in the periodic system, only carbon possessed an oxide which could be liberated repeatedly from acid solutions under oxidizing conditions—a fact which made it clear that the activity observed was, in fact, isotopic with carbon.

The new probe target, with its improved mode of bonding, withstood much more intense probe beams; in 1 week a probe inserted in the south port of the 37-inch cyclotron withstood 13,500 microampere-hours of bombardment with 3- to 4-Mev deuterons. The activity obtained was 10 to 20 times the counting background and sufficient to show that the isotope was indeed C^{14}; that the beta-energy maximum lay in the neighborhood of 120 kilovolts; and that the half-life was certainly greater than 20 years. I was able to make an estimate for $\tau_{1/2}$ on the basis of considerations as follows. The first probe sample, after 5700 microampere-hours, had shown a total activity of ~100 disintegrations per second. From a knowledge of the cross section at 3 to 4 Mev for the reaction $C^{12}(H^2,H^1)C^{13}$, and from the assumption that the cross-section for $C^{13}(H^2,H^1)C^{14}$ was similar, it could be calculated that the ratio of C^{14} nuclei produced to the number of deuterons stopped in the graphite would have been about 1/60,000 if 100 percent of the carbon were C^{13}. Hence $1/(6 \times 10^6)$ was assumed for the graphite, which had the normal isotope content of 1 percent C^{13}. The total number of deuterons was $\sim 1.2 \times 10^{20}$ (5700 μamp-hr), hence the number of C^{14} nuclei produced ($N_{C^{14}}$) was $1.2 \times 10^{20}/(6 \times 10^6)$, or 2×10^{13}. Since $N_{C^{14}}$ and $dN_{C^{14}}/dt$ (100 disintegrations per second) were known, it was simple to deduce the $\tau_{1/2}$ as $\sim 4 \times 10^3$ years. This value was remarkably close to the true disintegration half-life of ~5700 years, determined many years later, but the agreement was quite accidental, as this 1940 estimate was uncertain by as much as an order of magnitude in either direction. However, it did shed light on the reason for the negative results of previous years: the half-life of C^{14} was too great to permit production of the isotope in significant quantities until the internal-target technique had been developed to the point where 5000 microampere-hours and more of bombardment was possible. Moreover, it was clear that C^{14} had an enormously long half-life—a result most surprising on theoretical grounds, as I remarked previously.

All of these investigations were based on the assumption that the (H^2,H^1) reaction with C^{13} would be much the most likely to succeed. A reaction of this type exhibited the largest cross-section among those excited by charged particles and had the advantages that the target chemistry was simple and that dilution of isotopic material was minimal. The reaction of slow neutrons with N^{14}, which had led to the initial postulation of the existence of C^{14}, was regarded as a possible, but not promising, process for producing C^{14}. It may come as a surprise to many readers that this impression prevailed in 1940, in view of the fact that the $N^{14}(n,H^1)C^{14}$ reaction is the method of choice now.

There were many cogent reasons for neglecting the slow-neutron reaction. (i) The neutrons produced in the cyclotron were not primaries but were secondary particles with ranges up to many meters in dense media, so that only a fraction could be captured by N^{14} nuclei, even with the best possible geometry. On the other hand, all deuterons produced as primaries with very small ranges could be absorbed in a minimal amount of target. (ii) Cross sections for slow-neutron capture were high only for the (n,γ) process, with which the (n,H^1) process was expected to compete poorly. (iii) The recoil C^{14} nuclei produced would not be expected to reach equilibrium in chemical species sufficiently uniform to permit simple, efficient extraction. Nevertheless, two carboys, each containing 5 gallons of saturated ammonium nitrate solution, were placed near a good source of neutrons—the deflector region of the 60-inch cyclotron—in January. Prior to exposure, the solutions were acidified with dilute nitric acid, aspirated with CO_2-free air to remove contaminant carbonate (which would dilute excessively any radioactive carbonate formed—not that we expected to see any!), and sealed tightly. The success with the graphite probes had completely distracted my attention from these carboys, and I was busily engaged in an attempt to improve the (H^2,H^1) yields by fabricating C^{13}-enriched graphite probes when an angry deputation from the 60-inch cyclotron paid me a visit and demanded that the carboys, which had sprung leaks and were proving an intolerable nuisance, be removed. The deflector region was in constant need of adjustment, and the cyclotron crew was weary of the constant pushing and pulling required to move the box and get at the deflector controls, especially since the box was wet with acid.

So, with no great enthusiasm, I went over to the 60-inch cyclotron with a cart and moved the box to Ruben's laboratory in the ramshackle hut affectionately labeled the "Rat House." Ruben and I decided to make a gesture and aspirate some air, freed of CO_2 by passage through soda lime, through the carboys in the hope that some C^{14} might be entrained and removed as $C^{14}O_2$. A copious precipitate of $CaCO_3$ which formed in the $Ca(OH)_2$ trap after passage of the effluent gases through a combustion train did not encourage us, since it indicated that large quantities of CO_2 had diffused into the ammonium nitrate solutions and that any activity formed was likely to have been lost because of excessive dilution. To our astonishment, we found that a small fraction of this precipitate was so active it completely paralyzed the screen wall counter! In a short time we ascertained that we had several microcuries of C^{14}—a quantity greater by two or three orders of magnitude than any we had seen from the probe bombardments. Needless to say, our interest in the $C^{13}(H^2,H^1)C^{14}$ reaction vanished, never to return.

Where had I gone astray in assessing the slow-neutron process? All the assumptions about poor cross sections and complex target chemistry were eminently sound and eminently wrong! As it developed later, the (n,H^1) process for producing N^{14} was favored heavily over the (n,γ) process—possibly the only exception to the general rule. It is remarkable that the only other instance of appreciable yield from the (n,H^1) process with slow neutrons also involves production of an important radioactive tracer (22)—S^{35} from the (n,H^1) reaction on Cl^{35}. Moreover, as we found in further experimentation (*23*), and as was later confirmed by Yankwich, Norris, and Rollefson (*24*), well over 80 percent of the recoil C^{14} found its way into the volatile oxides of carbon (CO and CO_2) and so made possible a simple, practically quantitative recovery of the C^{14} from any amount of bulk solution. When all these facts were known there was some talk of forming a syndicate to build a battery of cyclotrons designed solely for the production of C^{14}.

In the meantime, Lawrence authorized construction of a special set of stainless steel cans with aspirator inlets and outlets to be mounted as a permanent shield around the 60-inch cyclotron. This setup was expected to produce hundreds of microcuries of C^{14} each month. After these cans had been in place for a month, however, worry over the possibility, however remote, that ammonium nitrate solutions were an explosion hazard induced Lawrence to order them removed. A few years later, in 1944, these cans served as a source of C^{14} in the first tracer researches with C^{14} to be reported in a scientific publication—research which I carried out in collaboration with Barker (*25*).

The story of the birth of C^{14} ends here. But, of course, there were many chapters to come. One of these was the expansion of C^{14}-production from the microcurie to the curie level which followed the development of nuclear reactors, and the resultant proliferation of C^{14} as a tracer isotope in every area of biological research. Another chapter (which provides a thread from the early history up to 1940) concerns something that may prove of great significance in the future of nuclear theory—the anomalously low rate of C^{11} decay. All through the period from 1938 to 1940 the search for C^{14} was conducted in the belief that the half-life of C^{14} was of the order of seconds, or less. When it was seen, by July of 1940, that the half-life of the material we had produced was certainly of the order of years—in fact, millennia—doubt was expressed that the observed activity was isotopic with carbon. Even the testimony of algae, which absorbed the activity photosynthetically, and the chemical behavior of the activity failed to still these doubts at the time. The question raised—Why is C^{14} so long-lived?—remains with us today.

Explanations have been offered seriatim; (i) that there is a change in parity; (ii) that C^{14} is wholly $^1S_0$ and N^{14}, purely ^3D, hence, that a transition between them is ΔL forbidden; (iii) that there is a fortuitous cancellation in the matrix element for decay (*26*). The third suggestion is favored at present (*27*) but is not wholly acceptable. The first two are definitely excluded on experimental as well as theoretical grounds (*26*, *27*). It is apparent that the answer to the riddle of C^{14} decay will be an important part of the future history of nuclear theory. In conclusion, I quote, as a moral for our story, the words of the late psychiatrist E. Winzholz: "We never let our theories interfere with our practice."

References and Notes

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