HISTORY OF RADIOCARBON DATING

W. F. LIBBY
DEPARTMENT OF CHEMISTRY AND INSTITUTE OF GEOPHYSICS,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIF.,
UNITED STATES OF AMERICA

Abstract

HISTORY OF RADIOCARBON DATING. The development is traced of radiocarbon dating from its birth in curiosity regarding the effects of cosmic radiation on Earth. Discussed in historical perspective are: the significance of the initial measurements in determining the course of developments; the advent of the low-level counting technique; attempts to avoid low-level counting by the use of isotopic enrichment; the gradual appearance of the environmental effect due to the combustion of fossil fuel (Suess effect); recognition of the atmosphere ocean barrier for carbon dioxide exchange; detailed understanding of the mixing mechanism from the study of fallout radiocarbon; determination of the new half-life; indexing and the assimilation problem for the massive accumulation of dates; and the proliferation of measurement techniques and the impact of archaeological insight on the validity of radiocarbon dates.

INTRODUCTION

The neutron-induced transmutation of atmospheric nitrogen to radiocarbon, which is the basis of radiocarbon dating, was discovered at the Lawrence Radiation Laboratory in Berkeley in the early thirties. Kurie [1a], followed by Bonner and Brubaker [1b], and Burcham and Goldhaber [1c], found that the irradiation of air in a cloud chamber with neutrons caused proton recoil tracks which were shown to be due to the nitrogen in the air, and in particular to the abundant isotope of nitrogen of mass 14. The neutrons producing the tracks appeared to be of thermal, or of near thermal energy, and the energy of the proton therefore gave the mass of the ^{14}C produced; from this it was concluded that the beta decay of ^{14}C to reform ^{14}N from ^{14}C should release 170 kV energy (2.7×10^{-7} erg). So the work of Kurie, Bonner, Brubaker, Burcham, and Goldhaber laid the foundation in the reaction

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

The thermal-neutron absorption cross-sections for the elements were measured systematically by the Rome group, under Fermi, and it was found that the element nitrogen had an effective cross-section of about 1.7 b (one barn is 10^{-24} cm^2) which is large, compared to most materials. This indicated that the (n, p) reaction (1) is unusually probable and that, in fact, thermal neutrons in air would be expected to be converted essentially quantitatively into carbon-14 by this reaction.

At this early time, in 1936, the Table of Isotopes showed that there was a blank at the position mass 14 in the element carbon, and indicated therefore that there might be a radioactive isotope of this mass. Therefore, following on the reporting of the (n, p) reaction with nitrogen, it seemed reasonable to try to produce radiocarbon by irradiating nitroge-

nous materials with neutrons. This was attempted by the author's group at the University of California at Berkeley by placing 100 kg or so of ammonium nitrate near the target of the newly completed cyclotron in the Lawrence Radiation Laboratory. The idea was that the neutrons would produce radiocarbon which would be trapped in the ammonium nitrate crystals as carbon monoxide, or carbon dioxide, and which would be released on dissolving in water. In the early research of Yost and collaborators [2] at the California Institute of Technology it was shown that carbon produced by a similar reaction behaved chemically, as one would expect, and formed CO and CO_2. Therefore, it was supposed that any radiocarbon produced by the neutrons could be collected and measured for radioactivity. This was undertaken by Samuel Ruben for his doctoral thesis under the direction of the author in the Chemistry Department at the University of California at Berkeley. However, it was mistakenly supposed that the number of atoms needed would correspond to something like the case of sulphur-35, with which experiments had been made. Sulphur-35 has an average life of four months and it was thought that, since the 170 kV decay energy expected for radiocarbon was close to that observed for sulphur-35, the lifetime would be similar. Bombardments were therefore planned on the assumption that this would be the case. Actually, of course, the lifetime is 8300 yr on average, so Ruben and the author made only 1/25 000 of what was needed; therefore there was failure to detect any radiocarbon produced in this first experiment. It is known today that the procedures used were quite adequate and radiocarbon would have been found if it had been irradiated more intensely with neutrons; but the attempt was doomed to failure because of ignorance of the long lifetime. It is fair to say that, even today, the reason for the long lifetime is unknown, and in those early days there was discussion of very rough relationships between transition energy and lifetimes in analogy to the case for alpha radioactivity where tight relationships hold. Of course, it is most fortunate for radiocarbon dating that the lifetime is so very unexpectedly long.

Ruben went on to take his degree with the author on other subjects in physical radiochemistry and, after having finished, joined forces with Martin Kamen, who had come to the Lawrence Radiation Laboratory from Chicago a couple of years before to have another try at radiocarbon. This time they succeeded [3]. By bombarding graphite with a strong deuteron beam from the cyclotron, the (d, p) reaction on the ^{13}C present in the natural mixture gave enough radiocarbon for them to detect. On the basis of this they gave the tentative value of 25 000 yr as the lifetime. This was in 1940. World War II came, Ruben died, and after the war Kamen went on to biochemical work. However, before his death, Ruben published a most distinguished series of papers on the use of radiocarbon in the study of photosynthesis.

The next step in the history of radiocarbon dating was the discovery by Korff that neutrons are produced in the atmosphere by cosmic rays. A counter had been developed at Berkeley by Korff and the author's group which was capable of detecting neutrons [4]; they found, on flying this counter on a balloon, that its count rate increased with altitude to a maximum at some 50 000 ft, after which it fell off again (Fig. 1). It was a reasonable assumption at the time that the neutron was radioactive with respect to the formation of hydrogen, but its lifetime was

unknown. (Subsequently it was shown that the mean life is 18 min.) It was clear, therefore, that there would be little chance that the neutrons found would be cosmic-ray primaries, since they would not have been able to survive the long times in flight which cosmic-ray primaries undoubtedly require. Further, the fall-off at the top of the atmosphere was conclusive evidence that they were not primaries for, had they been, there would have been little, if any, fall-off; it appeared that the fall-off must be due to their having escaped the Earth. In his first reference to this work Korff [5a] pointed out how the (n, p) reaction on nitrogen would undoubtedly make carbon-14; from the data of Korff and Hammermesh [5b] it was possible to estimate that, on average, one or two atoms of carbon-14 would be produced in this way each second for each cm^2 of the Earth's surface.

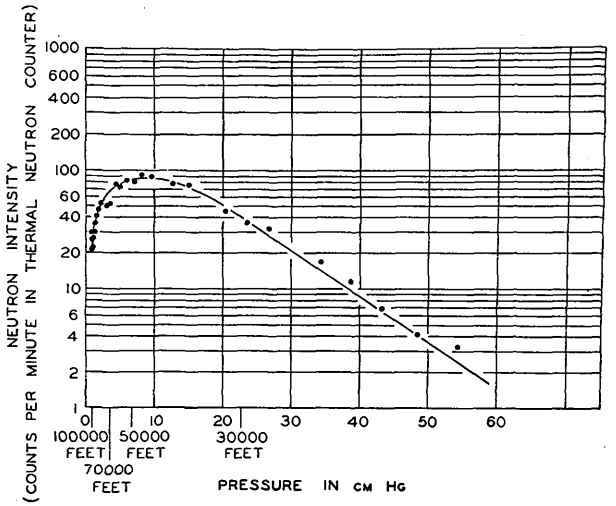

FIG. 1. Neutron density in free atmosphere versus altitude at Princeton, N.J. (8 Jan. 1949) (Phys. Rev. 74 (1948) 504; 76 (1949) 1267; 77 (1950) 728; Bull. Am. Phys. Soc. 23 2 (1948) 21)

After World War II the story was taken up again when, in a general study of the effects of cosmic rays on the Earth, the author's group at Chicago decided to concentrate on carbon-14 and tritium made by the cosmic-ray secondary neutrons in the atmosphere. In an earlier research at Berkeley [6] Cornog and the author had shown that fast neutrons on nitrogen make tritium (radioactive hydrogen of mass 3 and mean life 18 yr) and carbon-12, somewhat in analogy to reaction (1) by which slow neutrons on nitrogen make ordinary hydrogen of mass 1 and carbon-14. The plans for this research were outlined at that time [7].

HISTORY OF RADIOCARBON DATING

The real beginning of the history of radiocarbon dating as such was in the realization that the cosmic-ray production of radiocarbon in the

high atmosphere leads to a continuous labelling of the biosphere and living matter, which is terminated at death. It is difficult to know exactly when this idea was born, but it was very soon after the author's plan was fixed to detect the effects of cosmic rays on the Earth's atmosphere. It was necessary to know how a test could be made for the radiocarbon that must be present on Earth, according to Korff's measurements; in considering where to look for this natural radiocarbon, and how to detect it, it was realized that the supply of radiocarbon from the well-mixed system, consisting of the carbon dioxide in the air, and the dissolved salts in the ocean and in the biosphere, would be cut off to any living being at the instant of death. From this, of course, the principle of radiocarbon dating was obvious – namely, that the decay of the radiocarbon normally present during life would measure the time elapsed since death – half of it being lost every 5730 yr.

The first step to be taken to develop the idea was to look for natural radiocarbon in living systems; the second was to measure the half-life accurately, so that if radiocarbon dating proved practical, it would be possible to give the dates accurately. At that time there was very considerable uncertainty that the Ruben and Kamen value of some 25 000 yr still stood. However, within a year or two, as a result of researches in the laboratory of the author's group at the Argonne Laboratory, and at the University of Chicago, together with a number of other teams, the value of 5568 yr [8a] was established; the radiocarbon dates have always been given on this basis, even though it is now known that it is some 3% low compared to the latest value of 5730 yr [8b, c, d]. This convention has been adhered to for the purpose of avoiding confusion [9].

The first task was to analyse living matter for radiocarbon to see whether it was true that about one atom in 10^{12} of the carbon in living systems was radiocarbon. The estimate of the amount of diluting carbon (the 10^{12} factor) was difficult, for it was not known at that time whether the oceans mixed in the lifetime of radiocarbon; it was clear that the ocean would contribute the dominant amount if it did mix. It was assumed that the mixing was rapid, essentially on an ad hoc basis, although comfort was taken from the argument that the thermal heat from the floor of the ocean was very likely to be adequate to mix the ocean, if nothing else did. Now, twenty years later, it is known that the assumption was correct, for the mixing time has been measured, using radiocarbon dating, and it has been found to be something less than 2000 yr, on average. It was hoped, as this crucial assumption was made, that it was so, because radiocarbon dating could not have been as successful if the oceans were not equilibrated rapidly with the atmosphere and biosphere. The stability of the reservoir that is given by the ocean could not have been obtained in any other way; as the ice ages came and went, and the amount of living matter on Earth changed considerably, the diluting reservoir would probably have fluctuated wildly. Therefore the concentration of radiocarbon in living matter in times past would not have been constant and would have been difficult to estimate (Table I). It is the essence of the radiocarbon dating method that at the instant of death the radiocarbon concentration is known accurately. The facts that the carbon in the ocean is some 30 times as abundant as that in the biosphere and the atmosphere combined, and that the volume and compo-

TABLE I. EXCHANGE RESERVOIR
(g C/cm^2)

	Anderson and Libby	W.W. Rubey [a]
Ocean "carbonate"	7.25	6.95
Ocean, dissolved organic	0.59	
Biosphere	0.33	{0.78
Atmosphere	0.12	0.125
Total	8.3	7.9

[a] RUBEY, W.W., Bull. Geol. Soc. of Amer. 63 (1951) 1111.

sition of the oceans have not fluctuated seriously during the last several tens of thousands of years, gave every reason to hope that, if the oceans mixed, the radiocarbon concentration in living matter would have been constant. There was, therefore, concern regarding the question of ocean mixing; the fact had to be faced that one did not know. However, it was clear that, if it were mixed, radiocarbon dating had a chance.

This mixing of the atmospheric carbon dioxide with the oceans, which was hoped for so ardently, did however cause one difficulty. The factor of 30 of dilution involved pushed the concentration of radiocarbon which was expected (some 10 to 15 dpm/g carbon) out of the range of sensitivity of the existing instruments and measurement techniques. The author's group at Berkeley had developed a sensitive instrument – the screen wall Geiger counter – for the measurement of feebly radioactive substances, and it would have been possible to detect natural radiocarbon with it at a level some 30 times higher than that expected on the assumption that the mixing of the ocean was rapid. It used essentially a good fraction of a square foot of solid sample surface in intimate contact with the sensitive gas volume, so that something like 35 to 40% of all the radiation leaving the sample surface would pass through the sensitive volume of the counter, and be recorded. However, the radiation of radiocarbon is very soft (it is reduced by the factor 1/2.718 by a thickness of any light element absorber weighing 3 mg/cm^2 area); effectively, only the top 3 mg on each square centimeter of area would be recorded. Therefore, with the screen wall Geiger counter, with a sample area of about 600 cm^2, it was expected to have about 2 g carbon disposed for measurement at about 35% efficiency (providing pure carbon was mounted). This would present 20 to 30 dpm total, of which about one third would be directed inwards towards the counter's sensitive volume, giving an expected count rate of between 7 and 10 cpm for pure carbon from the biosphere. However, it is a very well-known fact that Geiger counters have a kind of irreducible background due to cosmic-ray secondaries which are too penetrating to be shielded out with thick iron or lead shields (μ mesons) and this rate for the screen wall counter was expected to be about 100. Because of this, the 7 to

10 cpm looked too small to find with certainty; thus the task of enriching the natural radiocarbon was undertaken so that it could be detected (Figs. 2, 3).

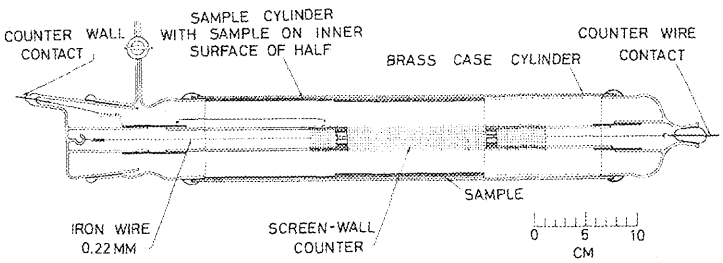

FIG. 2. Cross-section of screen wall counter

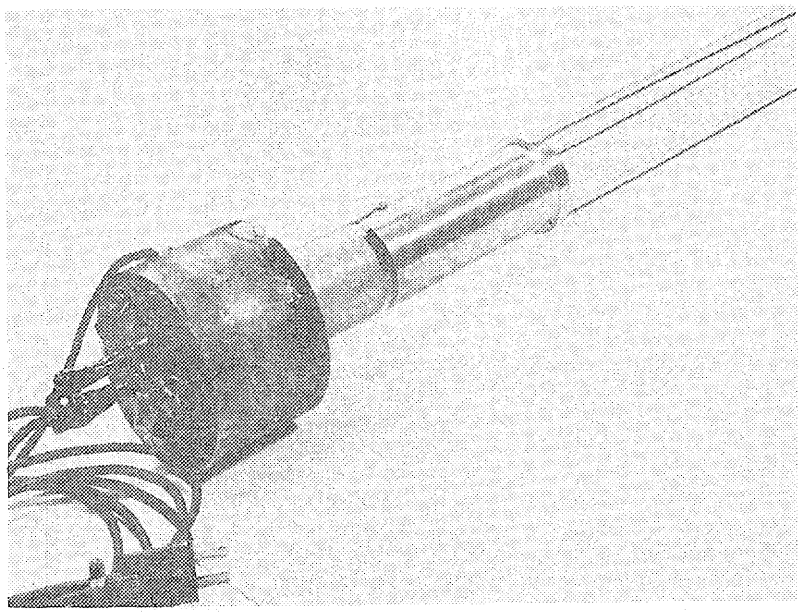

FIG. 3. Screen wall counter (front view)

Very fortunately, a friend, A. V. Grosse, was in the business of concentrating carbon isotopes, using methane as a process gas in a thermal diffusion column, and he was asked to join in the search for natural radiocarbon. The next task then was to find methane which was alive, in the sense of not having been too long out of the biosphere. Methane from an oil well would obviously contain no radiocarbon, since it would be far too old. This was accomplished by Grosse by asking Joseph Pew, of the Sun Oil Company, to persuade the mayor of the city of Baltimore to permit sewage methane from the Baltimore City sewage disposal plant

to be used. It was this methane which Grosse concentrated in his thermal diffusion column at Marcus Hook, Penn. , and shipped to Chicago, where it was measured in the author's counters. Grosse's concentrates were measured for ^{13}C enrichment, and from the observed ^{13}C enrichment the expected ^{14}C enrichment was readily calculated [11].

The enriched methane gas was placed directly in an ordinary cylindrical Geiger counter, rather than making carbon of it and using the screen wall, because the enrichments calculated were somewhat larger than the bare minimum. Unenriched methane was used for the background measurement. A plot was made of the difference in count-rates for the enriched and unenriched methane, using thick shielding (a foot or so of iron and lead in all directions) to eliminate the background from radioactivity in the laboratory and leave only the meson level (Fig. 4).

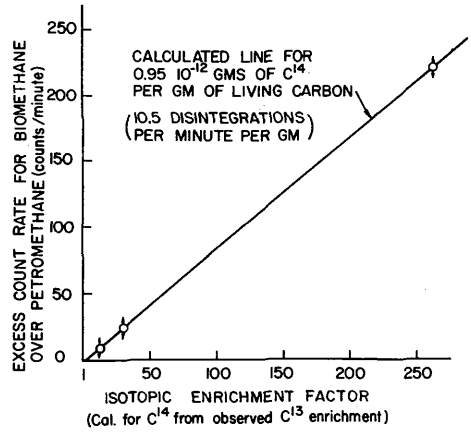

FIG.4. Radioactivity of biomethane samples versus isotopic enrichment (6.5-mm Hg pressure in 1900-cm^3 counter at room temperature)
ANDERSON, E.C., LIBBY, W.F., WEINHOUSE, S., REID, A.F., KIRSHENBAUM, A.D., GROSSE, A.V., Phys. Rev. 72 (1947) 931.

In this way a rise with enrichment, that fitted the theoretical curve well, corresponding to about the concentration predicted, was observed. The methane was then burned, and the CO_2 was precipitated as calcium carbonate and was measured in the screen wall counter to observe its activity and to prove that it was chemically carbon. Finally, an absorption curve was run with aluminium foils placed over the calcium carbonate in the screen wall counter; thus it was possible to show that the radioactivity had the penetration characteristics of synthetic radiocarbon (absorbed to 1/e intensity by 3 mg/cm^2) (Fig. 5).

The good fortune in many stages of this research was most miraculous. As one example, it would have been difficult indeed to have done the research without Grosse's thermal diffusion columns, which one could not have afforded to construct. They just happened to be ready, and operating. As a second example, without the experience in the measurement of small amounts of radioactivity which the group had gained in other connections over the years, it would not have been possible to measure even the most concentrated samples. As a third example,

the oceans do mix. As a fourth, no one in Baltimore had used synthetic radiocarbon from the Atomic Energy Commission for research at the time of the study, so it was quite certain that the radiocarbon found in the sewage was natural.

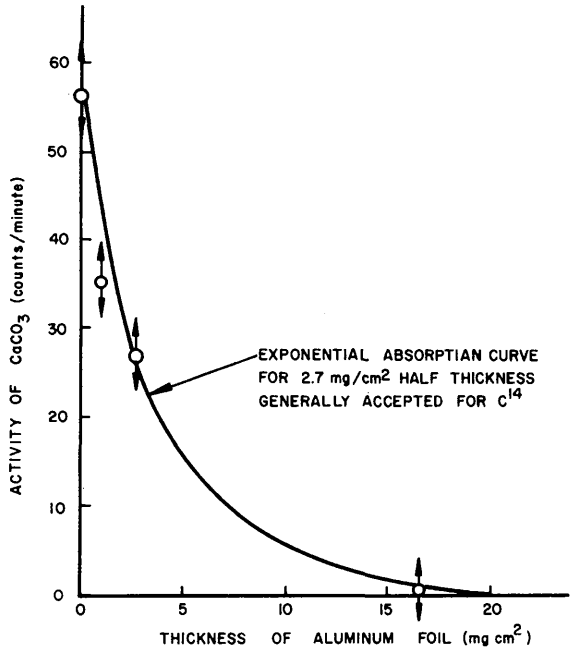

FIG. 5. Absorption of $CaCO_3$ radiation in aluminium and aluminium-absorption curve for synthetic radiocarbon (^{14}C)
(ANDERSON, E.C., LIBBY, W.F., WEINHOUSE, S., REID, A.F., KIRSHENBAUM, A.D., GROSSE, A.V., Phys. Rev. 72 (1947) 931)

After the discovery of natural radiocarbon, the question arose again as to how to measure the feeble amount of radioactivity accurately, for it was clear that radiocarbon dating would never be of practical use if each sample had to be enriched as Grosse had done. The dates would have been far too expensive; so, the 100 cpm of meson background remained a problem. The unshielded screen wall counter had a background rate of about 500 cpm sitting on the laboratory table, and this dropped to about 100 cpm when the counter was put behind heavy iron and lead shielding to shield the gamma radiation from radioactive materials in the walls and floor – uranium, thorium and potassium. (This was before radioactive fallout was noticeable.) Further shielding did little good. It was known that the residual background was due to the cosmic ray μ mesons, that they were extremely penetrating and that there was hardly any hope of absorbing them short of several hundred feet of rock. This problem remained for some weeks until the idea of anticoincidence shielding occurred.

Noting that, if a shield of counters in close contact were to be placed around the radiocarbon dating counter, any mesons passing through the dating counter would certainly have to pass through one of the guard counters, it was realized that coincidences in time would always exist between the guard counter counts and those from the dater for those rays. Therefore, if coincidental counts were always eliminated from the record, it would be possible to be rid of the meson background without appreciable loss in the radiocarbon count rate, since the shut-off time could be as little as one thousand of a second per meson (Fig. 6). There-

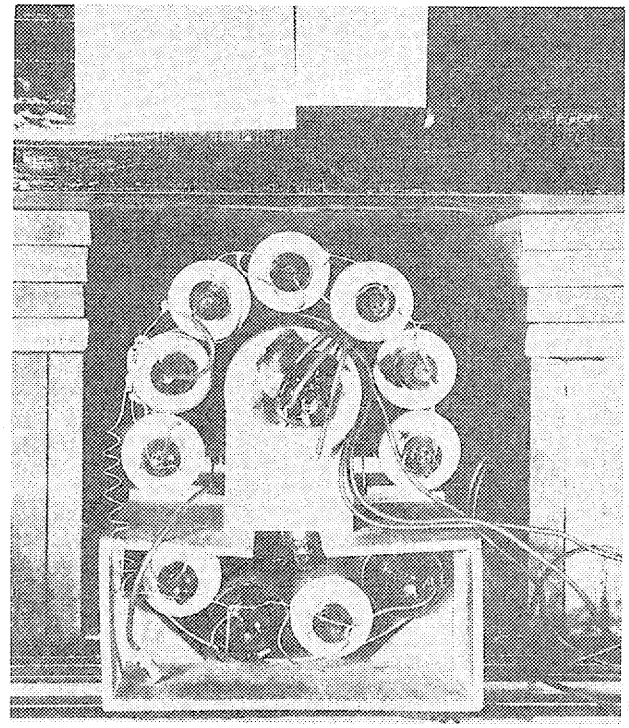

FIG. 6. First AC set and shield

fore, the trial set was built, the mesons thus eliminated, and the background reduced by a further factor down to something like 6 cpm, to about 1% of the unshielded value. With this value it was then possible, with pure elementary carbon, to detect and measure the natural radiocarbon accurately at something like 7 to 10 cpm above background.

The next procedure was to develop the technique for reducing the carbon dioxide obtained by burning the object to be dated to pure carbon black for measurement in the screen wall counter. Today one uses the carbon dioxide gas itself. The carbon was formed by heating the CO_2 with magnesium metal turnings until a flame was formed by the reaction

$$2\,Mg + CO_2 = 2\,MgO + C \qquad (2)$$

Unfortunately, the magnesium-oxide ash produced clung to the carbon formed and it was never possible, even with extraction at length by hydrochloric acid solution, to obtain the carbon black entirely free of ash (Fig. 7). Therefore, one had to be content with the consequent reduction in count rate which sometimes amounted, in extreme cases, to 20 or 30%.

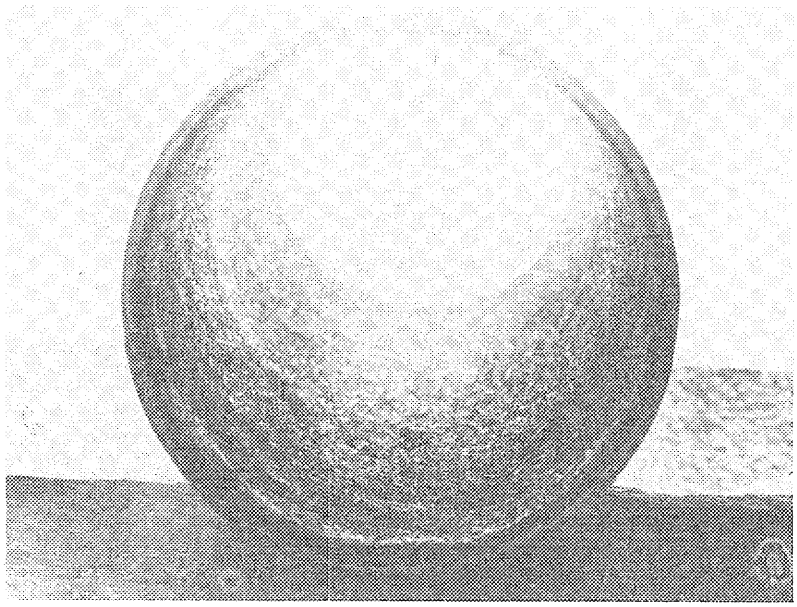

FIG. 7. Carbon black sample

It was found, however, that, by using the anticoincidence counter shield and a good heavy iron and lead shield, and the ash containing carbon, natural radiocarbon could be comfortably measured. On a background of about 6 cpm the rate was approximately doubled when the carbon black sample was placed on the counter wall. The screen wall counter is constructed in such a way [10] that the sample cylinder slides, so with the sensitive part of the counter in the middle third of the over-all length, the sample cylinder, with the sample disposed on half, has two positions, one with the bare wall in contact with the counter, and the other with the carbon sample in contact. In this way background readings can be obtained without tampering with the counter gas filling. It was this consideration which led to the use of the screen wall counter rather than the gas proportional counter which is now generally used. The first counting was done with gas counters with methane filling, as mentioned earlier; this could have continued, but there was the problem of background constancy and the necessity with gas counters of measuring the background with a separate gas filling. With the enriched samples the count rate was too large for this uncertainty to be a problem. (This is done routinely now, and very successfully,

with the carbon-dioxide proportional counters.) The screen wall counter and the carbon black method was used, because the background could be reliably measured throughout the run. The routine was to alternate between the sample and background positions of the sample cylinder every few hours during some 48 h or so to accumulate about 10 000 counts from the carbon sample being measured. From the laws of statistics 10 000 counts are necessary for something like a 1% error in the count and so, at the rate of about 7 cpm above a background rate of about 6, it was necessary to measure something like 24 h in each position. Other subtleties were involved in the use of the screen wall counter also. The filling required a quenching gas, and the best quenching gas at that time was ethyl alcohol, which was avidly absorbed by the highly porous carbon black. This, of course, raised two problems – the radiocarbon in the alcohol (one had to be certain that it was derived from fossil fuel) and its absorbing effect on the ^{14}C radiation from the carbon black. It was therefore necessary to make a further correction for the alcohol absorbed. After the runs the carbon samples were then bottled. About 700 samples were measured by the carbon black method, and the original bottles are still in the laboratory in Los Angeles, although some of them have been given to other radiocarbon dating laboratories for check measurements, using the more modern gas counting techniques.

Following the development of the counting technique, E.C. Anderson[1] proceeded to make measurements of biological materials from all over the world, using wood and flesh from various latitudes. He found, as was hoped, that the mixing was so good that, even though the cosmic-ray intensity varies strongly with latitude, the long lifetime of radiocarbon and the relatively short time that it stays in the ocean and the biosphere means that it is thoroughly mixed (Fig. 8). Thus, this assumption was found to be correct, and it was possible to continue towards radiocarbon dating itself (Table II).

At this stage James Arnold, of Princeton University, joined the group to test the radiocarbon dating method. To review, in the principle of radiocarbon dating it is assumed that the cosmic rays have been constant and have been irradiating the Earth at the present intensity for several radiocarbon lifetimes, i.e. perhaps 30 000 yr. There was evidence for this in the agreement observed between the concentration of radiocarbon in nature, as seen in the Baltimore sewage, and that calculated from Korff's measurements. It was therefore expected and hoped to observe in ancient matter radiocarbon concentrations corresponding to the time elapsed since death, using the exponential law of radioactive decay, with Anderson's value for the concentration in living matter as the initial value. An object that had been dead 5730 yr (5568 yr was the figure for the half-life actually used, as it still is in radiocarbon dating tables) should have half the radiocarbon content, that is about 7.5 dpm/g carbon, and one quarter, or about 3.75 dpm/g after 11 460 yr, or two half-lives. In this way the decay should proceed until, at 5/300 yr, there would be only one part in 1024 (2^{10}) of what was there at the beginning.

Radiocarbon dating, therefore, is limited to the first 50 000 yr or so, the problem being that, even if the small amount of radioactivity left after that time could be measured, the problem of contamination, and of

[1] Dr. E.C. Anderson wrote his Ph.D. thesis on natural radiocarbon.

TABLE II. ACTIVITY OF TERRESTRIAL BIOSPHERE SAMPLES

Source	Geomagnetic latitude	Absolute specific activity (Dpm/g)
White spruce, Yukon	60°N.	14.84 ± 0.30
Norwegian spruce, Sweden	55°N.	15.37 ± 0.54
Elm wood, Chicago	53°N.	14.72 ± 0.54
Fraximus excelsior, Switzerland	49°N.	15.16 ± 0.30
Honeysuckle leaves, Oak Ridge, Tenn.	47°N.	14.60 ± 0.30
Pine twigs and needles (12 000-ft. alt.), Mount Wheeler, New Mex.	44°N.	15.82 ± 0.47
North African briar	40°N.	14.47 ± 0.44
Oak, Sherafut, Palestine	34°N.	15.19 ± 0.40
Unidentified wood, Teheran, Iran	28°N.	15.57 ± 0.34
Fraximus mandshurica, Japan	26°N.	14.84 ± 0.30
Unidentified wood, Panama	20°N.	15.94 ± 0.51
Chlorophora excelsa, Liberia	11°N.	15.08 ± 0.34
Sterculia excelsa, Copacabana, Bolivia 9000-ft. alt.	1°N.	15.47 ± 0.50
Ironwood, Majuro, Marshall Islands	0°	14.53 ± 0.60
Unidentified wood, Ceylon	2°S.	15.29 ± 0.67
Beech wood, Tiera del Fuego	45°S.	15.37 ± 0.49
Eucalyptus, New South Wales, Australia	45°S.	16.31 ± 0.43
Seal oil from seal meat from Antarctic	65°S.	15.69 ± 0.30
Average	.....	15.3 ± 0.1*

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

LIBBY, W.F., Radiocarbon Dating, University of Chicago Press Chicago (1955).

the validity of the sample, becomes insuperable. At 57 300 yr a contamination of one tenth of one percent doubles the radiocarbon content and reduces the age as calculated by 5730 yr. Of course, in principle, one could take a very large amount of sample and enrich it isotopically with techniques similar to those used by Grosse. DeVries [12] did exactly this with one or two samples years later. However, the problem of the integrity of the sample is obviously dominant in radiocarbon dating of very old materials.

Arnold and the author gave first attention to the question of sample integrity, as it was conceivable that there would be nothing left of the original material in an ancient tomb. The question is twofold: "Is it possible that contamination can be removed from a piece of ancient carbon-containing matter?"; and "Is it possible that, after decontamination, sizeable amounts of matter can be found which consist of the same atoms that were present when the object was alive?". There was hope that this was so because of the unique nature of biochemical processes. It seemed very likely that only living processes can produce the molecules

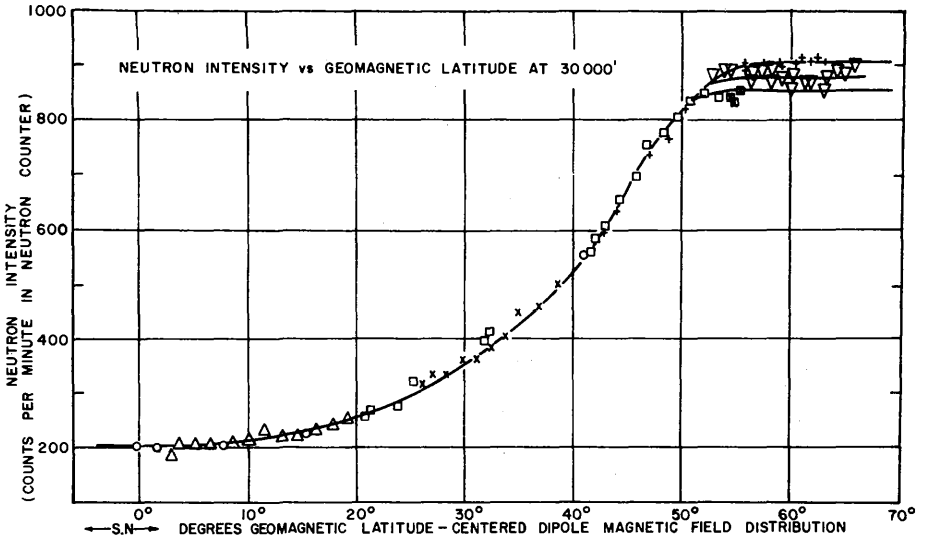

FIG. 8. Latitudinal variation of cosmic-ray neutron intensity
(After SIMPSON, J.A., Jr., Phys. Rev. 73 (1948) 1389)

of which living things consist; thus the remains would retain their individuality in death, and contaminants would not imitate them so closely as to be inseparable. The contaminants would be of higher molecular weight in general and chemically distinguishable. Of course, there was the problem of sheer physical contamination, but it seemed possible that this could be solved by careful examination and cleaning. Thus a technique was developed for cleaning samples and authenticating them, which involved mechanical washing followed by chemical treatments to remove contaminants such as the humic acids from soil and calcium carbonate from limestone, etc. The proof of the adequacy of these techniques necessarily lay in finding the same age for a given site with a variety of different materials. Thus it was gratifying to observe that on the Two Creeks Forest bed in Wisconsin, made during the last glacial advance, the peat in the soil gave the same date as large pieces of wood from the trees that had been felled by the southward moving glacier as it advanced some 11 400 yr ago (Table III). Similar tests in other sites and contexts showed that it is indeed possible to find matter containing carbon clean enough and authentic enough to give reliable radiocarbon dates. Charcoal has been found to be one of the best types of material.

TABLE III. RESULTS FROM TWO CREEKS FOREST BED, WIS. SHOWING AGREEMENT WITH DIFFERENT KINDS OF SAMPLES

UNITED STATES OF AMERICA	
Two Creeks; wood and peat from Two Creeks Forest Bed, Manitowoc Co., Wis. Underlies Valder's Drift. Spruce forest pushed over and buried by last ice sheet	
Sprucewood, Wilson, Mass. – C-308	10 877 ± 740
Tree root, Bretz, Chicago – C-365	11 437 ± 770
Peat in which root was found, Bretz, Chicago – C-366	11 097 ± 600
Sprucewood, Horberg & Bretz, Chicago – C-536	12 168 ± 1500
Peat, Horberg & Bretz, Chicago – C-537	11 442 ± 640
	11 404 ± 350
FED. REP. OF GERMANY	
German Alleröd: Zone IIb, northwest Germany.	
Firbas, Germany – C-337	11 044 ± 500
UNITED KINGDOM	
Alleröd I: peat, Hawks Tor, Cornwall. Late Glacial, Zone II. Godwin, Cambridge – C-341	9 861 ± 500
Godwin: lake mud, Neasham, near Darlington, Zone II.	
Blackburn & Godwin, England – C-444	10 851 ± 630
REPUBLIC OF IRELAND	
Irish Mud: lake mud, Knocknacran, County Monaghan.	
Late Glacial Zone II. Mitchell, Dublin – C-355	11 310 ± 720

It is found very widely and is associated with human occupation in most sites, for man is apparently the only animal that has learned to build fires. It is cleaned by picking out rootlets, washing, treating with sodium hydroxide solution to remove the soil acids, with hydrochloric acid to remove contaminant calcium carbonate, and finally with distilled water and drying, before burning to collect the carbon dioxide. Other good materials are wood (although tree rings need to be watched and considered in the data calculation since the rings are of different age), cloth, and, in some cases when well preserved, sea shell – here the carbon is liberated by adding hydrochloric-acid solution since the shell is chemi-

cally calcium carbonate. Thus it was found that there is no shortage of material which can be used.

The amount of material needed depends of course on the method of measurement. At the present time, with gas counters, as little as 1 g can be used under special circumstances. The black carbon method, which was used by Arnold and the author, needed about 10 g carbon per run, or something like two ounces of a sample of average composition for duplicate measurements with normal processing losses. The modern CO_2 proportional carbon technique requires 4 to 5 g of elementary carbon per run and thus uses less material than the old black carbon method. Oeschger [13] recently reported being able to measure radiocarbon dates on samples of two or three hundred milligrams.

The earliest experience on ancient matter obtained by the author was with Egyptian material from the Oriental Institute at the University of Chicago, and the first measurement gave a satisfactory date. However, the second measurement gave the supposedly Egyptian sample a modern or zero age. This was puzzling until it was learned with great relief that there was indeed a possibility that the material was modern. Fortunately this happened very seldom, as otherwise faith in radiocarbon dating would have been rapidly shaken and the research abandoned (once again good luck held!).

Research into the accuracy of radiocarbon dates was necessarily in co-operation with archaeologists and geologists, so a request was made for a committee of experts of the American Archeological Association and the Geological Society of America to be appointed to assist in the selection and acquisition of samples for measurement. A very distinguished committee, consisting of Frederick Johnson of the Peabody Institute in Amherst, Richard Foster Flint of Yale, Froelich Rainey of the Philadelphia Museum of the University of Pennsylvania, and Donald Collier of the Chicago Museum of Natural History, was appointed and served to select and acquire the materials to test the method. It also served to make a selection from samples offered throughout the first years and Johnson and Flint are still active in this role[2].

As the method has been perfected, and accuracies have increased, it has been discovered, as might have been anticipated, that there are significant deviations between radiocarbon dates and the true dates, but during the early years good checks were found by the author's group [14], since the measurement errors gave dates accurate to only two centuries or so (plus or minus 100 yr) (Figs. 9, 10, 11). Apparently, and fortunately, the deviations are normally small in the periods of recorded history [15], being of the order of 1 or 2% in radiocarbon content (1% is 80 yr). A curve of correction has been published by Suess and others [16a, b, c, d, f, g] which can be used to about three thousand years ago to give results which are apparently fully concordant (Fig. 12).

It is very intriguing to try to understand what it is about the basic assumptions of radiocarbon which causes these deviations. A phase is now being entered where radiocarbon dates are used to test the validity of the geophysical parameters involved; for example, the constancy of the Earth's magnetic field, as was pointed out years ago by Elsasser,

[2] The Radiocarbon Supplement of the American Journal of Science, in which most radiocarbon dates are reported anually, is edited at Yale University by R.F. Flint, E.S. Deevey and Irving Rouse.

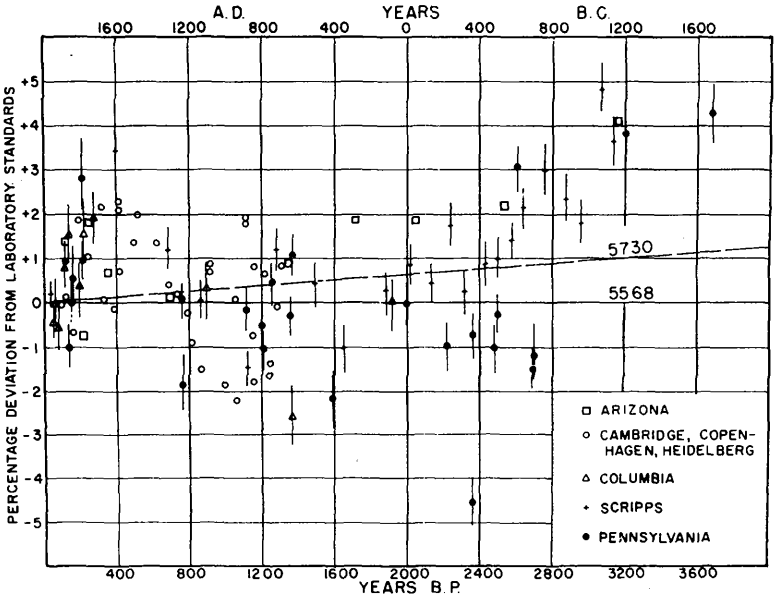

FIG. 9. Some tree-ring-dated samples

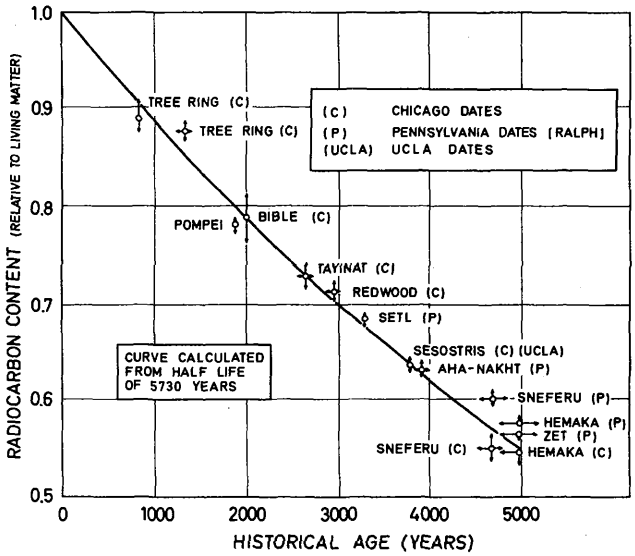

FIG. 10. Samples of known age

Ney and Winkler [17a]. Changes in the Earth's magnetic dipole would cause a change of the radiocarbon production rate through changing the degree to which incoming cosmic rays are deflected away from the Earth and, therefore, agreement between radiocarbon and historical dates is indirect evidence for the constancy of the Earth's magnetic dipole [17b, 18, 19]. Of course, there is the matter of sensitivity for

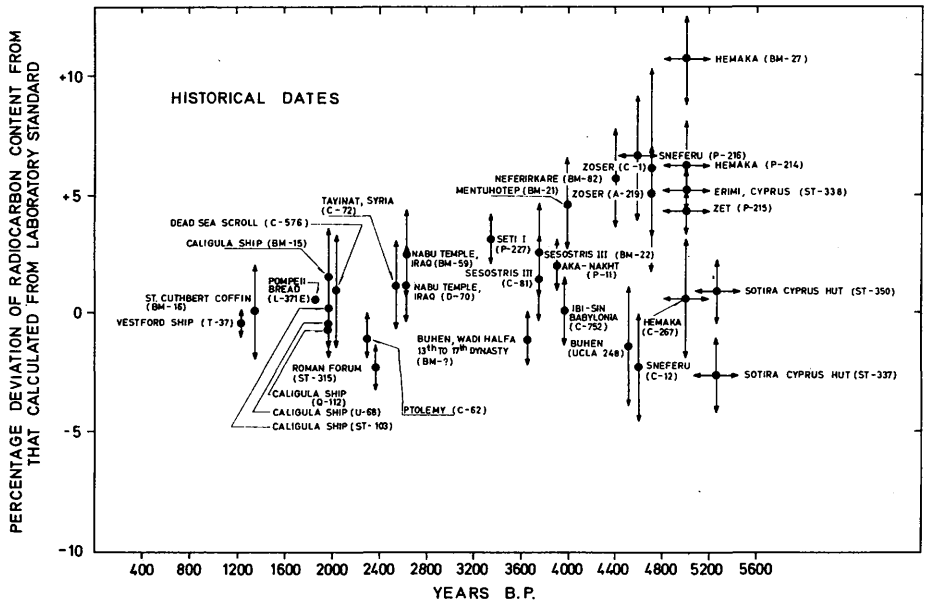

FIG. 11. Samples of known age

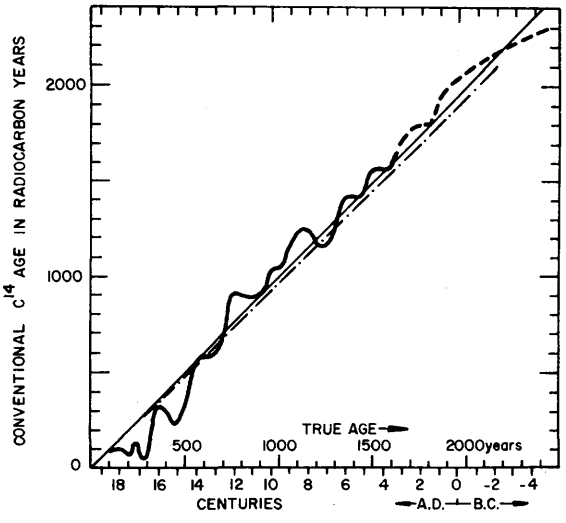

FIG. 12. Correction curve of Suess
Approximate empirical relationship between conventional radiocarbon dates (assuming $T_{\frac{1}{2}}$ = 5568 yr) and dendrochronologically determined wood ages as derived from La Jolla $\Delta^{14}C$ determinations. The diagonal broken line refers to data calculated with a ^{14}C half-life of 5730 yr
(SUESS, H.E., J. geophys. Res. 70 (1965) 5937)

each effect. With a lifetime of 8300 yr considerable inertia exists in the system, and one cannot expect to record changes immediately a change in the production rate occurs [19]. However, if the change in

TABLE IV. CHRONOLOGIES OF THE EGYPTIAN DYNASTIES I-XII IN YEARS B.C.

	Historical chronologies		Radiocarbon chronologies $t_{\frac{1}{2}} = 5730$			
	Hayes [a]	Helck [b]	Arizona [c]	British Museum [d]		UCLA [a]
Beginning of dynasty			Beginning 2500	2490		2695
			Early	2690		2465
I	c.3100	2950	Middle			2410
			End 2540			2320
II	-	-				2335
					(Early)	2225
III	2691	2650	2330			2140
			2340			2220
IV	2617	2579		1910		2185
V	2497	2460				
VI	2347	2322				
VII-X	-	-				
XI	-	-				1655
XII	1991	1995		1480,1550		1650

a) HAYES, W.C., in Cambridge Ancient History, Ch. VI, 1 (1962).
b) HELCK, W., in Handbuch der Orientalistik (1967) (in press).
c) DAMON, P. et al., Uncorrected dates, Radiocarbon, 10 (1968).
d) EDWARDS, I.E.S. et al., Uncorrected dates, British Museum, Radiocarbon Advisory Committee Mtg. (7 Dec. 1966).
e) BERGER, R., LIBBY, W.F., Radiocarbon 9 (1967) (in press).

production is large enough (and due to the fact that the mixing of the ocean is not an instantaneous process, requiring possibly ten years on average for the top layer of the ocean and the atmosphere to mix, and about twenty or thirty years for the top layer of the ocean to mix with the great depths), it can be expected that very sudden changes will be detected if they amount to 10% or more. A kind of amplification occurs for a brief period, which lasts for fifty years or so. For example, at present, due to the testing of nuclear weapons in the atmosphere, the radiocarbon level in the atmosphere and continental biosphere is about twice as high as the natural level (Fig. 13). At the same time

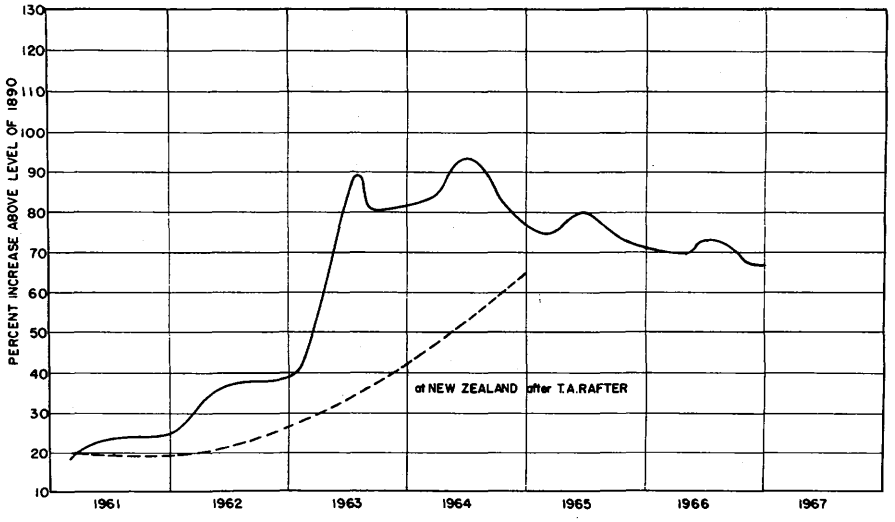

FIG. 13. Level of atmospheric carbon dioxide activity at China Lake, Calif. (RAINER BERGER and LIBBY, W.F.)

it has not increased more than about 20% in the top ocean layer and is even less in the great depths. Therefore, for the next thirty to fifty years the radiocarbon level in the continental biosphere and the atmosphere will be higher than in the ocean and will gradually fall until, when mixing with the ocean has occurred thoroughly, the level will be about 3% above the natural level. This condition will last for the lifetime of the radiocarbon, in diminishing degrees, losing half every 5730 yr. Variations in the production rate of radiocarbon can be traced if they last for periods which are appreciable with respect to the lifetime of radiocarbon.

As for possible sources of deviation, other than the Earth's magnetic dipole, Suess and others [16c, d, e] suggested that it is quite conceivable that deviations are a measure of solar activity, the correlation being with climate; thus, deviations during warm periods, when the sun is quite active, correspond to additional shielding of the cosmic rays by the solar wind, which the sun then emits in higher intensity, with the result that the production rate of radiocarbon is reduced, the opposite being the case during cold periods.

A new set of samples from the first twelve dynasties of Egypt was recently obtained by the British Museum to test whether, by chance, the Egyptian samples previously used were misleading (Table IV).

In general, measurements of these samples confirmed earlier work, and there appears to be a deviation in the fifth millenium of about five or six hundred years, the radiocarbon date being younger than the historical date. It is conjectural whether the deviation is real, or whether the Egyptian historical dates are incorrect, or possibly both.

Other evidence indicates that it is the radiocarbon which deviates towards being too young. This evidence is from the Bristle Cone Pine tree rings. These trees live to be very ancient and, when carefully studied, can give tree-ring dates. Although the method of dating with these trees has not been so certainly established, especially in the fifth millenium, as has been the dating with other kinds of trees in the first three millenia, there is a tendency for the radiocarbon dates to be younger than the Bristle Cone Pine tree-ring dates, as the radiocarbon dates are younger than the historical dates of the Egyptian fifth millenium. Some radiocarbon dating experts believe that the discrepancy in the fifth millenium is about 10% at 500 B.P., or about 800 yr. The question is open at the moment, because the Bristle Cone Pine dating technique remains to be established to the point of certainty needed, and the historical dates are themselves uncertain during the period 2000 B.C. to 3000 B.C.

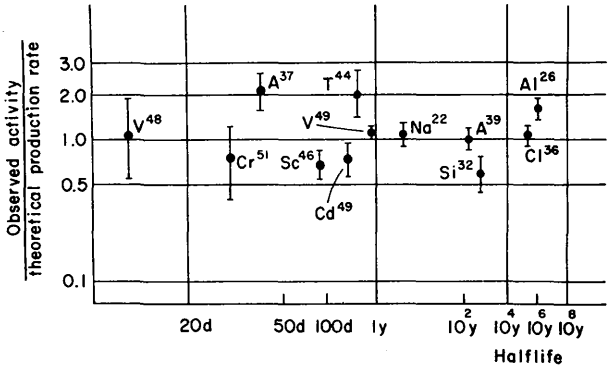

FIG. 14. Ratio of observed activity to theoretical production rate of spallation products in Aroos iron meteorite versus half-life
(GEISS, J., OESCHGER, H., SCHWARTZ, U., Space Scie. Rev. 1 (1962) 197)

The cosmic-ray flux is one possible cause of deviation. However, studies of meteorites by Arnold and others [20a, b] have shown that the most likely cosmic rays have been quite constant (Fig. 14). Although the accuracies are less than desired, there seems to be no systematic tendency for cosmic rays to change in intensity over periods of hundreds of years. This is judged by the relative amounts of cosmic-ray-produced radioactivities of lifetimes varying between a few years and hundreds of millions of years. The meteorites travelling outside the Earth's magnetic shield are subject to solar wind shielding only, and thus serve more closely as a measure of the true extra-terrestrial flux. Therefore questions may arise regarding variation in the terrestrial and solar magnetic shields. The solar shield acts mainly through patches of plasma which are sent out by the sun, called solar wind, and which serve to scatter the cosmic rays [17b] away from the solar system. On this basis, as Suess has pointed out, there may be a correlation between the

activity of the sun and the production rate of radiocarbon. On the other hand, the Earth's magnetic dipole may have undergone changes (Fig. 15). (It is noted that its direction is known to have changed; some evidence from the magnetism of rocks indicates that it has reversed its direction completely in periods during the last several millions of years. However, the mixing of radiocarbon is so effective that a change in direction in the Earth's dipole would not affect radiocarbon dates.) There is a third possibility that the mixing of the ocean, which now takes about two thousand years on average, may have changed in times past. However, this seems quite unlikely, and it is probable that the cause of any deviations will have to be found in the cosmic-ray intensity, as the atmosphere of the earth records it, this change probably being due to change in solar activity, or changes in the Earth's magnetic field, or both [18].

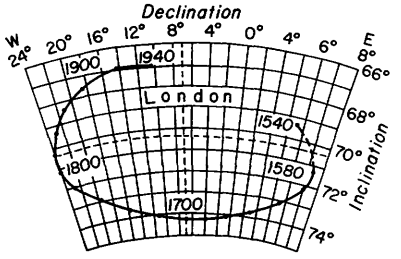

FIG. 15. Observed changes in the annual mean direction of the Earth's magnetic field at London since 1580 A.D. The continuation to 1540 A.D. is extrapolated from observations at Rome (After BAUER, L.A.)

The techniques of measuring radiocarbon dates greatly improved with the introduction of the CO_2 proportional counting method of deVries and Barendsen [21]. At present it is the most popular method. Other possibilities exist, and it is hoped that these will be investigated in practice but, on the whole, radiocarbon dates are probably measured now as accurately as is required in most cases. Further improvements to reduce the required sample size would be helpful.

Of course, in the prehistoric period there are no dates historically fixed with which to check. Therefore, radiocarbon is entirely alone. Arnold and the author were merely able to use consistency checks, such as the onset of the last ice age 11400 yr ago (Table V). This was seen to be true throughout the northern hemisphere, and was possibly world wide. Apparently the method passes all known tests of consistency and there is no reason to doubt that it is not systematic and reliable. There is,however, reason to doubt that the years, as written down, are chronologically accurate. Some indirect evidence exists that they are not far off, in the absolute sense, even in the prehistoric period, but the evidence is not conclusive.

It is difficult indeed to see how the checks can be improved, although it is to be hoped that possibilities exist of checking with other radioactive time clocks not as yet developed. The great gap between the radiocarbon time scale and that of ^{40}K needs filling badly, for dating purposes. It is possible that something may be found in the cosmic-ray isotope, ^{10}Be, with a half-life of 2.5 m.y., and ^{26}Al, with a half-life of 0.75 m.y. However, these are all very difficult to use, for one reason or another, and it is by no means clear that a practical method of dating by means

TABLE V. APPARENT COINCIDENCE OF GLACIAL ADVANCES[a)]

UNITED STATES OF AMERICA	C-308	10 877 ± 740
	C-365	11 437 ± 770
	C-366	11 097 ± 600
	C-536	12 168 ± 1500
	C-537	11 442 ± 640
FEDERAL REPUBLIC OF GERMANY	C-337	11 044 ± 500
UNITED KINGDOM	C-341	9 861 ± 500
	C-444	10 851 ± 630
REPUBLIC OF IRELAND	C-355	11 310 ± 720
NEW ZEALAND	NZ-339, 112	11 500 ± 170
	NZ-340, 334	11 900 ± 200

a) BERGER, R., Proc. 37 Int. Congr. of Americanists, Argentina (1966).

of any of them can be developed. Ionium, as supported by the decay of uranium in sea-water, offers some promise as measured in sea sediments. The lifetime of ionium, about 120 000 yr, is of the proper order to check radiocarbon, and the evidence at present indicates that radiocarbon dates do not deviate greatly, judged by ionium. However, it is not possible to say at present that radiocarbon dates are known to be absolutely correct, unless one is restricted to the first 3000 yr where, after the application of the Suess corrections, there is evidence that this may be so.

In terms of physical principles of course, a method which works for three thousand years might extend all the way to fifty thousand. However, this is mere conjecture, and until more solid evidence is available, the fact that radiocarbon is known to be not absolutely accurate in the prehistoric period has to be accepted and the radiocarbon time scale for this period must suffice.

During the trial period of the method, which has taken fifteen years, various improvements in technique have occurred which should be cited. In particular, there are the improvements in counting technique previously mentioned. In addition, the use of bones for dating has been accomplished by the development of a gentle method of acid dissolution of the bone mineral which leaves the bone protein, collagen, unhydrolysed [22]. In many cases bone is the only certainly authentic material available.

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