

ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 5 NUMBER 9 SEPTEMBER, 1972

Dating by Radiocarbon

WILLARD F. LIBBY

Department of Chemistry† and Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California

Received January 18, 1972

History

The cosmic ray production of radiocarbon in matter is the basis of radiocarbon dating. It is made from the most abundant atom in air, nitrogen of mass fourteen. Radiocarbon—carbon-14 or ^{14}C —lasts 8300 years on the average (see Appendix on radioactive decay for explanation on “half-life” and “average-life”) before reverting by radioactive decay to nitrogen-14. During this time it enters all living things as well as sea water and air. Chemically, carbon dioxide is the food of life, and presumably the freshly produced ^{14}C atom is oxidized sooner or later (probably in a few days, although this time is not at all well known) to $^{14}\text{CO}_2$ which is mixed with the ordinary carbon dioxide (0.03% in air) by the winds.

The process which converts CO_2 into plants—photosynthesis—is the means whereby the radiocarbon is introduced into living beings. In principle and in theory one could understand that if organisms were to live off coal or oil, radiocarbon dating would not work for them. They would not be in touch with the cosmic rays through recent photosynthesis. The long time that coal or oil have been underground ensures that the original radiocarbon in the plants which produced them would long since have disappeared.

Perhaps at this point we should stop and clearly state the basic principles of radiocarbon dating: (1) the cosmic rays make living things radioactive with ^{14}C to a certain level fixed by the environment; (2) at death the intake of food stops, so no replenishment of the ^{14}C steadily lost by the immutable radioactive decay can occur. The degree to which decay is observed to have occurred gives the time lapse since death (radiocarbon age). Thus 5730 years (the half-life of

^{14}C) corresponds to a reduction to 50% of the concentration in living matter.

The cosmic rays actually produce radiocarbon only indirectly. In the first step of the process they strike the nuclei in the air atoms and disintegrate them. Among the fragments are many strange, short-lived particles most of which transform almost immediately into longer-lived entities. Radiocarbon is produced by the interaction of one of these secondary particles, the neutron, with the nitrogen of the air. The neutron has been with us now since the early thirties and has come to be part of our daily life since it is the purveyor of atomic energy. Neutrons at high altitudes are found in the maze of general debris formed in the collisions of great cosmic-ray primaries with the nuclei of nitrogen or oxygen atoms.

The first clue to radiocarbon dating came in 1939 when Professor Korff of New York University sent up neutron-sensitive detectors on balloons and found a positive response with a peak intensity at some 16-km altitude. These data, taken together with the previously demonstrated fact that the chief interaction of neutrons with air was to produce radiocarbon, was the first hint that radiocarbon dating might be feasible. However, World War II intervened and our quest which had gelled into theory during the 4 war years came to a test at the University of Chicago in 1945. The first move was to publish the general thought that cosmic-ray-produced atoms could accumulate in the atmosphere. In addition to ^{14}C , tritium (radiohydrogen of mass three) and its stable daughter, ^3He (which also probably is produced directly by the cosmic rays as well), were cited.¹ Then a strenuous program to measure accurately the radiocarbon decay rate was undertaken.² (We know the average life of 8300 years now to about 1 or 2%, but at that time the uncertainty was much larger. One figure was as large as 30,000 years!) However, our major objective was to search for natural radiocarbon and thus to test

Professor Libby received all his higher education at the University of California, Berkeley, receiving his Ph.D. in 1933. He remained at Berkeley on the teaching staff until 1941, when he took a leave of absence to work on the Manhattan Project at Columbia University. He worked at Chicago in radiochemistry until 1954, particularly on natural carbon-14 and its application to dating archaeological artifacts and on natural tritium and its use in hydrology and geophysics. For this work he received the Nobel Prize in Chemistry in 1960. In 1959, he moved to the University of California, Los Angeles, where he is presently Director of the Institute of Geophysics and Planetary Physics and Professor of chemistry. Professor Libby has devoted considerable energy to numerous scientific and technical advisory appointments, including 5 years on the Atomic Energy Commission (1954–1959). His awards and affiliations are too numerous to list.

† Contribution No. 2944 from the Department of Chemistry, UCLA. This research was sponsored by National Science Foundation Grant No. GA-628.

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

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

whether the whole theoretical fabric was false in some way.

The theoretical structure was in a sense simple—the cosmic rays make radiocarbon atoms at a steady rate of about two per square centimeter of area of the Earth per second and have been doing so for tens of millenia. Thus at present, there should be an equilibrium inventory in which about two radiocarbons revert to nitrogen every second for each square centimeter of area. Therefore, we should find about 2 disintegrations per second for every 8 g of carbon in living beings, or dissolved in sea water, or in the atmospheric CO_2 , for the total carbon in these three categories adds to 8 [7.5 g/cm² in the oceans, $\frac{1}{8}$ g/cm² in the air, $\frac{1}{4}$ g/cm² in life forms, and perhaps $\frac{1}{8}$ g/cm² in humus; some of these figures are not accurately proven, but since the ocean is the largest and is best known (5% error or better) the total is known to about 10%]. Thus we expected to find this concentration of radiocarbon in living matter, and the job was to test for it.

Unfortunately at that time no instrument was sufficiently sensitive, so my colleague, Dr. E. C. Anderson, and I were stumped for the time, until we recalled that an old friend from World War II days had a carbon isotope separator with which he was making concentrated ^{14}C for isotope tracer work in cancer research. This expensive machine was operating at Marcus Hook near Philadelphia, and we enlisted Dr. A. V. Grosse's aid to enrich the natural ^{14}C by some hundredfold in concentration so we then could detect the radioactive rays it gives in reverting to ^{14}N in our Geiger or methane-filled proportional counters. [A Geiger-Muller counter is a metal cylinder with a fine wire down its axis and is filled with a special gas mixture. A potential is applied between the wire (positive) and the cylinder (negative) of 1–2 kV depending on the pressure and composition of the gas. Under these conditions, uniformly sized voltage pulses are delivered whenever ionization (separation of one or more electrons from a neutral atom or molecule) occurs, even if it is only one event, *i.e.*, one free electron and one positive ion. *It is one of the most sensitive radiation detectors known.*]

The ^{14}C radiation makes about 1500 ion pairs on the average over a path length of about 2.5 cm in air. It is measured best in the counter gas itself since the radiation will not easily traverse the counter wall nor escape efficiently from it. Hydrocarbons and carbon dioxide, which are the richest carbon-containing gases, will not serve in Geiger counters, but will serve in proportional counters. (Proportional counters operate below the voltage for the onset of the uniform pulse size required in Geiger counters and give pulses which are approximately proportional to the number of ions delivered by the particular ray being registered, thus qualifying for the term "proportional." The voltage pulses are smaller and require more electronic amplification.)

Dr. Grosse's equipment operated on methane (CH_4). Therefore we needed to find a source of "live" methane, *i.e.*, methane of recent origin. We found it in the gaseous

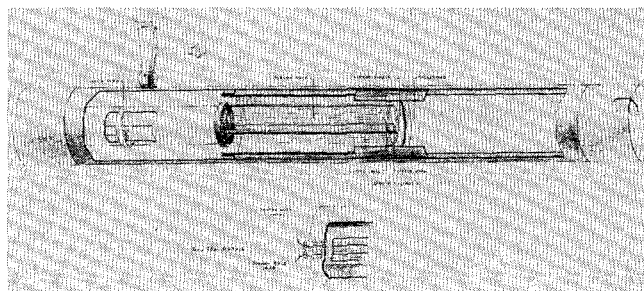


Figure 1. Screen wall counter.

effluent of the sewage disposal plant of the city of Baltimore. Methane (in natural gas) from oil wells would be completely devoid of ^{14}C because its age is so great, but the sewage gas methane should, of course, have its full complement of ^{14}C .

Dr. Grosse after obtaining the sewage methane proceeded to enrich it to varying degrees (as measured by the ^{13}C enrichment) and Dr. Anderson and I excitedly put the enriched methane in our proportional counter and recorded the counting rate. We used the heaviest shield we could assemble, since the counter was responding in the main to laboratory radioactivity present in the building and equipment and to the cosmic radiation reaching the Earth's surface at Chicago. Strangely enough this whole thing worked and we did find about the anticipated ^{14}C concentration as a small additional counting rate for the enriched methane, compared with the rate for unenriched methane or for petroleum natural gas methane. Further confirmation came when the carbon dioxide formed by burning the methane was found to be radioactive as well and to display a radiation with an average penetrating distance equivalent to 2.5 cm of air, just as had been found to be true for man-made radiocarbon. This was done by precipitating the carbon dioxide as solid calcium carbonate which then was spread as a thin layer to minimize self-absorption of the radiation. Thin aluminum foils were placed over the deposit and the decrease in count rate in a special screen wall counter was measured (see Figure 1). (The special screen wall counter was necessary because the β radiation is of such low energy.) A layer of aluminum weighing some 2.5 to 3 mg cm⁻² was found to effect a 50% reduction just as is the case for synthetic reactor produced ^{14}C .³

The question of the rate of oxidation of the freshly made ^{14}C atom in the high atmosphere remains, for as said previously we really do not know this rate. The main part of the ^{14}C is produced in the stratosphere—the top 20% or so of the atmosphere lying above the cloud tops. We know now (although we only guessed it in 1945) that the stratospheric air mixes downward with the lower air—the troposphere—only in a matter of years. This information has been gained from studies of the radioactive debris of nuclear explosions

(3) E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirschenbaum, and A. W. Grosse, *Science*, **105**, 576 (1947); A. F. Grosse and W. F. Libby, *ibid.*, **106**, 88 (1947); E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirschenbaum, and A. V. Grosse, *Phys. Rev.*, **72**, 931 (1947).

introduced into the stratosphere by the high rising fireballs. At the present time we still are detecting such fallout from explosions in 1962. Thus we see that if the carbon atoms are oxidized in a year or two that is soon enough for our purposes in radiocarbon dating. It seems likely from laboratory experiments that the first step is the formation of carbon monoxide and that this occurs very rapidly. Following this is a slower oxidation of CO by oxygen, or possibly ozone, or by sunlight exciting the CO, or some other process. More research is needed on the details of this mechanism.

However, there is a great saving grace—the 8300-year average life of radiocarbon. In this great span of time there is adequate opportunity for the CO₂ to form, for the atmosphere to mix, for the oceans to mix, and for the biosphere to cycle many times, *i.e.*, die, decay to CO₂, and be reborn in photosynthesis. This grand system is continually stirred. Living matter is a part of this until death occurs and thus all living things have the same ratio of ¹⁴C to natural carbon.

At death isolation from the life cycle occurs and the radiocarbon clock starts sticking. The isolation is complete. There remains only the relatively straightforward problem of separating the ancient matter to be dated from modern contamination. The fact that it is possible to do this “laundry” job so completely ranks with the near-constancy of the cosmic rays as one of the real breaks of good fortune in radiocarbon dating.

The “laundry” of the dating materials is done by common sense and understanding. For example, charcoal is a favorite type of material for ¹⁴C dating since man is the only animal able to make fire. Charcoal is never attacked chemically. The first move with a charcoal sample is to examine the material under a low-power magnifying glass and to remove with tweezers foreign materials such as plant rootlets. Then an acid wash is used to remove carbonates and this is followed by an alkaline wash to remove humic acids. Normally this is adequate and the treatment ends with a thorough distilled water washing before drying and burning to give carbon dioxide for proportional counters operating at 1-atm pressure and with about 5000-V potential drop, although some favor other methods, such as methane or acetylene proportional counters, or scintillation counters using liquid benzene synthesized from the purified sample.

The method of counting contains a story: after we had found natural radiocarbon we had to face the fact that we could hardly expect Dr. Grosse to use his very expensive apparatus on all our dating samples which would most likely be very numerous. So we went to work on the problem of how to increase the sensitivity of detection of the low-energy, short-ranged radioactive carbon radiation by two or three orders of magnitude. The task was commanding for the Grosse samples left no serious doubt at this point that natural radiocarbon did exist. The only question was whether

we could use it, and it was completely clear that if every time we wanted a radiocarbon date we had to isotopically enrich the sample, the cost would be prohibitive. Dr. Grosse had spent enough money on this Baltimore sewage sample to run many archaeological museums for a month!

The natural counting rate for a Geiger or proportional counter is about 5 counts min⁻¹ cm⁻² of cross-sectional area or 30 counts min⁻¹ in.⁻². Thus, a counter 15 cm in diameter and 60 cm in length would count at the enormous rate of about 4300 counts min⁻¹, whereas the expected radiocarbon from 1 atm of carbon dioxide or methane filling the counter would be about 45 counts min⁻¹ or about 1%! Furthermore, in order to make meaningful use for dating purposes this rate would have to be measured to better than 1 count min⁻¹.

We began our task by making an analysis of the sources of the background radiation and found them to be many and varied. The material of which the counter itself was made—the metallic cylinder, the central wire, and the insulating end plugs—all could contain radioactive materials, such as uranium and thorium and their radioactive daughters, or potassium which is naturally radioactive. In addition, the laboratory floor, ceiling, and walls, the workbench, and the electronic equipment all were potential sources of penetrating γ radiation (very high energy X-ray-like radiation emitted by many radioactive substances in addition to the α (helium nuclei) and β (negative electron) particle radiations).

The internal counter contaminants registered mainly the α and β rays, whereas these would not be able to penetrate the counter wall. External sources contributed to the counter background only through the more penetrating γ rays [a typical γ ray may require 7 to 12 cm of water or a corresponding mass of denser material to be absorbed to 50% intensity; a typical α , about 0.005 cm; and a β , 0.065 cm (¹⁴C emits a particularly soft β and has a “half-thickness” of about 0.0025 cm of water or plastic or paper)]. Thus, we knew that: (a) we must build our counter of clean materials, (b) we must shield the counter with clean nonradioactive matter, preferably a few meters thick for light materials or about 30 cm thick for dense materials such as lead or iron.

We tested several samples of metal tubing by cleaning them carefully and building counters with them, using plastic end plugs to avoid glass which contains potassium. Thus, we obtained what we thought was a clean counter. We next assembled some lead bricks, built ourselves a little house, and lined the inside with iron plates about 2.5 cm thick to avoid radioactivity of the lead. The slagging operation in the iron metallurgy seemed to us to be a good way of purifying iron from radioactive contamination, since most natural radioactivities have a stronger reducing potential than iron. The contaminants should occur as oxides or silicates in the molten slag floating on the liquid iron. Placing our counter in this shield (which had a heavy

door on rails so we could close it) we obtained a counting rate of 800 counts min^{-1} for the counter described above!

This was discouraging but not unexpected since we knew the cosmic rays were able to penetrate many meters of rock. We took our apparatus to the cyclotron building and placed it underneath the iron magnet yoke which was 3 meters thick and found about 600 counts min^{-1} . So it was clear that we either had to put our counter in a deep mine or we had to do something about these penetrating rays. The water table in the city of Chicago is only two or three meters below the surface, so we would have had to move our laboratory by many miles to some abandoned mine inland.

We were on the point of doing just that when we had an idea which solved the problem. The cosmic ray muon (the muon is one of the transitory particles produced high in the atmosphere) has the very strange property that it does not react readily with atomic nuclei, and yet ionizes matter easily. So it is not stopped by nuclear disintegration as are the primary cosmic rays. Thus, it is the culprit which has the great range and trips the counters deep in the atmosphere. This was the clue which showed us the way over our hurdle. If the muon moves in essentially straight lines, then all we need do is to surround our counter with a layer of protecting counters set to switch off the central counter containing the CO_2 gas to be dated whenever the shield counters are activated. This is commonly called an anticoincidence arrangement. Since the radiocarbon radiation is of too low an energy to pass through the counter walls, it will not trip the shield counters. Therefore, the radiocarbon radiation will register on the dater counter except during that certain small fraction of the time when the dater counter will be deactivated by the shield counters. This will constitute a loss factor which fortunately is small. By putting the bundle inside the heavy shield the muon rates are essentially all that is left for the shield counters to handle. The deactivation time need be only a fraction of a millisecond, so the loss fraction is about 1% or less.

We tried it. Figure 2 is a picture of the first apparatus and it was successful immediately. In terms of the hypothetical counter (actually the present UCLA dater) the background now dropped from 600 to 13 counts min^{-1} .

The nature of the remaining counts is not known at present. They may be due to a number of effects. In our UCLA laboratory over the last 10 years or so the background has decreased rather steadily from 15 down to something between 12 and 13, as though some slow decay were involved.

Having acquired a sufficiently sensitive and practical technique, we went to work to test the main assumption on which radiocarbon dating was based. This problem, the natural distribution and concentration of radiocarbon, actually was Dr. Anderson's doctoral thesis project. He took wood samples collected about the turn of the century from widely dispersed places,

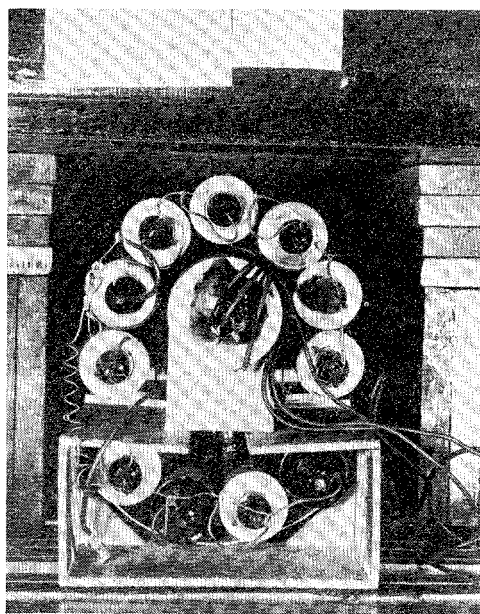


Figure 2. The first anticoincidence counter.

as well as seal meat and oil from Antarctica (the source was Admiral Byrd's last expedition). All gave the same result (*cf.* Table I). This result still stands. At the Nobel Symposium XII on Radiocarbon Dating held in Uppsala, 1970, several papers once again reaffirmed Dr. Anderson's conclusions.^{4,5} The mixing is excellent.

The next step was to try the dating method. Dr. J. R. Arnold of Princeton joined us for this test. He is a physical chemist, as are both Dr. Anderson and I, but his father, a lawyer, was an enthusiastic amateur archaeologist and this brought him to us in the proper mood.

Straight off we had to face the question: "How can you expect a museum keeper to give precious, invaluable materials for you to destroy?" We worried about this a great deal and finally decided there was nothing for it but to enlist the aid of recognized experts to advise us and acquire the materials for us. So we appealed to the American Archaeological Association and the Geological Society of America to give us a committee of experts, which they did. The chairman was Frederick Johnson of the Peabody Museum at the Phillips Academy in Andover, and the other members were Froelich Rainey of the Philadelphia Museum at the University of Pennsylvania, Donald Collier of the Field Museum in Chicago, and Richard Foster Flint, the geologist from Yale. Three archaeologists and one geologist—these gentlemen did it right. They immediately directed us to the Breasted Egyptian collection in the Oriental Institute at the University of Chicago and to John Wilson, a senior professor in the Institute. Through Professor Wilson

(4) W. F. Libby, "XII Nobel Symposium. Ruminations on Radiocarbon Dating. Radiocarbon Variations and Absolute Chronology," I. U. Olsson, Ed., Almqvist & Wiksell, Stockholm, 1971.

(5) W. F. Libby, E. C. Anderson, and J. R. Arnold, *Science*, **109**, 227 (1949).

Table I
Activity of Terrestrial Biosphere Samples

Source	Geomagnetic latitude	Absolute specific activity, d min ⁻¹ g ⁻¹
White spruce, Yukon (Frederick Johnson)	60° N	14.84 ± 0.30
Norwegian spruce, Sweden (Donald Collier, Chicago Natural History Museum)	55° N	15.37 ± 0.54
Elm wood, Chicago (author)	53° N	14.72 ± 0.54
<i>Fraxinus excelsior</i> , Switzerland (Donald Collier)	49° N	15.16 ± 0.30
Honeysuckle leaves, Oak Ridge, Tennessee (C. H. Perry, Clinton Laboratory)	47° N	14.60 ± 0.30
Pine twigs and needles (3650 m alt.), Mount Wheeler, N. M. (Robert Fryxell)	44° N	15.82 ± 0.47
North African briar (John Hudson Moore, Inc.)	40° N	14.47 ± 0.44
Oak, Sherafut, Palestine (Donald Collier)	34° N	15.19 ± 0.40
Unidentified wood, Teheran, Iran (M. Hessaby)	28° N	15.57 ± 0.34
<i>Fraxinus mandshurica</i> , Japan (Donald Collier)	26° N	14.84 ± 0.30
Unidentified wood, Panama (John Simpson)	20° N	15.94 ± 0.51
<i>Chlorophora excelsa</i> , Liberia (Donald Collier)	11° N	15.08 ± 0.34
<i>Sterculia excelsa</i> , Copacabana, Bolivia (9000 ft alt) (Donald Collier)	1° N	15.47 ± 0.50
Ironwood, Majuro, Marshall Islands (Donald Collier)	0°	14.53 ± 0.60
Unidentified wood, Ceylon (Donald Collier)	2° S	15.29 ± 0.67
Beech wood ("Nothofagus"), Tiera del Fuego	45° S	15.37 ± 0.49
Eucalyptus, New South Wales, Australia (Donald Collier)	45° S	16.31 ± 0.43
Seal oil from seal meat from Antarctic (Byrd Expedition through H. J. Deason)	65° S	15.69 ± 0.30
Average	—	15.3 ± 0.1 ^a

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

we obtained precious materials from the earliest pyramids and proceeded to burn and date them. (About 30 g of material was used in each measurement.)

The agreement obtained was well within our counting uncertainty of a few centuries (1% in the count is 83 years in the radiocarbon age, since the average life is 8300 years).⁶ So we began, and now 20 years later with perhaps 30,000 dates and some 70 dating laboratories we can take a reviewing look at the method.

One additional point in the story—we actually used carbon black and the screen wall counter instead of the present carbon dioxide proportional counter, so we had to be extremely careful of contamination of the highly absorbent carbon black (obtained by reacting the CO₂ from the combustion with hot metallic magnesium). This nearly derailed us because the errors and uncertainties could be substantial. The carbon

black had a tendency to retain magnesium oxide in a strangely adherent way which protected it from the hydrochloric acid leach applied routinely after the magnesium treatment. This ash correction was large. As a final step we mounted the carbon black on the inside of the screen wall counter wall by moistening it with ethyl alcohol to make a slurry, which then was dried in a stream of warm air. However, a certain amount of the alcohol usually remained on the highly absorbent carbon black, and this contributed an error due to the counts in the grain alcohol used. Only one other laboratory (New Zealand, Dr. G. Fergusson) ever used the black carbon method, and we gave it up with great relief when it was shown (Fergusson in New Zealand and de Vries in Holland) that CO₂ proportional counting worked well. By that time, however, we had laboriously processed several hundred samples. Incidentally, we still have the carbon blacks for most of these early measurements in case anyone would like to check the dates.

Retrospect and Prospects

The long experience with radiocarbon dating has taught us two things: on simultaneity it apparently is reliable, but on absolute dates it can be incorrect by as much as 600 or 700 years. The peak of the deviation occurs some 7000 years ago. The simultaneity principle states that two samples taken from any place in the world for any past epoch will give the same date. This, of course, follows from the principle of good mixing described previously, *i.e.*, Dr. Anderson's result that the same concentration of ¹⁴C in natural radiocarbon is found all over the world and in different life forms.

The bristlecone pine tree ring chronology of Fergusson and Bannister⁴ has made possible the determination of the extent of the deviations of the radiocarbon dates by Suess, Ralph, and Damon⁴ back to some 7500 years ago. The dates appear to start falling slightly too young about 3000 years ago and continue deviating in that sense until what may be the peak deviation of some 700 years is reached about 5000 years ago. The deviation then appears to level off. There is some evidence of a decrease in the variation back toward agreement at 10,000 to 11,000 years. This evidence is from the Swedish varve chronology, according to Tauber and others.⁴ In addition to the broad general sweep of the main deviation there appears to be a short-term fine structure of somewhat erratic nature, according to Suess⁴ (*cf.* Figure 3).

The speculation at the moment is that the main deviation is due to a weakening of the Earth's magnetic field observed by Bucha and others⁴ according to the principle pointed out by Elsasser long ago. The fine structure is then due to variations in the intensity of the solar wind which fends off the cosmic ray. The Earth's field normally deflects about half the cosmic rays, so weakening of the magnetic field could cause the observed effect. A third possibility is that solar cosmic rays also play a role. It appears to be unlikely

(6) J. R. Arnold and W. F. Libby, *Science*, **110**, 678 (1949).

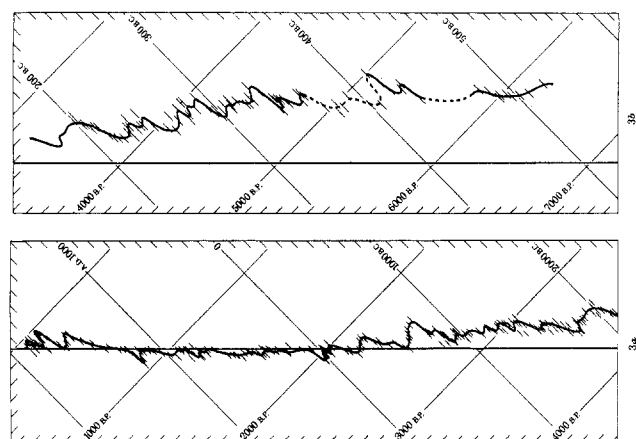


Figure 3. Empirical correlation between conventional radiocarbon ages based on 5568-year half-life and bristlecone pine tree-ring ages after Suess.

that the intensity of the galactic cosmic rays varies, since the radioactivities found in meteorites seem to agree only with the assumption of constancy, *i.e.*, the long-lived and shorter-lived radioactivities occur in intensities which fit only this assumption. Unfortunately the accuracy with which this assertion can be made is limited due to the paucity of data. A benefit for radiocarbon dating has been gained here from the Moon samples. Their large size and freshness allows more accurate measurement of the intensities of the radioactivities induced by the cosmic rays in the surface rocks. High-energy protons from accelerators are used to calibrate for the relative efficiencies of production of the various radioactive atoms.

The question of the solar proton contributions remains somewhat open at the moment. Counters on space probes seem to say that there must be some such contribution, but the energy spectrum and the intensity remain uncertain. The Earth's magnetic shield is so strong that it may be difficult for these relatively low-energy cosmic rays to play a role.

The argument for the finely structured deviations being due to some solar cause is persuasive, but just how the effects occur is less clear, and further work is necessary. It may be anticipated that when these points are settled the information may prove to be of value to astrophysics.

The main effort now under way is the bristlecone pine program of Fergusson, Suess, and Damon,⁴ but the work of Stuiver⁴ on lake sediments is very promising as well. His results seem to agree with the bristlecone curve in many respects, but they do not seem to agree with the Swedish varve results in the older periods beyond 7500 years ago. Since the method is questionable (the counting of annual layers of sediment and the association of organic matter in a particular layer with that layer), as is true also of the Swedish varve method in some respects, we are left uncertain about the course of the curve prior to 7500 years ago. So we are driven back to the bristlecone pine method to extend the chronology backward to glacial times about 11,000 years ago.

Fergusson reports finding a piece of wood in the White Mountain (California) area which radiocarbon dates at about 9000 years. So, presumably, if an overlapping piece or pieces can be found there, the chronology could be extended from the present 7500-year limit in the White Mountain area back to 9000. A second area near Ely (Nevada) has a bristlecone chronology reaching back to about 5000 years. There are several bristlecone stands which have not been dated dendrochronologically, but it would seem that they offer some additional hope for future work. Every effort should be made to preserve the ancient wood on the ground in these forests, for they are of prime scientific value possibly embodying our main opportunity to check radiocarbon dates back to 10,000 years.

The principle of simultaneity means that radiocarbon dates are the same at any given epoch over the entire Earth, so a calibration at any one locality is equivalent to a world-wide calibration.

The corrections to the radiocarbon dates are of fundamental interest to geophysicists and astrophysicists. The source of the Earth's magnetic field remains unknown, although evidence accumulates suggesting that it is related to the metallic nature of the Earth's interior and the Earth's rotation. Venus has no magnetic field and is of about the same size as the Earth; it presumably has a metallic interior but does not rotate: 241 Earth days to a Venusian day. Mars also has no magnetic field, is much smaller, and may have no metallic interior even though it rotates at about the same rate as the Earth. The Moon is smaller still. None of these bodies has a magnetic field. Jupiter, on the other hand, has a very strong field—about fifty times stronger than the Earth—and it rotates more rapidly, 10 hr, and is larger than the Earth.

Thus, the evidence seems to indicate that the overall strength of the Earth's magnetic field decreased substantially perhaps 7000 or 8000 years ago, and then subsequently renewed its intensity about 5000 years ago. It is only the overall strength that matters, since world-wide mixing is so efficient. A mere shift of direction (which is well known to have occurred in historic times) would not be recorded by radiocarbon.

On a longer time scale—millions of years—it has been discovered that complete reversal of the direction actually occurs repeatedly. These very ancient data seem to give little evidence about overall intensity. However, it is natural to suppose that the fact of reversal at least suggests the possibility of intensity variation.

The astrophysicists expect to learn about the constancy of solar activity over the last 40 millenia as more work is done on radiocarbon dating. They also can expect strict limits to be set on the intensities of past super novae bursts since these could have given γ -ray bursts which would have given short-termed peaks (of the order of 50 years wide) in the deviation curve of Lingenfelter.⁴

A short-termed perturbation as we have had recently in the atmospheric nuclear explosions which have raised the ¹⁴C content of the atmosphere and biosphere

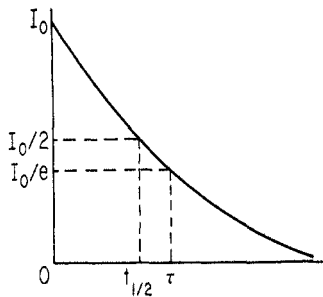


Figure 4. Half-life ($t_{1/2}$) vs. average life (τ).

by about 50% lasts about 50 years before mixing with the ocean occurs and gives a dilution of some 30-fold (Figure 4). Thus radiocarbon is particularly sensitive to short-term perturbations, but the method requires samples from the particular years involved. Thus, it has been shown, by measuring wood from tree rings in the years following that the Siberian meteorite of 1908 could not have contained antimatter (Cowan, Atluri, and Libby, 1965).⁷ Had it contained antimatter in the amount needed to cause the large explosion observed, it would have produced neutrons (and thus ^{14}C) in about the same amount as the tests of 1962 which gave about 100% increase in the biospheric concentration of ^{14}C .

The correction curve itself is primarily of interest to historians and archaeologists. With it we now can say that the Egyptian chronology currently accepted probably is nearly correct. Further work is needed to clarify detailed points and the possibilities of substantial clarification of the history of the first dynasties appear to be good. The opportunities for predynastic Egypt extending back into the palaeolithic seem to be very substantial (Save-Soderbergh and Wentdorf).⁴

In Europe the main new result seems to be a redating of the Neolithic,⁴ at about 2 millenia older than previously believed, although further work is needed.

In the Americas it has given a quantitative chronology with relatively few surprises, except for the continued search to firmly establish preglacial man. A great deal of information about the history of the climate has been obtained (*cf.*, for example, Wells and Berger).⁸

(7) C. Cowan, C. R. Atluri, and W. F. Libby, *Nature (London)*, **206**, 861 (1965).

Earth scientists are interested in the curve itself for dating vertical earth movements and the eustatic rise of the seas following the last glacial period. Climatologists use radiocarbon dates to establish climatic changes on a world-wide basis.

The method itself has been improved in several respects. It now is possible to date bone using the small protein content. The prospects for developing a reliable method for shell samples appear to be brighter (Wentdorf⁴).

The study of the nuclear test radiocarbon and its rate of movement into the sea promises to give detailed understanding of the mechanism and the rate of uptake of CO_2 from the air by the sea—a matter of concern as the rate of burning of coal and oil continues to increase. It also will allow more quantitative evaluations of the fine structure in the deviation curve. A somewhat unexpected result that the rate may be controlled by an enzyme has recently been obtained (Berger and Libby)⁹ by studying subsurface sea water (60 m deep) and finding that it equilibrates more rapidly with atmospheric CO_2 than does surface water (Santa Monica, Calif., beach) and that the surface water can be brought into agreement by addition of the enzyme carbonic anhydrase in a few parts per million.

A general early treatment of the method is available¹⁰ and the dates themselves are published in *Radiocarbon*.

Appendix. Half-Life and Average Life

The law of radioactive decay is $2^{-t/t_{1/2}}$ or $e^{-t/\tau}$ where e is the Napierian base and $t_{1/2}$ and τ are the half-life and average life, respectively. If you average the life you obtain τ . For instance

$$\int_0^{\infty} 2^{-t/\tau} t dt = \tau$$

$$\int_0^{\infty} 2^{-t/t_{1/2}} t dt = \int_0^{\infty} e^{(t/t_{1/2}) \ln 2} t dt$$

So $\tau = t_{1/2} / \ln 2$. Figure 4 shows this less mathematically.

(8) P. V. Wells and R. Berger, *Science*, **155**, 1640 (1967).

(9) R. Berger and W. F. Libby, *ibid.*, **164**, 1395 (1969).

(10) W. F. Libby, "Radiocarbon Dating," 2nd ed, University of Chicago Press, Chicago, Ill., 1955.