Fifty Years of Radiocarbon Dating.

by R. E. Taylor

The history of radiocarbon dating through the 20th century is presented, focusing on the work of Willard F. Libby, who introduced radiocarbon dating in 1949, and its application during the following 50 years. Topics include an explanation of radiocarbon dating, by which the age of organic matter can be determined; difficulties Libby encountered in developing processes for accurate measurements; and the manners in which accelerator mass spectrometry aided radiocarbon dating.

This widely applied technique has made major strides since its introduction a half-century ago at the University of Chicago

Since the 1350s, when a linen fabric bearing full-scale front and back images of what appeared to be a crucified man was first displayed in a small village in France, many people debated whether this famous cloth--later enshrined in the Cathedral of St. John the Baptist in Turin, Italy--could have once served as the burial shroud for Jesus of Nazareth. Arguments raged for six centuries about the "Shroud of Turin;" then, during the 1980s, a group of scientists decided to seek a final answer to the question of authenticity. Investigators in England, Switzerland and the United States analyzed swatches from the linen shroud (along with other ancient textile samples of known vintage). They applied the now-famous technique for determining the age of organic materials using the radioactive carbon isotope [C.sup.14]--or carbon-14. These measurements showed that the flax from which the linen was produced grew sometime in the 13th or 14th century A.D.--far too recently to have had anything to do with the death of Jesu s.

Assigning a reliable age to this medieval artifact is just one of a long string of notable accomplishments since Willard F. Libby and his colleagues at the University of Chicago introduced radiocarbon dating in December of 1949 (an achievement that brought Libby the 1960 Nobel Prize for chemistry). A 1974 article by the late Elizabeth K. Ralph and Henry Michael of the University of Pennsylvania recounted for readers of American Scientist the first quarter-century of progress since Libby and his coworkers made their pioneering determinations of age using [C.sup.14]. Here I review the entire five decades of development of this remarkable technique, one that today requires no more carbon than what can be found in a few strands of hair.

Long Ago and Far Away

Radiocarbon dating depends on a chain of natural events, some having taken place in deep space long ago. The sequence begins in various parts of the galaxy, where charged particles are accelerated to immense velocities, forming what are known as cosmic rays. A fraction of these particles eventually rain down on the earth and strike molecules of atmospheric gas, producing neutrons. Some of these neutrons in turn react with nitrogen, [N.sup.14], to form [C.sup.14], which quickly combines with oxygen to form molecules of radioactive carbon dioxide ([[CO.sup.14].sub.2]). By the time the radioactive [[CO.sup.14].sub.2] reaches the earth's surface, it has mixed fully with normal carbon dioxide and accounts for about one molecule in 10 [12].

The vast majority of this [C.sup.14] eventually enters the oceans. But 1 or 2 percent goes into the terrestrial biosphere, because plants absorb carbon from [CO.sub.2] in the air during photosynthesis. Thus vegetation, and the animals that feed on it, are tagged with [C.sup.14].

Living things maintain a [C.sup.14] content that is about equal to the atmospheric concentration because the carbon atoms that undergo radioactive decay within their bodies are continually replaced. But once an organism dies and its metabolic processes cease, the amount of [C.sup.14] begins to diminish. The rate of decline is measured by the [C.sup.14] half-life, about 5,730 years.

Recognizing these phenomena, Libby realized that the age of ancient organic matter can be found from its residual [C.sup.14] content, as measured by the radiation emitted by the matter. For the radiocarbon age to correspond with its actual age, several conditions must be satisfied. First, the atmospheric ratio of [C.sup.14] to normal carbon ([C.sup.12]) must have remained essentially constant. Second, the ratio of carbon isotopes in the measured material must not have changed--except by the radioactive decay of [C.sup.14]--since the death of the organism. Third, there should have been rapid and complete mixing of [C.sup.14] through the various carbon reservoirs. Finally, the method assumes that the presumed half-life of [C.sup.14] is correct and that suitable analyses can reveal small concentrations of radiocarbon with appropriate levels of accuracy and precision.

Libby's means of measuring [C.sup.14] employed elemental carbon in amorphous form ("carbon black"),

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which he placed in a special type of Geiger counter. He originally built this type of apparatus for his dissertation research at U.C.

Berkeley in the mid-1930s, while he was studying the radioactivity of rare-earth elements. Testimony by those who labored with Libby at the University of Chicago, James R. Arnold and Ernest C. Anderson, records the great difficulties they encountered-and overcame-in making radiocarbon dating practical.

The key was finding an effective way to distinguish between background radiation and the relatively weak and infrequent beta decay from 14C in natural samples. Their solution was anti-coincidence counting, a technique that had been employed in the study of cosmic rays since the 1930s. Following this approach, they compared pulses from the counter containing the sample with pulses received from a ring of surrounding Geiger counters, the "guard ring." Signals that did not also register on the guard ring, that is, those in "anti-coincidence," reflected radioactive decay inside the sample. With this scheme, Libby and his young collaborators were able to demonstrate the inverse relation between the 14C content and age for a series of known-age samples, publishing their first "Curve of Knowns" in December 1949.

Successful as they were, these procedures were destined to change a great deal within just a decade. The production of massive amounts of artificial radiocarbon from the atmospheric testing of nuclear weapons complicated the use of elemental carbon for low-level 14C measurements. The problem is that solid carbon, like a charcoal filter, tends to absorb stray compounds, and many of the organics in the environment at that point had become mildly radioactive. So by the mid-1950s, proportional gas and liquid scintillation counting, techniques that involve only purified [CO.sub.2] or hydrocarbon gases (such as acetylene and methane) or liquids (such as benzene), had largely replaced the original method. These strategies became the basis on which tens of thousands of radiocarbon dates have since been determined in more than 40 laboratories scattered throughout the world.

Unfortunately, none of these facilities can date with any precision samples that are less than about 300 years old, except under very special conditions. This limitation stems from the natural fluctuations in [14.sup.C] production combined, more recently, with two effects of modern civilization: the release of enormous quantities of fossil fuel carbon dioxide and the production of "bomb" [14.sup.C] from atmospheric nuclear testing. The maximum ages that can be inferred depend on characteristics of the instrumentation and other details of the experimental configuration--sample-blank values, counter size, length of counting and, to some degree, the amount of material available for analysis.

Modem laboratories with counters designed to work with older material can readily measure moderately sized pieces of organic matter that are as much as 40,000 to 50,000 years old. Employing somewhat larger samples, a few laboratories have developed the capability to obtain age estimates up to about 70,000 years. And with isotopic enrichment, some investigators have measured a small number of specimens that are as much as 75,000 years old--a truly remarkable feat considering that this interval represents 13 half-lives, or a diminution of more than 8,000 times in the original, tiny radioactivity of organic matter. But improvements in measurement are just part of the story of the past 50 years: Specialists in radiocarbon dating have also made considerable progress in understanding the surprisingly complicated relationship between [14.sup.C] content and elapsed time.

Calibrating Radiocarbon Time

A early as 1958, the pioneering [14.sup.C] investigator Hessel de Vries (of the University of Groningen in the Netherlands) noted certain discrepancies between radiocarbon ages and true ages. Seeking an understanding of the geophysical implications of these variations, several investigators, notably the late Hans Suess of the University of California, San Diego, along with others, such as Paul Damon at the University of Arizona and Mimze Stuiver at the University of Washington, began to study this phenomenon. Suess quickly recognized a long-term trend on which were superimposed shorter-term components, later dubbed De Vries effects or, less formally, "wriggles," "wiggles," "kinks," "windings or "time warps." The presence of these deviations in the [14.sup.C] time scale indicated that at least one of the postulates of the method--most probably the assumption of a constant concentration of [14.sup.C] in the atmosphere--is violated to varying degrees.

Among the investigators studying these so-called secular variations were Ralph and Michael, who used their 1974 article in American Scientist to focus attention on early sets of measurements that illustrated clearly the systematic anomalies in the [14.sup.C] time scale. They and others were able to document the amount of offset between " [14.sup.C] time" and "real time" for the past 7,000 years by measuring the radiocarbon ages of wood from California giant sequoia and bristlecone pine--samples for which the true ages could be determined by counting the many yearly growth rings in these venerable trees. These findings sparked a series of further efforts to calibrate the radiocarbon method, allowing true

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ages to be calculated by adding or subtracting the appropriate offset.

When Ralph and Michael wrote their review, many workers were assuming that the longterm component of the variation follows a sinewave function, with a maximum deviation of 800 to 1,000 years for materials living about 7,000 years ago. But that surmise proved premature. In the past 25 years, investigators have succeeded in extending the 14C calibration much further back in time. For instance, comparisons between 14C and tree-ring counts of Irish oak and of German oak and pine pushed the limit to about 11,800 years ago.

Probing the discrepancy between conventional radiocarbon ages and true ages by counting tree rings is currently not possible for earlier periods. But investigators have nevertheless extended the calibration using other materials and other radioisotopic clocks. For instance, the measurement of trace amounts of uranium-234 and thorium-230 in samples of ancient coral (calcium carbonate) provide estimates of their antiquity. So by pairing 23U/230Th ages with 14C ages from such coral samples, geologists, geochemists and oceanographers working together over the past decade have extended the calibration to about 24,000 years ago (or, as expressed in uncorrected 14C time, to about 20,300 years before 1950, the unspoken reference date specialists commonly use when they give a number of radiocarbon years "before present"). Rather than displaying a sine wave, the long-term offset appears to slowly diminish, from its value of about 3,700 years for that time to less than 200 years for the past two millennia.

For earlier intervals, the offsets between ages obtained from 14C and other dating methods show discrepancies in many cases. For example, using materials from aboriginal hearths found near Lake Mungo, Australia, investigators have compared radiocarbon ages with those obtained from hearth stones using thermoluminescence dating, a technique that measures the photons released from quartz when internal high-energy electrons are freed by heat. Because sunlight can also liberate these trapped electrons, thermoluminescence dating gauges the amount of time an object has been buried. The differences between thermoluminescence and 14C ages for these hearths suggest that the offset in the radiocarbon time scale for about 29,000 years ago may have been in the range of 3,500 to 5,000 years. But comparisons between 14C results and ages obtained from mineral specimens by assessing the radioactive decay of potassium into argon suggest less of an offset for this same period.

Studies of ancient changes in the intensity of the earth's dipole magnetic field (and thus its ability to shield the planet from cosmic rays)--currently considered to be a major cause of the long-term offsets in [C.sup.14] ages--also cast doubt on the magnitude of the discrepancy found using thermoluminescence as a yardstick. One interpretation of the geomagnetic evidence argues for a slowly decreasing offset in radiocarbon ages, one that starts in the range of 1,500 to 2,700 years for material living between 25,000 and 40,000 years ago. Interestingly, deductions drawn from the geomagnetic measurements predict that [C.sup.14] ages should be largely correct for carbon that is about 45,000 to 50,000 years old.

Further work will be needed to confirm that the systematic error in radiocarbon ages for 500-century-old material is truly so small and to examine the short-term secular variations at such remote times. But investigators now have a good handle on the "wiggles" in the calibration for the last twelve millennia. These variations are well documented, yet they cause considerable problems because they introduce built-in uncertainties in dating: Calendar ages can often be expressed only as broad ranges, even when the [C.sup.14] concentrations are known precisely. Thus radiocarbon dates for some time periods will be inherently less precise than those for others.

Radiocarbon specialists have considered various strategies to increase precision. Some employ Bayesian statistics--a technique for combining stratigraphic ordering and [C.sup.14] ages--to prevent the error bars in a ordered series of samples from overlapping. Among other things, such a strategy assumes that samples from lower beds must be older than those obtained higher in the stratigraphic column. Another novel calibration procedure is "wiggle-matching." This maneuver requires a sequence of [C.sup.14] measurements for closely spaced tree rings taken from a sample of wood of unknown age. Matching the shifts in these values against the known pattern of short-term de Vries effects in the calibration curve permits a more precise age of the sample to be found. For example, Austin Long and his colleagues at the University of Arizona used this strategy to determine the cutting date for a timber from a 4th-century Japanese tomb with an uncertainty of only five years.

Accelerated Progress

So in some cases radiocarbon dates are dearly becoming more accurate. They are also becoming easier to obtain. The chief difficulty in the past was that a considerable amount of material was needed to measure radiocarbon concentration--and thus age--by counting decay events with an ionization or scintillation detector. Decay counting registers only a tiny fraction of the [C.sup.14] atoms present. For example, of the 60 billion atoms of [C.sup.14]

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in 1 gram of pre-industrial carbon, fewer than 14 of these atoms will, on average, decay during each minute of measurement.

Practitioners tolerated the inherent inefficiency in decay counting from Libby's first work in 1946 until 1977, when physicist Richard Muller of the University of California, Berkeley proposed that radiocarbon concentrations could be found directly with a cyclotron. This high-energy accelerator, which sends particles along a spiral trajectory, could be used as an ultrasensitive mass spectrometer to distinguish ionized carbon isotopes by their chargeto-mass ratio. Detecting [C.sup.14] in this way was possible, but consistent results proved difficult to achieve despite years of effort.

Another type of accelerator mass spectrometry, as this approach was called, was described independently by two groups of physicists within months of Muller's initial publication. Both groups-one led by D. Erle Nelson at Simon Fraser University and the second involving a collaboration of investigators at the Universities of Toronto and Rochester, and the General Jonex Corporation-noted that there were no known stable negative nitrogen ions. By using negative ions, the accelerator would discriminate against [N.sup.14], the ion that would create the most difficulty in measuring [C.sup.14]. Both groups also used tandem electrostatic accelerators. As the name implies, these devices employ two stages: A negative ion beam is first accelerated and passes through a "stripper," which removes electrons, converting the beam to positive ions. These particles are then further accelerated. The stripping process breaks up molecules of mass 14; which would otherwise interfere with the detection of [C.sup.14]. A mass spectrom eter, essentially a large electromagnet, separates the isotopes of carbon so that the [C.sup.14] atoms can be counted directly.

The advent of accelerator mass spectrometry at the end of the 1970s brought about an enormous boost in detection efficiency, one that promised three important advantages. First, the amount of carbon required should plummet from grams to milligrams. Second, counting times should be reduced from days, weeks or even months to just minutes. Finally, the sensitivity of detection should increase so that the maximum age datable with radiocarbon might extend from the then routine 40,000 to 50,000 years to as much as 100,000 years.

Over the last 20 years, investigators have indeed realized the first two of these anticipated benefits. For both sample sizes and counting times, thousand-fold reductions have been possible. However, the projected third advance has not materialized. Why not? It turns out that sensitivity is limited not by the detector but by the tainting of samples with modern carbon, which is commonly introduced as the materials are prepared for analysis. Much of this contamination stems from the current requirement in most laboratories that samples be converted to graphitic carbon for measurement with an accelerator mass spectrometer. So investigators at these facilities face the same problem that hampered Libby's use of solid carbon samples a half-century ago. Even a few parts per million of modem carbon in a sample will limit the effective maximum ages that can be resolved. So in practice, [C.sup.14] dating with accelerator mass spectrometry has not broken through the age barrier established by decay counting: In routine application, it still lies somewhere between 40,000 and 50,000 years; only rarely can 60,000 be achieved.

Also, the ages estimated with particle accelerators are no more or less accurate or precise than those obtained by decay counting. But the new approach provided a way to measure samples with extremely small amounts of carbon. Experiments that would not have been mounted or would not have been practical with conventional decay counting were suddenly possible. In the biomedical sciences, for example, clinicians could use natural concentrations of [C.sup.14] to trace the flow of a compound within a patient's body, rather than having to administer a more highly radioactive solution. This advance thus permitted studies that were previously deemed to be overly dangerous.

In archaeology, the leap was no smaller. Very quickly, scientists could be quite selective about what they wanted to measure. A good illustration of the gains that ensued comes from a 1989 study of maize specimens excavated from two rock shelters in the Tehuacan Valley of Mexico. The Zea mays found at those sites had been regarded as among the earliest example of cultivated maize in the New World, seemingly as much as seven millennia old. But this idea was established at the beginning of the 1970s, when it was not possible to measure the radiocarbon content of the small amount of maize recovered. Archaeologists had to obtain age estimates from pieces of charcoal that were thought to date from the same period. (Charcoal, unlike unburned wood, can survive many centuries of burial.)

In 1989, Long and his colleagues measured the [C.sup.14] content in milligram amounts of maize with accelerator mass spectrometry and found that the seeds were less than 5,000 years old. So over the past decade, archaeologists have had to rethink their ideas about just where the center of maize domestication in Mesoamerica may have been.

Accelerator mass spectrometry has also helped to address one of the most acrimonious debates in New World archaeology--the nature and timing of the peopling of the

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Western Hemisphere. Historically, arguments have centered on two issues: the strength of the evidence for human presence and its dating. Many archaeologists have questioned the validity of materials with radiocarbon dates in excess of the well-documented Clovis period, for which the ages of artifacts range from about 10,890 to 11,570 radiocarbon years.

Beginning in the mid-1970s, my colleagues and I undertook a direct examination of bone from human skeletons found at different archaeological sites in North American that, on various grounds, had been declared to be preClovis in age. The sensitivity of accelerator mass spectrometry eventually permitted us to obtain [C.sup.14] ages from different chemical fractions of these bones, including amino acids and other highly specific organic constituents. We could thus judge whether the bones might have absorbed older carbon, for example, from the ground in which they were buried.

The work of several laboratories revealed that all of the alleged pre-Clovis ages were unreliable. Although there now is evidence that at least one site in South America (Monte Verde in Chile) may have been occupied about 1,000 years before the Clovis period, no human skeleton from North America has yielded ages any older than 11,000 radiocarbon years.

So the peopling of North America probably begins, as most prehistorians have long believed, at the very end of the last ice age. But the story is certainly not a simple one, and the final chapter has not been written. Our recent [C.sup.14] measurements on human skeletons recovered from Kennewick in Washington and Spirit Cave in Nevada hint at some of the complications. These remains, between 8,000 and 10,000 years old, seem to show skeletal features similar to those of early South Asian populations, unlike more recent Native Americans. It appears that the late ice-age inhabitants of North America may have been much more genetically diverse than was previously imagined.

An Impressive Half-Century

Now, at the 50th anniversary, it is difficult for many people to appreciate just how dramatically the advent of radiocarbon dating transformed archaeology. Libby's invention made the study of world prehistory truly possible, contributing a time scale that may not have been perfect (particularly at the outset) but that transcended the former jumble of regional schemes.

Radiocarbon dating continues to provide the chronological foundation, directly or indirectly, for most investigations into the past 500 centuries of prehistory. And it regularly contributes to many other fields of science, from geology to astrophysics, a breadth that is perhaps fitting for a method that owes its current level of sophistication to workers in so many disciplines.

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Bibliography

Arnold, J. R., and W. F. Libby. 1949. Age determinations by radiocarbon content: Checks with samples of known age. Science 110:678-680.

Bard, E., B. Hamlin, R. G. Fairbanks and A. Zindler. 1990. Calibration of the [C.sup.14] timescale over the past 30,000 years using mass spectrometric U-Th ages from Barbados corals. Nature 345:405-410.

Kline, J., J. C. Lerman, P. E. Damon and E. K. Ralph. 1982. Calibration of radiocarbon dates: Tables based on the consensus data of the workshop on calibrating the radiocarbon timescale. Radiocarbon 24:103-150.

Ralph, E. K,. and H. N. Michael. 1974. Twenty-five years of radiocarbon dating. American Scientist 62:553-560.