ChemMatters February 1989 Page 12

Carbon-14 Dating

by Clair G. Wood

Archaeologists must have accurate dates to understand our history. Ashes from a prehistoric campfire may be evidence of a human migration, but only if the date of the campfire can be fixed. Seeds from a funerary jar in Central America may indicate when the Mayan culture collapsed, if the age of the seeds can be determined. Until about 40 years ago artifacts had to be dated indirectly. For example, a document of unknown age might contain written reference to a prominent astronomical event that could indicate when the document was written. Or a "marker," such as a coin, found with the artifact could indicate the minimum age of the artifact. In 1946 Willard F. Libby, a University of Chicago professor, developed a method by which most carbon-containing artifacts could be dated directly. The artifact's own atoms can reveal its age, back to about 50,000 years. Libby's discovery revolutionized archaeology and earned him the Nobel Prize for chemistry in 1960.

Unstable carbon

Libby's method, called radiocarbon dating, is based on the fact that all living things contain carbon, yet not all carbon atoms are the same. Your own body contains three isotopes of carbon: ^{12}C, ^{13}C, and ^{14}C. The atoms of ^{12}C and ^{13}C are stable and have been around for millions of years. However, the nuclei of ^{14}C atoms are relatively unstable and emit radiation as they decay. The amount of ^{14}C remaining in an artifact is the key to determining age. The rate at which ^{14}C decays is well known, and the amount of ^{14}C in an artifact can be measured in the laboratory. If the amount that was originally in the artifact can be estimated, then the decay time—the age of the artifact—can be calculated.

This chain of logic depends on knowing the original amount of carbon in the object. If a wooden axe handle is recovered from an ancient campsite, how can anyone possibly know the amount of ^{14}C that it contained, say, 10,000 years ago? The answer came from the work of physicist Serge Korff who, in 1939, discovered that ^{14}C is continually being created in the upper atmosphere. High-energy cosmic rays can eject neutrons from the nuclei of atmospheric gases, and the free neutrons collide with the nuclei of nitrogen atoms, changing them to carbon-14 and releasing a proton. Much later, the ^{14}C decays, emits beta radiation (electrons) and reverts to nitrogen. The half-life for this final step is 5570 years, which means that half of the existing carbon-14 atoms will decay in 5570 years, and half of the remaining carbon-14 atoms will decay in an additional 5570 years.

Throughout the entire atmosphere, the interaction of cosmic rays with nitrogen produces only about 7.5 kg (16.5 pounds) of ^{14}C per year. This small amount of carbon, in the form of carbon dioxide, becomes distributed evenly worldwide and finds its way into the carbon cycle. The carbon dioxide is taken up by plants, which may be eaten by animals. When the plants and animals die and are consumed by decay organisms, the carbon is released to the atmosphere, largely as carbon dioxide and methane, CH_4 (see Figure 1). There is continual formation of carbon-14 high in the atmosphere, exchange of carbon-14 between the oceans, atmosphere, and biota, and gradual decay of carbon-14 atoms. This dynamic process keeps the proportion of carbon-14 in living things fairly constant.

Libby used the "constancy" assumption as the basis for his dating method. He assumed that the ^{14}C ratio (the ratio of ^{14}C to stable carbon, ^{12}C and ^{13}C) would be the same in all terrestrial organisms for thousands of years. This ratio is about one atom of ^{14}C to every trillion atoms of stable carbon. When the organism dies, ^{14}C disintegrates without being replenished by the carbon cycle, and the ratio begins to decrease.

Up in flames

The standard laboratory measurement of the ^{14}C ratio requires sacrificing part of the sample. The object must be cleaned of any living material and washed with both acid and alkali to remove any extraneous carbon compounds. If the object is made of wood, approximately 10 g is burned, and the resulting carbon dioxide is collected, dried, and purified. Gaseous contaminants, primarily oxides of sulfur and nitrogen, are removed chemically, and the purified carbon dioxide is then converted to benzene, C_6H_6.

The final task is to measure the amount of radioactivity being given off by the ^{14}C within the sample. About 10 mL of the benzene is mixed with a scintillant, an organic compound that emits a flash of light when it is struck by beta radiation, and placed in a scintillation counter—a device with "electric eyes" that patiently counts each flash of light. The older the wood the lower the count.

If archaeologists are to have confidence in the dates produced from radioactive carbon, it is necessary to compare the carbon dates with dates determined by other methods. The most accurate method of dating wood is also the simplest: counting the growth rings of trees.

Rings of truth

Bristlecone pines are among the oldest living organisms on Earth. One specimen in California is between 4600 and 4900 years old. Moreover, the pines' resinous wood and dry, high-altitude environment help preserve them even after death. By 1969, overlapping of rings from many samples had given a complete chronology for the bristlecone pine dating back to nearly 7000 B.C. This made the bristlecone ideal for "calibrating" the ^{14}C dates, that is, converting the calculated ages to true calendar ages. Without this calibration, the dates could be off by as much as 800 years.

Verification of carbon-14 dates is important because the principle of constancy is not 100% true. Over the millennia, the 14C ratio has varied enough to cause up to 10% error in dates if they are not calibrated by comparison with tree rings.

Needle in a carbon stack

In any sample of carbon the amount of ^{14}C is so small, compared with stable carbon, that it is difficult to measure. Furthermore, as the sample ages the ^{14}C diminishes. The disappointing facts are:

- One milligram of carbon from a 110,000-year-old artifact contains only 50 atoms of ^{14}C.
- The slow decay rate of ^{14}C means that if all the disintegrations in a sample were counted for 80 years, only 1% of the ^{14}C would be detected.
- At low counts-per-minute levels, it is difficult to separate the ^{14}C counts from background radiation, which adds to the dating error.

These difficulties mean that a relatively large sample of the artifact must be used—and destroyed. This led researchers to seek a more effective method of determining the ^{14}C ratio in an artifact. They turned to an instrument called the mass spectrometer.

The mass spectrometer, or MS, is a sophisticated combination of vacuum chamber, magnet, detector, and computer that can count atoms

of different mass directly, rather than waiting for them to decay and counting their radiation. However, in order to measure the minute amount of ^{14}C present, it is necessary to separate it from 99.9999999% of all other atoms in the sample, and this can only be done by the most sophisticated accelerator-type instruments, such as the tandem accelerator mass spectrometer (TAMS) operated by the University of Arizona (see box "Accelerated dating").

The TAMS's ability to detect individual ^{14}C atoms gives it two advantages over the radiocarbon decay method. The size of the sample that must be destroyed is reduced to a few miligrams, and a sample can be measured in only about an hour— a real advantage compared to days or weeks needed for the method of measuring radioactivity.

Bible dates

One of the most fascinating applications of ^{14}C dating has been in the field of Biblical archaeology. For example, ^{14}C dating of the Dead Sea scrolls gave a reading of 1920± 200 years—well within the time frame in which literary scholars believed they had been written.

One of the most controversial religious artifacts has been the Shroud of Turin. A linen cloth over 4 m long, it bears a striking image of a crucified man, which many people believed to be the image of Jesus. The shroud was kept at the Cathedral of St. John the Baptist in Turin, Italy, for nearly 400 years, and records indicate that it was at least two centuries older than that.

In 1978, a team of scientists from many disciplines conducted an extensive investigation on the shroud. They concluded that the image had not been painted on the cloth by any traditional method—but the scientists were unable to say how the image got on the cloth (see "Studying the Shroud," page 8).

To determine whether the cloth was a hoax, it was important to learn the age of the linen. If the linen was made from flax grown during Biblical times, the shroud might be authentic; if dated from medieval times, the shroud was definitely not authentic. Dating the shroud by its ^{14}C content could help resolve the controversy. In 1978 the only method available was the radioactive counting technique—which requires destroying a sizeable sample. The church authorities refused permission to conduct the test, preferring to keep the shroud intact. However, in 1987 permission was granted to cut from the shroud a piece of linen just 1-by-7 cm—more than enough to perform TAMS dating. In 1988 three postage-stamp-size pieces were sent to TAMS laboratories at the University of Arizona, Oxford University, England, and the Swiss Federal Technical Institute in Zurich, Switzerland.

The verdict

In October 1988, the Archbishop of Turin released the test results. The linen is about 660 years old—far too young to be the burial cloth of Jesus. Because of the statistical nature of the measurements, Timothy Linick, scientist at the TAMS laboratory at the University of Arizona, prefers to give the official date this way: "There is a 95% chance that the flax from which the linen was made was grown between 1260 A.D. and 1390 A.D. Pushing the statistics further, there is about 1/100 of 1% chance that it is older than 1200 A.D, and essentially zero chance that it was made at the time of Jesus."

SIDE BAR

Accelerated dating

When the 2-by-1-cm piece of the shroud arrived at the University of Arizona laboratory, it was cut into four pieces, which were locked up in different locations. The pieces were later cleaned of any modern carbon (such as sweat compounds) by rinsing with HCI, distilled water, NaOH, detergent, and a surfactant. The sample was then heated in a sealed glass tube with some copper(II) oxide. Some of the CuO decomposed, releasing enough oxygen to burn the linen to carbon dioxide and water vapor.

$$2CuO \Rightarrow Cu_2O + 1/2\ O_2$$
$$\text{linen} + O_2 \Rightarrow CO_2 + H_2O$$

Dry ice was then used to chill the mixture of gases, which caused the water, but not the carbon dioxide, to freeze. The gases were then passed over heated silver powder to remove impurities containing sulfur and chlorine.

$$5Ag + SO_2 \Rightarrow AgS + 2Ag_2O$$
$$2Ag + 2HCl \Rightarrow 2AgCl + H_2$$

The remaining gas was then chilled with liquid nitrogen, and the CO_2 condensed, forming a frosty film on the glass walls. The now-purified carbon dioxide was transferred to an apparatus that contained powdered zinc and powdered iron in separate, but connected, glass tubes. When the apparatus was heated, the CO_2 was reduced to carbon in two connected steps:

$$CO_2 + Zn \Rightarrow ZnO + CO$$

$$2CO \xrightarrow{\text{Fe catalyst}} CO_2 + C \text{ (graphite)}$$

The CO_2 produced by the second reaction reentered the first reaction until all of the carbon ended up as graphite. The sooty product was removed from the vessel, poured into a small hole in a sample holder, and compressed into a piece of graphite about the size of a pencil point.

Two samples containing carbon from the shroud were slipped into the target wheel, along with three control samples containing carbon of approximately known age, four modern standards containing known amounts of ^{14}C, and one sample prepared from limestone from which all ^{14}C had decayed. The loaded target wheel was then inserted into the TAMS source chamber, which was then sealed and pumped to a vacuum.

The measurement of ^{14}C begins with the boiling of a small amount of cesium metal. The vapor is passed through a porous disk of hot titanium, which removes electrons from the easily ionized cesium. The heavy Cs^+ ions are attracted to the negatively charged target wheel, where they strike the carbon sample (Figure 2). The impact dislodges and ionizes some of the carbon, and the negative ions that are formed are repelled from the negative target wheel, travel through a long vacuum tube, and pass between the poles of a large magnet. This "injection magnet" deflects the ions with mass 14 into the accelerator section of the instrument and leaves most of the ions of other masses behind. The stream entering the accelerator contains $^{14}C^-$ and other ions with the same mass such as $^{14}C^-$ and fragments such as $^{12}CH_2^-$ and $^{13}CH^-$.

A terminal at the center of the accelerator carries a positive electrical charge of 1.8 million volts, which attracts the negative ions. This intense charge accelerates the ions and pulls them through the dime-size entrance to the "stripper." Once inside, the negative ions collide with a thin cloud of argon gas, lose some of their outer electrons, and change their charges from 1 - to 2+, 3+, or 4+. Now positively charged, the ions are repelled by the positive voltage and, because they carry multiple positive charges, the ions accelerate away even faster than they approached. (The pull-push action is reflected in the instrument's name: the tandem accelerator.) Any molecular fragments become positively charged, and those with charges of 3+ or more (such as $^{13}CH^{4+}$) become unstable and break apart.

Exiting the accelerator at very high speed, the ions pass between a pair of oppositely charged plates that deflect the C^{3+} ions just enough to follow the next bend in the vacuum tube; meanwhile, the C^{2+} ions are deflected too little and the C^{4+}, too much, so they are removed from the stream. The ions are deflected by two more magnets that are adjusted to allow particles of mass 14 to pass and send other particles crashing into the walls. The ions then pass through a thin film of Mylar (to slow them down slightly) and finally enter an electronic detector that measures the energy of each particle. A computer draws a spectrum-like graph showing the number of impacts that occurred in each energy category. Carbon-14 can be distinguished from nitrogen-14 (abundant in the atmosphere) because, as the nitrogen-14 atoms pass through the Mylar film, they are slowed more than the carbon and strike the detector with less energy.

After 50 sec of counting ^{14}C, the injection magnet is adjusted to admit ^{13}C for 10 sec—measurement time is shorter because of the far greater abundance of ^{13}C. This 50-sec, 10-sec cycle is repeated 10 times for each sample before the target wheel is rotated to the next sample, and full measurements are made for five revolutions of the wheel. The computer calculates the $^{14}C/^{13}C$ ratio, and from this number calculates the age of the ^{14}C, which is then corrected for environmental variations to give the final statistical range of possible ages.

(David P. Robson)

CAPTIONS

Figure 1. The carbon cycle.

A bristlecone pine in Yosemite National Park. Some bristlecone pines are over 4,000 years old, making this the longest lived of all species.

Figure 2. The TAMS accelerator at the University of Arizona is so long that only about half of it is shown in this photo. The stack of paper next to the computer printer contains the results of a TAMS test.

BIOGRAPHY

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