# Radiodating: Direct Detection Extends Range of the Technique

Carbon-14 dating may be extended from the present practical limit of about 50,000 years to 100,000 years or more with new techniques in which accelerators designed for nuclear physics are used as sophisticated mass spectrometers. Other radioactive elements may also be used to date geological samples as old as 50 million years, and previously unmeasurable trace concentrations of radioactive elements in the environment may be detected with the new techniques. The capability of the accelerators to identify radioactive elements without waiting for a disintegration to occur opens new vistas for archeology, geology, pollution monitoring, and nuclear waste disposal.

Conventional radiocarbon dating relies on measurement of the $\beta$ decay of carbon-14 present in a sample containing organic materials. The amount of carbon-14 in the atmosphere is constant because it is produced from nitrogen atoms by cosmic rays at the same rate that it decays. The amount in living tissues is equal to the amount in the atmosphere. When the organism dies, however, no new carbon-14 is incorporated and the carbon-14 present at the time of death begins to decay with a half-life of 5730 years. By monitoring $\beta$ decay and determining the ratio of the amount of carbon-14 in the sample to the amount in contemporary materials, it is possible to date reliably objects as old as 60,000 years—although practical considerations often limit the age to 40,000 years or less. For older samples, the amount of carbon-14 still present is so small that it becomes extremely difficult to separate its radiation from that of the background.

### Detect Atoms Directly

One alternative to monitoring $\beta$ decay is to detect the carbon-14 atoms directly. Several investigators have attempted to do this with conventional high-resolution mass spectrometers, but without success. The concentration of carbon-14 is so small that its signal is completely overwhelmed by that from nitrogen-14. The use of accelerators not only increases sensitivity and resolution by several orders of magnitude compared to even high-resolution mass spectrometers, but also makes it feasible to eliminate nitrogen-14 and other contaminants.

Two independent approaches to the problem have been developed in the last year, one in which the 88-inch cyclotron at Lawrence Berkeley Laboratory is used and the other in which the tandem Van de Graaff accelerators at the University of Rochester and McMaster University are used. The high energies to which ions can be accelerated in these devices make possible several things that cannot be accomplished with conventional mass spectrometers.

The cyclotron was first used in this fashion in 1939 by Luis W. Alvarez and Robert Cornog of the University of California at Berkeley, to demonstrate that tritium is the radioactive element with an atomic weight of 3 rather than helium-3, as was previously believed. The technique thereafter lay unused until it was exhumed in 1975 by Alvarez and several associates for their unsuccessful search for quarks with a charge of +1. Richard A. Muller, a member of that team, recognized the potential of the cyclotron as a mass spectrometer and began experiments using it to detect trace concentrations of elements. The principal problem in the cyclotron mass spectrometer, as in a conventional instrument, is separation of carbon-14 from ions with nearly identical masses. At the high energies to which ions are accelerated in the cyclotron (typically 35 million electron volts or more, 1000 times more than those in a mass spectrometer), ions of different atomic number can be distinguished by the distance that they travel through various substances. Tritium ions travel a greater distance through aluminum than do helium-3 ions, for instance, and carbon-14 ions travel farther than nitrogen-14 ions. Undesirable ions can thus be filtered out, and each desired ion can be identified with a silicon detector.

In his first experiments, Muller found that a thin foil of aluminum would block all helium-3 ions accelerated to a given voltage while permitting passage of all tritium ions accelerated by the same potential. In this fashion, he was able to measure the concentration of tritium in a 24-year-old sample of water and date the sample (an accomplishment that can, of course, also be performed by conventional techniques). The same technique did not work well for carbon-14, though, because the foils were not sufficiently uniform to separate it completely from nitrogen-14. After some experimentation, Muller, Edward J. Stephenson, and Terry S. Mast of Berkeley found that a cell containing xenon gas does the job well; carbon-14 travels about 1.3 times farther through xenon than does nitrogen-14 at the voltages employed. They recently used the xenon cell successfully to date a carbon sample approximately 6000 years old.

Independently, a group of investigators headed by Harry E. Gove of the University of Rochester, Albert E. Litherland of the University of Toronto, and Kenneth H. Purser of General Ionex Corporation pursued an old idea that the separation could be accomplished by working with negative ions in a tandem Van de Graaff accelerator (the cyclotron works only with positive ions). Negative carbon ions are stable and can be accelerated, but negative nitrogen ions tend to lose their charge so readily that few are accelerated. Using a cesium sputtering source developed by Roy Middleton of the University of Pennsylvania, nitrogen-14 is thus eliminated at the ion source. The small amount that remains in the beam can be eliminated by electrostatic fields.

### Eliminate Molecular Ions

Partway through the acceleration process, the negative ion beam is passed through a carbon foil to convert the negative ions to positive ones. This process eliminates molecular ions such as $^{12}CH_2^-$, $^{13}CH^-$, and $^{11}BH_3^-$, which fall apart when they are stripped of three or more electrons. A similar approach was developed about the same time by a team composed of Erle Nelson and Ralph G. Korteling of Simon Fraser University and William R. Stott of McMaster University, using the accelerator at McMaster.

In their initial report last year, Gove and his associates demonstrated that they could detect amounts of carbon-14 comparable to those in organic samples 70,000 years old. In a similar experiment, the McMaster group reported that they could detect carbon-14 in a sample of wood from the late 19th century. Similar results were subsequently reported by H. R. Andrews and his associates at the Chalk River Nuclear Laboratory in Ontario and by David Sinclair and his colleagues at Oxford University. Also


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recently, the Rochester group has reported dates as old as 48,000 years for archeological artifacts.

The limiting factor in the use of established accelerators for radiocarbon dating is contamination resulting from their previous use for nuclear physics. Interaction of accelerated particles with the carbon lining of the cyclotron or with residual gases in the tandem accelerators produces a background of carbon-14. The problem is moderate in the Rochester accelerator and, at present, limits the age of samples that can be dated easily to about 40,000 years. Contamination in the Berkeley cyclotron is worse by a factor of 10 and the practical limit there is now about 10,000 years. Both groups think that the contamination problem can be overcome. The McMaster group, in contrast, reports that there is no apparent contamination in the accelerator. Carbon-14 contamination should not be a problem at all in new instruments dedicated exclusively to dating. Purser says General Ionex is prepared to construct dedicated accelerators that will be free of machine background carbon-14 and guaranteed to detect quantities of carbon-14 comparable to ages of 60,000 years. The cost of such an instrument will probably be about $500,000.

### Contamination Problem

A second, and perhaps more serious, problem is contamination of samples with carbon-14 from contemporary sources. If 60,000-year-old samples are to be dated, Nelson says, contamination (from atmospheric carbon dioxide, plant roots touching the sample, and so forth) must be less than 0.01 percent. For each additional 20,000 years by which the range is extended, the contamination must be reduced by a factor of 10. For a 100,000-year-old sample, the contamination must be less than 0.0001 percent or 10 parts per million, a figure that may not be possible to achieve with current techniques. One way to minimize carbon dioxide contamination, Nelson says, might be to work only with macromolecules, perhaps proteins, that can be positively identified as having come from the sample.

Such an approach would be possible because the accelerator mass spectrometers can be used with very small samples. Even if the age limit for accelerators could not be extended beyond that for $\beta$ decay methods, this capability would still make the technique valuable. Because of background radiation from cosmic rays, Muller says, about 10,000 radioactive disintegrations must be observed for accuracy. For sample ages in the range 5,000 to 10,000 years, this requires 1 to 10 grams of carbon and counting times of 1.5 to 15 hours. Older samples require larger amounts of carbon, longer counting times, or both. In contrast, a typical cyclotron beam might consume about 2.5 milligrams of carbon per minute. At this rate, contemporary carbon would produce about 440 atoms of carbon-14 (counts) per minute. A rate of 1 count per minute would be equivalent to an age of 69,000 years, while a rate of 1 count per hour would imply an age of 94,000 years. A whole hour of counting would consume only 150 milligrams of sample. It should thus be possible to use a very small scraping for accelerator dating, while conventional radiocarbon dating might necessitate wholesale destruction of the sample. The Rochester group has achieved even greater efficiency and has dated 40,000-year-old objects with samples as small as 15 milligrams.

Carbon, of course, is not the only element that can be accelerated. Direct detection opens the door to measurement of a whole spectrum of radioactive elements whose half-lives are too long or whose concentrations are too low for counting. Tritium concentrations, for example, could be used to date water samples, as Muller has already demonstrated; mass spectrometric techniques can be used with enriched tritium samples, though, and accelerators are not really necessary. Older water samples could be dated with argon-39, which has a half-life of 265 years. Cosmic-ray-produced argon-39 is present in a known concentration in water that is in equilibrium with the atmosphere. By measuring its concentration in an underground water reservoir, therefore, it should be possible to tell how long it will take the reservoir to refill by natural seepage. It could also be used to date underground reservoirs to assess the long-term stability of proposed nuclear waste storage sites. If argon is present in the water in a proposed site, then that site is probably not sufficiently stable for waste storage.

Dating of older geological samples can be achieved with beryllium-10, which has a half-life of 1.5 million years. Beryllium-10 is produced in the atmosphere by cosmic rays at a low rate. It is relatively inert chemically and, after mixing into the ocean, settles out in sediment at the same rate that it is produced. Traces of beryllium are thus present in most sedimentary rocks and can be used to date them. Several investigators have concentrated beryllium in sediment by as much as five orders of magnitude and have used conventional dating techniques in studies of sea-floor spreading and formation of manganese nodules. Even with such concentration, however, dates beyond two half-lives are difficult to obtain.

In the cyclotron, Muller says, beryllium-10 can be detected easily and interfering ions, chiefly boron-10, can be removed with the xenon gas cell. Muller and his colleagues have demonstrated that beryllium metal with a $^{10}Be/^{9}Be$ ratio of $10^{-9}$ produces 800 counts of beryllium-10 per minute in the cyclotron. A blank containing no beryllium-10 produced no counts in a 5-minute period. This demonstrates, Muller says, that the technique can be used readily to date geological samples. Grant M. Raisbeck and his colleagues at the Laboratoire René Bernas du Centre de Spectrometrie de Masse in Grenoble, France, have used the cyclotron there to measure the concentration of beryllium-10 in sediments where the ratio is $10^{-10}$. This corresponds to an age of 10 million years. The amount of sample required, assuming a total beryllium concentration in the sample of 3 parts per million, is less than 10 cubic centimeters for ages under 35 million years.

### Other Isotopes Can Be Detected

Other relatively rare isotopes that can probably be detected with an accelerator mass spectrometer include aluminum-26, chlorine-36, manganese-53, krypton-81, and iodine-129. Chlorine-36, for example, has a half-life of 300,000 years and could be used for dating water in underground reservoirs in the same fashion as argon-39. It could also be used to detect leakage in groundwater near nuclear power plants and waste disposal sites. The Department of Energy has expressed interest in such possibilities and both the Berkeley and Rochester groups have shown that chlorine-36 can be detected at concentrations of one part in $10^{14}$.

In view of all these potential benefits and the rapid pace of the research, it seems likely that several institutions will acquire dedicated accelerators; some investigators are already writing grant proposals. Industry may also be interested in the instruments. The current market for radiocarbon dating has been estimated to be about $3 million per year (at $200 per date), and the capability of the accelerators to use smaller samples—as well as to use other isotopes—should increase that market substantially. The future for ultrasensitive accelerator mass spectrometers looks bright.

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