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RADIOISOTOPE DATING WITH ACCELERATORS

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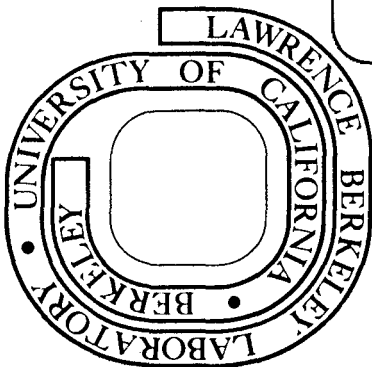
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Radioisotope dating with accelerators

Counting accelerated ions rather than decay events increases the sensitivity by several orders of magnitude so we can find the ages of much older and smaller samples.

Richard A. Muller

A new method of detecting radioactive isotopes promises to have a revolutionary impact on the field of radioisotope dating. The technique, which was developed over the past two and a half years, consists of counting individual atoms of radioactive isotopes that have been ionized, accelerated to high energies, and then selected and identified. By detecting all—or a substantial fraction—of the atoms in the beam, this method has much greater sensitivity than the standard method, which detects only the tiny fraction of the atoms that decay during the counting period. The new “direct detection” method therefore will allow one to use much smaller samples and to measure much greater ages than the older “decay detection” method.

One remarkable fact about direct radioisotope detection with accelerators is that six groups have already made very sensitive measurements with virtually unmodified existing accelerators. Dedicated accelerators are now being planned at Oxford University, the University of Rochester and the University of Arizona. Several additional groups either plan to begin measurements with existing accelerators, or have already begun. Samples a thousand times smaller than previously required have already been used to obtain dates. The radioisotopes carbon-14, tritium, beryllium-10, and chlorine-36 have served for measurements inconceivable with the older methods.

Carbon-14 is the most famous of the dating radioisotopes. It can be used for determining the ages of formerly living

materials because the ratio of C^{14} to C^{12} is approximately constant with time for carbon in the biosphere. This ratio is determined by the equilibrium between the production of C^{14} by cosmic rays, and its decay with a half-life of 5730 years. When a living object is taken out of equilibrium with the biosphere (when it dies) the C^{14} continues to decay without being replaced by fresh atmospheric C^{14} . The initial rate is 14 decays per minute per gram of carbon, and decreases with time, t , as $2^{-t/5730 \text{ yrs}} = e^{-t/8270 \text{ yrs}}$. Measurement of the decay rate gives an estimate of the “age” of the sample; the use of C^{14} for this purpose was developed by Willard F. Libby and coworkers¹ in the late 1940's. Alternately, with objects of known age (such as tree rings) one can study variations in the intensity of the cosmic rays or in the amount of diluting C^{12} ; such studies are yielding a fascinating record of the climate history of the Earth over the last 8000 years.²

Decay detection

Modern carbon-14 laboratories detect the disintegration of the remaining C^{14} atoms, typically by oxidizing the carbon to CO_2 and counting the decays in a proportional counter. Because of the low decay rate, the undistinctive nature of the decay (the emitted electron has a broad beta-decay spectrum with an average energy of only 45 keV) and problems with background radioactivities, typically 1 to 10 grams of carbon must be counted for 1 to 10 hours or more. Except in unusual cases when large amounts of material are available and long counting periods taken, one cannot obtain dates older than 30 to 40 thousand years.

For every decay per minute, there are 4×10^9 atoms of carbon-14 in the sample. The fundamental idea of the accelerator

technique is to take advantage of this very large number, and to estimate the ratio C^{14}/C^{12} in the sample by counting atoms rather than decays. Even with losses due to inefficiency in accelerating gas atoms into a beam (0.25 to 10^{-5}) the accelerator method allows one to use much smaller samples and to measure much older dates. Dates as old as 40 000 years have now been measured with only 0.015 gram of carbon (as compared with the 1 to 10 grams that are necessary for decay detection), and soon one may be able to date back 100 000 years.

Other cosmic-ray-produced radioisotopes³ accessible to the new method include H^3 , Be^{10} , Al^{26} , Si^{32} , Cl^{36} , Ar^{39} and Kr^{81} . The longer the half-life, the greater is the advantage of direct detection over decay detection. For example, in the case of Be^{10} (half-life of 1.5×10^6 yr) one decay per minute implies 10^{12} atoms of Be^{10} in the sample. Beryllium-10 may prove to be a particularly useful isotope in the study of sedimentary geology. It is produced by cosmic rays and some of it settles in the oceans and is trapped in the accumulating sediments. Although it has been detected in both sedimentary deposits and manganese nodules, its general usefulness has been severely limited by the very low decay rate. Potential applications of the other radioisotopes span many areas of research, from astrophysics to theology.

History of direct detection

Perceptive scientists have recognized for decades that direct detection is potentially more sensitive than decay detection, and that the problem was to invent a practical method for accomplishing it. The key to the solution was the use of high-energy beams. In this section I will try to reconstruct the history of the cross

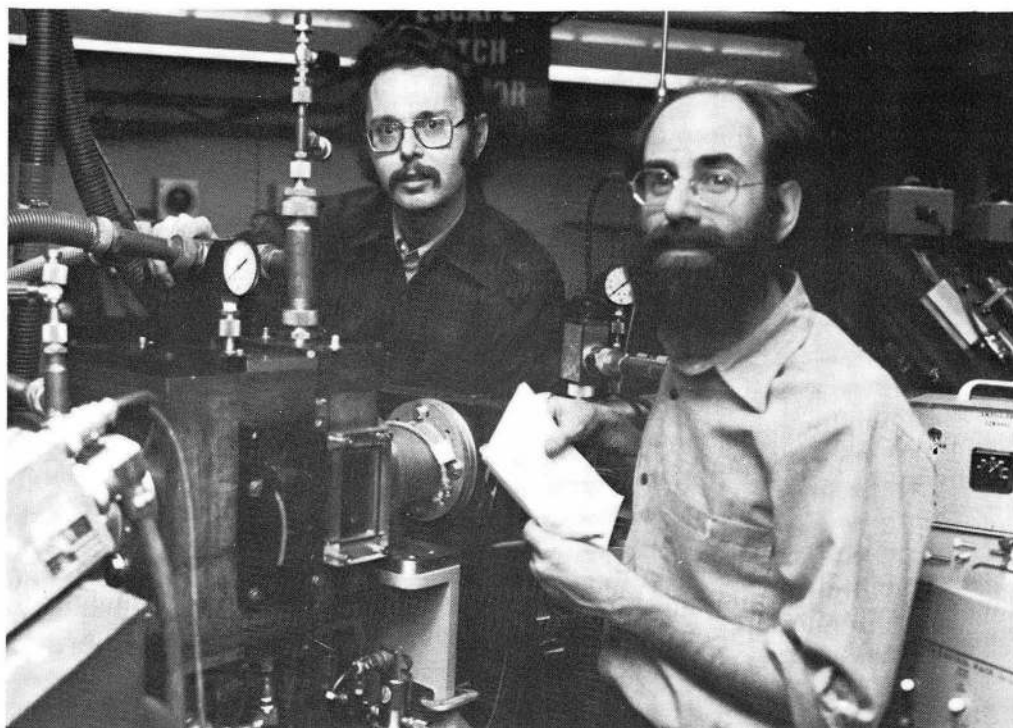
Richard A. Muller is an associate professor of physics at the University of California at Berkeley. He holds a joint appointment at the Lawrence Berkeley Laboratory and the Space Science Laboratory.

fertilization that brought nuclear physicists into the radioisotope-dating business. I have discussed this history with, and corresponded with, most of the scientists who played a major role in the solution of the problem, and although memories differ on some points and opinions differ on the relative importance of some events, I will do my best to relate the history leading directly to the use of high-energy beams for dating and to the successes of the past two and a half years.

One of the early sensitive attempts at direct detection was made by Michael Anbar and coworkers⁴ at SRI International, using a mass spectrometer specially designed for that purpose. Unfortunately, a mass spectrometer has difficulty distinguishing the radioactive ion from background ions with the same charge-to-mass ratio. For example, if $(C^{14})^{6+}$ ions are used, then there are inevitably $(N^{14})^{6+}$ ions in the beam in sufficient numbers to swamp the carbon. Anbar used $(C^{14}N^{15})^-$ molecular ions, and although his group solved many problems, they were ultimately limited by background (Si^{29})⁻ and lack of funds; they never achieved sufficient sensitivity to detect C^{14} at natural levels.

The clue to direct detection lay in the revival of the method of *high-energy* mass spectrometry by Luis W. Alvarez in a search for quarks of integral charge, which he proposed to our group in 1974. In our search we used the 88-inch cyclotron at Berkeley as a mass spectrometer. (The only prior use of a cyclotron for mass spectrometry, as far as I know, was reported by Alvarez and R. Cornog in 1939.⁵) Although the cyclotron is an extremely good mass spectrometer (resolution of 10^{-3} to 10^{-4} with negligible tails at beam currents of 10 microamp), the key feature was the high energy of the emerging beam, which allowed the atomic number Z of the individual atoms to be determined through ionization measurements. Thus potential "quarks" could be distinguished from background ions of higher charge on a particle-by-particle basis. About a year after the quark search was begun, Kenneth Purser⁶ of the General Ionex Corporation proposed and patented a system using a tandem Van de Graaff accelerator combined with a mass spectrometer for the detection of atmospheric chlorine and fluorine compounds.

The quark search concluded in 1976 with the result⁷ that the ratio of integrally charged quarks to other singly charged nuclei (hydrogen) was less than 3×10^{-19} in the mass range of 3 to 8 amu. I was struck by this remarkable sensitivity, much better than that of virtually any other method of trace-element analysis. In looking for other potential applications, I realized that the new technique could be used for radioisotope dating. (Although I was "unaware" of Anbar's



work at this time, I discovered later that my familiarity with the need for direct detection was due to a colleague who had read Anbar's proposal.) In a colloquium at the Lawrence Berkeley Laboratory in July 1976, I reported the first age obtained using the new idea: we had dated a sample of deuterium known to be about 25 years old (about one tritium mean-life) by measuring the ratio of tritium to deuterium. I also described the techniques that would be required for the direct detection of beryllium-10, carbon-14 and other natural radioisotopes. Attending the colloquium was Grant M. Raisbeck, who initiated a program using a cyclotron for direct Be^{10} detection upon his return to France. Edward Stephenson and Terry Mast joined the effort at Berkeley, and together we worked on the development of the beam line and particle detectors necessary for the efficient detection of Be^{10} and C^{14} .

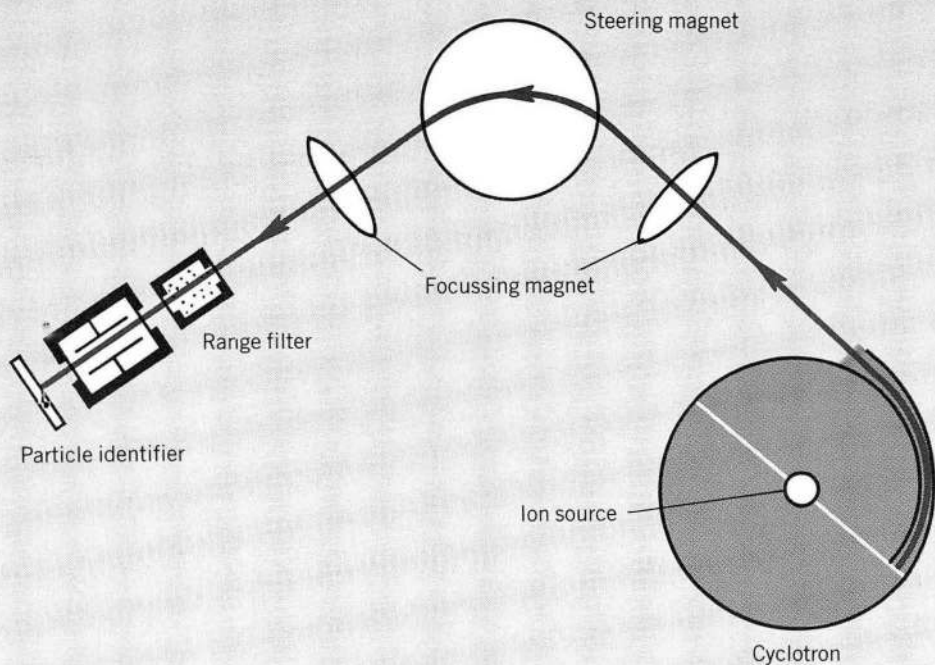
A key event in the next phase of experiments was an archeometry conference in Pennsylvania in March 1977. Among the speakers there familiar with our work was R.E.M. Hedges, who spoke about the plans at Oxford for direct detection of carbon-14 using a system that combines laser enrichment with a mass spectrometer. Hedges had spent several months in Berkeley collaborating with C. Bradley Moore on isotope enrichment; although he had visited our laboratory and read my preprint⁸ it was not yet obvious that the mass-spectrometer section of his plans should be replaced by an accelerator, especially since we had not yet obtained a date using carbon-14.

According to Roy Middleton of the University of Pennsylvania and Ted Litherland of the University of Toronto,

at this meeting and afterwards they and several others discussed informally the possible use of a tandem Van de Graaff accelerator for direct detection of carbon-14. They had already been thinking about direct detection for some time. Earle Nelson of Simon Fraser University heard of Middleton's thoughts from Gordon Brown. He immediately became interested in the application of accelerators to dating, and he says that he decided to pursue the technique after learning from my article⁸ how particle-identification techniques could be used to eliminate the expected backgrounds. Nelson, Ralph Korteling and William Stott made extremely sensitive measurements of C^{14} at natural levels, in their first experiment at the McMaster tandem.⁹

A month after the archeometry conference, Litherland met with Purser and Harry Gove, of Rochester, at the Washington meeting of The American Physical Society, and they planned an experiment at the Rochester tandem. (They were not aware of our paper¹⁰ at the same conference in which we described our first results with carbon-14, nor had they seen my article, which had appeared in *Science* several days earlier.) Others soon joined this Toronto-General Ionex-Rochester ("TIR") collaboration, and in their first experiment¹¹ they detected C^{14} with great sensitivity. Within a short time they were dating objects known to be as old as 40 000 years, using samples of 15 mg and less.¹²

The quick successes of the three groups inspired others to try, and in April 1978 a topical conference was held at Rochester¹³ at which six groups reported results. The TIR group described new measurements¹¹ with C^{14} and Cl^{36} ; our group in



Particle filters and identifiers of the Lawrence Berkeley cyclotron dating system (opposite page). Richard Muller (left) and Terry Mast are checking out the system. The large box in the center contains the xenon range filter, whose pressure is adjusted so that nitrogen-14 ions are absorbed while carbon-14 ions pass through to be counted. The filter reduces the nitrogen background by better than 10^{-14} . Figure 1

The dating system at the Lawrence Berkeley Laboratory's 88-inch cyclotron (this page). Positive ions are accelerated by the cyclotron, which also acts as a q/m filter. The range filter removes much of the background ioncurrent, and the remaining particles are identified by their energy-loss rate and total energy. The diagram is only schematic. Figure 2

Berkeley presented results¹⁴ with C^{14} , Be^{10} , and Cl^{36} . Nelson and his colleagues¹⁵ described their ongoing work in Canada; G. Raisbeck and his collaborators at Orsay and Grenoble reported¹⁶ measurements of Be^{10} with the Grenoble cyclotron. Hedges and collaborators¹⁷ at Oxford had incorporated an existing tandem in their system, and without isotope enrichment had detected C^{14} at natural levels; and Robert Andrews and his coworkers¹⁸ had detected natural C^{14} with the Chalk River tandem. Optimism was rampant at the conference, and most participants felt that the accelerator technique would soon be making important new measurements in areas inaccessible to the decay-dating method. Indeed, a few months later the TIR group¹⁹ had increased their sensitivity for Cl^{36} to the point where it was virtually assured to be an important new tool for dating old ground water, with an immediate application to nuclear-waste storage problems. And in July 1978 Raisbeck and his collaborators²⁰ reported measurements of Be^{10} in 1000 and 5000 year-old Antarctic ice, in samples that were unmeasurable by any other technique. They conclude their article with the observation that accelerator dating had moved "out of the phase of exploration and into that of exploitation."

Cyclotron techniques

The five basic stages involved in the cyclotron technique are

- ▶ ionization of the sample,
- ▶ acceleration of the isotope of interest,
- ▶ separation in the high-energy beam of the radioisotope from intense stable backgrounds,
- ▶ identification of the individual ions

through ionization and kinetic-energy measurements, and

▶ normalization with respect to a stable isotope.

No separate stage of mass spectrometry is needed; the acceleration itself serves that purpose: only those particles with the proper charge-to-mass ratio (q/m), given by the cyclotron resonance equation, are accelerated. The ionization source can be external to the cyclotron, or located at the center. The sample can be introduced as a gas (CO_2 or CH_4 for C^{14} dating) or as a solid (Be metal or BeO for Be^{10} dating) and sputtered.

The sharp resolution and absence of "tails" in the cyclotron resonance plot is dramatic; one can tune the frequency of the cyclotron 1% away from the resonant frequency for a 10 microamp C^{12} beam, and observe *no* accelerated particles in an hour of operation. This sharp resonance response is a consequence of the many (100 to 200) turns made in the cyclotron during acceleration. Thus when we accelerate C^{14} the only other isotope accelerated is N^{14} ; *no* high energy C^{12} , C^{13} , N^{15} or other isotopes appear in the beam.

If the current is low enough, one can send the beam directly into a set of "particle-identification" detectors, which measure the ionization rate and kinetic energy of each ion; these two quantities serve to determine the atomic number Z and the atomic weight A of the ion. (The ionization rate is determined by the nuclear charge Z rather than by the initial charge q of the ion, because the ion is stripped of its remaining electrons soon after entering the particle detector.) In most cases the beam current from the stable background ion is too intense to allow this, and some preliminary separa-

tion is required. In the experiments done so far with H^3 , Be^{10} , C^{14} and Cl^{36} this separation has been accomplished by the range-filter method described in reference 7, although other approaches are possible. (See figures 1 and 2).

The range filter is based on the observation that the range of an ion in matter is approximately proportional to $1/Z^2$ where Z is the ion's atomic number. Thus the range of H^3 is approximately four times that of the background B^{10} ; and the range of C^{14} is approximately 1.36 that of the background N^{14} . For H^3 and Be^3 , a simple solid foil is sufficient to stop the background ions, and only the radioisotopes emerge to be counted by silicon detectors or gas ionization chambers (see figure 2). For C^{14} the background current of N^{14} was so large (1–10 nanoamp) and the range difference so small that the necessary separation of 10^6 was not obtained with a simple foil. Irregularities in the solid were responsible for sufficient straggling that we could not obtain a date, although we had sufficient sensitivity to measure C^{14} at approximately natural levels.¹⁰

We finally used gas for the stopping material to reduce the straggling from irregularities.^{14,21} Separating the gas from the cyclotron vacuum required windows strong enough to support the gas pressure yet thin enough to contribute little to straggling. The solution was to use 1/3-micron gold foil for the window material. It holds an atmosphere of pressure when supported with a set of grids (see figures 3 and 4) fine enough that the foil never spanned more than $1/3$ mm. The nuclear charge-exchange reaction $N^{14}(Z, Z+1)C^{14}$, could have produced a contaminating signal, but all the materials

inserted into the beam (xenon, gold, tungsten) have a high nuclear charge and the beam energy was kept low enough (≤ 60 MeV) that the Coulomb barrier suppressed the reaction. The filter totally eliminated the nitrogen; only carbon-14 emerged from the xenon gas. We estimate the suppression to be better than 10^{14} . In several hours of coincident detection, not a single nitrogen ion penetrated the xenon cell to be counted as a coincidence in our particle-identification detectors.

To determine the age of the sample, the detection rate of the radioisotope must be normalized with respect to a stable isotope. There are several ways to accomplish this:

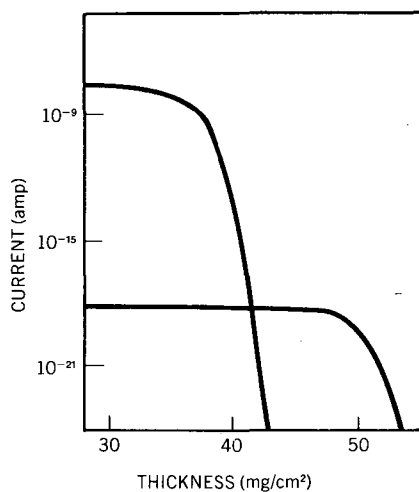
- ▶ by switching the cyclotron frequency so that the stable isotope is accelerated, and then measuring that isotope in the same beam line (although the sensitive silicon detectors must be replaced with Faraday cups capable of handling the microampere beam currents);

- ▶ by switching the sample with unknown age to one of known age, and measuring the ratio of radioisotopes in the two samples (the ratio of radioisotope to stable isotope is already known in the reference sample);

- ▶ by monitoring the beam currents exiting from the ion source. For example, one could magnetically separate the C^{12} from C^{14} prior to acceleration, and use the current of this isotope for normalization (provided that the acceleration efficiency is known). Possible isotope fractionation effects in the ion source may affect these experiments and one needs to account for them to obtain the fullest accuracy.

For the heavier isotopes the cyclotron technique is more difficult to implement, both because one cannot obtain high beam currents with present cyclotrons, and because the fractional range difference between neighboring elements decreases as $1/Z$. In the case of Cl^{36} there is an additional problem, because there is a stable isotope with lower Z (S^{36}), which is not removed by the range filter. However, we found that in our measurements the background S^{36} in the sample was low enough that the beam emerging from the range cell could be sent directly into the particle identifiers, which clearly distinguished the two elements.

By switching rapidly from an "unknown" to a reference sample, we have made carbon-14 measurements on several samples with ages up to 10 000 years. The real proof, however, is to measure a "blind" date, that is, one for which one does not know the answer beforehand. We have been the only group to try this so far; perhaps we were incautious; although we obtained the correct answer¹⁴ in one sample previously dated by Rainer Berger of UCLA, we also had a failure,²² which we believe was due to a systematic shift in C^{14} background level as we switched from the unknown to a reference sample.



Transmission through the xenon gas range filter, as a function of the mass of xenon in the beam. We plot the typical background nitrogen-14 current (black) along with the carbon-14 current (color) for a modern sample. Figure 3

The carbon-14 "background" comes from the cyclotron components themselves. The cyclotron dee is protected from the intense internal beam by graphite "beam scrapers." Graphite was chosen in the original cyclotron design because it remains relatively inactive when exposed to intense beams; virtually the only long-lived radioactivity produced on graphite is C^{14} , and of course nobody had anticipated use of the cyclotron for radiocarbon dating. The carbon-14 from the graphite has sufficient vapor pressure to contribute a small but annoying current of background C^{14} to our runs; no corresponding backgrounds are observed for our H^3 , Be^{10} , or Cl^{36} measurements. This background is presently limiting the sensitivity of our C^{14} measurements, and we have deferred the measurement of valuable and irreplaceable samples until it has been eliminated. We plan to do this by pre-accelerating the sample ions with an external ion source which is kept free of contaminants. Such an ion source is now under construction, and will be installed on the 88-inch cyclotron in a few months.

The 88-inch cyclotron at Berkeley is much larger than required for dating purposes; in fact we sometimes operate at such low energy that it is difficult to adjust the magnetic field to the required low level, due to hysteresis in the magnet iron. But the flexibility of this cyclotron has been very useful in exploring the range of techniques and isotopes accessible to accelerator dating. In spite of its large size, the cost of obtaining a date at this cyclotron is comparable to that of the decay method; although the machine is expensive to operate, the date can be obtained in less than an hour of running. A rough estimate of the cost of this hour can be calculated by taking the total operating budget of the cyclotron (scientists and engineers included) and dividing by the

number of hours devoted to experiments; the result is about \$250 per hour, or \$250 per date. There are numerous cyclotrons around the world that could be used for radioisotope dating; however, one can buy a new cyclotron of the minimum required size for about \$500 000. The cost is comparable for tandem Van de Graaff accelerators. Other types of heavy-ion accelerators could also be adapted for dating.

Tandem techniques

Many of the techniques used at the tandem accelerators are similar to those used at cyclotrons, and the general discussion given for the cyclotron need not be repeated. Negative ions are accelerated from ground to positive high voltage, stripped of orbital electrons, and then accelerated as they move from the positive potential back to ground. Because of the high charge of the stripped ion, the energy of the particle in MeV can be several times larger than the value of the high voltage measured in millions of volts. Since the tandem itself provides no mass selection, a separate mass spectrometer must be employed. Figure 5 shows the Toronto-General Ionex-Rochester system, which uses one stage of charge-to-mass (q/m) selection before acceleration, and three afterwards. Each "mass spectrometer" is simply a bending magnet with collimation slits. In the TIR system a final stripping foil changes the charge state from $4+$ to $6+$; molecular ions that survive to this point are broken up in the foil and eliminated in the final stage of q/m selection. The final beam enters a set of detectors that identify the nuclear charge Z and the atomic mass A of the ions through ionization and total energy measurements.

Several elements do not form stable negative ions; so the use of a negative ion source has important consequences for dating. In particular, because the negative nitrogen-14 ion is not stable, the primary stable background ion for carbon-14 dating is eliminated right at the source. This suppression of the nitrogen-14 background was a driving consideration in the plans of the tandem groups; the same advantage can be gained by using negative ions in a cyclotron. Molecular backgrounds such as $(C^{12}H_2)^-$ are broken up when they pass through the stripping foils, and then suppressed by the q/m mass spectrometers. Particle identification is still necessary, because some stable background ions such as C^{12} , C^{13} , and $C^{12}H_2$ do leak through the mass spectrometers. It is the high energy of the beam that allows the use of the particle-identification detectors and the stripping foils.

To normalize the count rate to that of a stable isotope, the magnets can be switched to select that isotope. However, it is also possible to include a wide-enough selection in the mass spectrometer so that

one can measure the stable and unstable isotopes simultaneously in different detectors, as Nelson has proposed. Dedicated tandems for radioisotope dating will certainly do this.

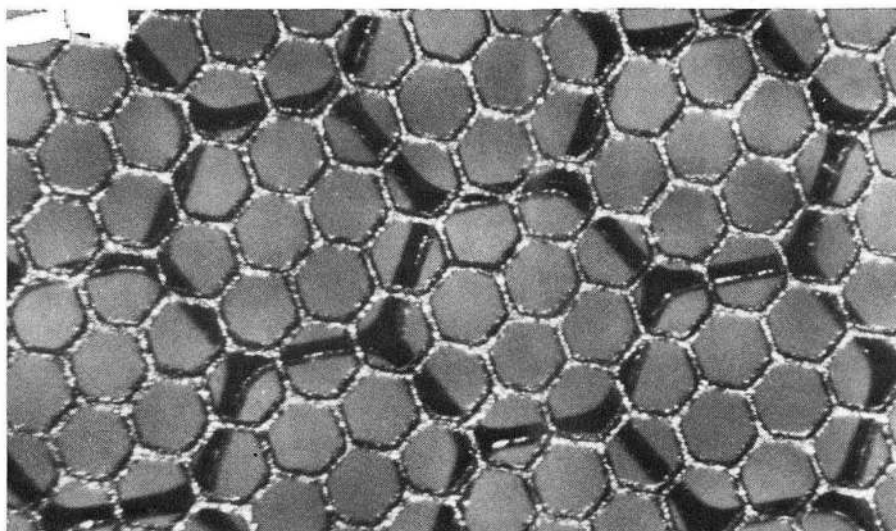
The table below shows a comparison of the most sensitive carbon-14 measurements reported to date by the TIR group¹², compared with measurements made using decay dating by the US Geological Survey.

The most impressive feature of the measurements is that the sample size was only 15 mg, except in the Mt Hood sample for which it was 3.5 mg. We show a typical output plot from their particle-identification detectors in figure 6; note the very clean separation between the C¹⁴ and other isotopes. It is premature to be concerned about the relatively large errors in the measurements. As systems are developed, stabilized and improved, the errors are certainly going to be reduced. We can estimate the present "maximum detectable age" for the Rochester tandem to be about 50 000 years: this is the measured age for the graphite blank known to contain no C¹⁴. The background C¹⁴ counts are believed to come from contaminant C¹⁴ in the tandem, just as the background C¹⁴ in our cyclotron comes from radioactive graphite in the cyclotron vacuum; it should be absent in a new machine dedicated to radioisotope dating. It may also be possible to eliminate the contamination in existing tandems with a specially designed ion source, the same approach we are pursuing at Berkeley.

Applications

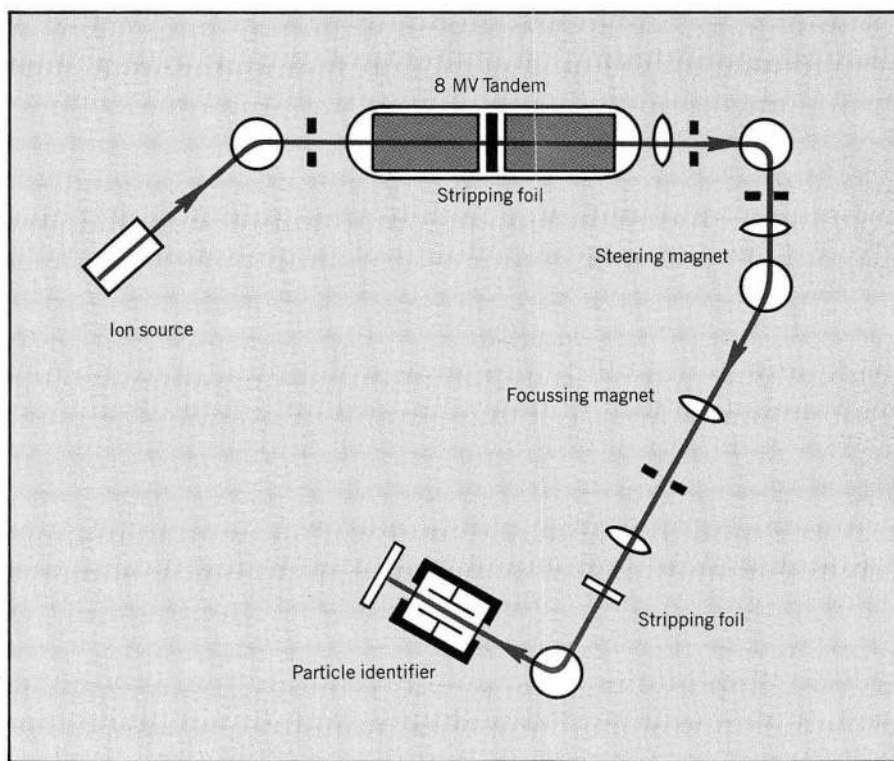
Many applications have been suggested for accelerator dating, especially for those radioisotopes that have already proven valuable with decay dating. An extensive discussion appears in the proceedings of the Rochester conference; I will draw heavily from this without individual attribution of the ideas.²³

For carbon-14 dating, it appears likely that the most important immediate application is to samples that are too small to have been dated before. In this category I include invaluable artifacts for which only a small bit can be sacrificed. Examples include manuscripts, bone fragments, cave paintings and the Shroud of Turin. Just as important is the ability to select, carefully, the carbon in the sample that is used, so that those carbon-bearing chemicals which exchange carbon with the surroundings can be avoided. Thus, for example, one can use only the collagen in bone, or perhaps only specific amino acids. C. V. Haynes gives the example that with the selection of certain organic compounds an entire mammoth skeleton might be required for decay dating; for the direct method a toe bone would suffice. One can date artifacts by selecting entrapped plant fragments, seeds, or insect remains. The



Microphotograph of the tungsten grid used to support the 1/3-micron-thick gold foil. The larger grid supports the finer grid, which supports the foil. The hexagons of the fine grid are 1/3 mm in diameter. The combination can support a pressure difference of greater than one atmosphere between the filter chamber and the cyclotron vacuum.

Figure 4



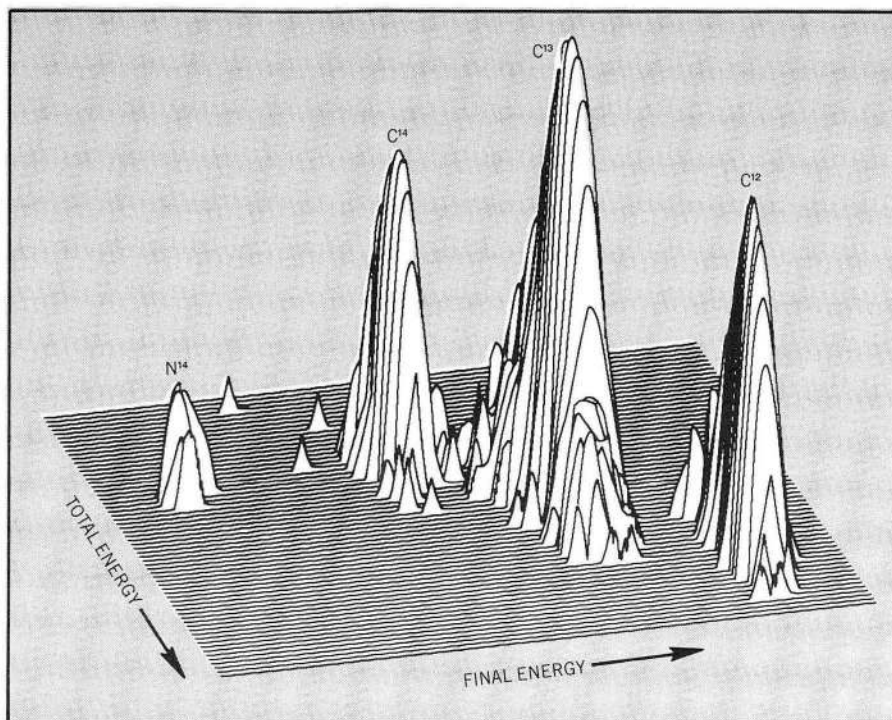
The TIR dating system at the Rochester tandem Van de Graaff accelerator. The sketch is not to scale and shows only the basic components. (Adapted from reference 11.)

Figure 5

Accelerator dates

Carbon Sample	Running time (min)	Accelerator age (yrs)	Decay date age (yrs)
Mt Hood	90	220 ± 300*	220 ± 150
Mt Shasta	180	5700 ± 400	4590 ± 250
Lake Agassiz	90	8800 ± 600	9150 ± 300
Hillsdale	400	41000 ± 1100	39500 ± 1000
Graphite	65	48000 ± 1300	∞

Based on reference 11
* assumed rate (used for calibration)



Measurements made in the particle identifier of the TIR system, for their 4590 ± 250 year-old sample from Mt Shasta. The logarithm of the heavy-ion counts is shown as a function of the total heavy-ion energy and the energy deposited in the final ionization detector. The clean separation of the carbon-14 signal from the various backgrounds is evident. The nitrogen-14 peak is from the $N^{14}H^-$ molecule. (From reference 12.)

Figure 6

small samples used for racemization dating can be cross-checked by comparison with carbon-14 dates. Glacial layers have been dated by trapped CO_2 ; in the future only a few liters of ice, rather than several tons, will yield a useful date. The ability to date ice layers can have important impact on our knowledge of the climate over the past 100 000 years, because the oxygen-18 concentration in these layers is related to the global temperature at the time they were deposited. The potential of the new C^{14} techniques to date beyond the present 40 000 year limit may allow the study of the climate in the period immediately preceding the most recent glaciation, which began about 80 000 years ago.

The C^{14} fluctuations in tree rings of known age (the "deVries effect") allow us to study climates over the past 8000 years. Presently it takes 10–20 adjacent tree rings to obtain enough material to measure the C^{14} content; with accelerators a single ring should be sufficient, allowing us to study the climate year by year.

Measurement of small samples will also simplify studies that make use of the sudden doubling of the atmospheric C^{14} content in the 1950's due to atmospheric thermonuclear bomb testing. (Such studies have been a primary concern to an ongoing program of small-sample counting at the National Bureau of Standards.) Particularly interesting is the origin of atmospheric gases and aerosols, including methane and CO_2 . If these originate from the burning of ancient hydrocarbons

then the C^{14} content will be low, whereas, if recent plants are the source, the C^{14} content will follow (with a delay) the thermonuclear increase.

Many other radioisotopes are produced by cosmic rays, but their detailed geochemistry is not yet worked out. Of these isotopes, J. R. Arnold suggests that Be^{10} holds the most interest, partially because its half-life of 1.5 million years matches the time scale of the evolution of Man and of the ice ages. Be^{10} has been detected in sea-floor sediment and manganese nodules. Measurements of Be^{10} in individual layers of manganese nodules should elucidate their history and help determine whether they have always sat on the sea floor or have been periodically buried. Since the Be^{10} concentration depends on not only the age but also the sedimentation rate, it is necessary to have an additional measurement to untangle these. One possibility is "double dating"^{3,7} with another radioisotope such as Al^{26} . According to J. C. Higdon and R. E. Lingenfelter²⁴ an anomaly in the ratio of Be^{10} to Al^{26} suggests the detonation of a nearby supernova in the recent past; it will be interesting to study the effect in more detail.

Longer-lived radioisotopes such as Kr^{81} (2×10^5 yr) and I^{129} (1.7×10^7 yr) can be used to study the constancy of the cosmic rays, provided they are detected in materials of known age, such as materials that have been potassium-argon dated. Iodine-129 is particularly interesting for this measurement, because its half-life is

long compared to the estimated trapping time of cosmic rays in the Milky Way galaxy. Other radioisotopes from deeply buried samples (such as Kr^{81} or Pb^{205}) may someday be measurable with sufficient sensitivity to study neutrino interactions.

One of the first "practical" applications of accelerator dating may be for hydrological tracing. A 1977 workshop on the dating of old ground water²⁵ concluded that the development of a chlorine-26 (3×10^5 yr) method of dating and the continued development of carbon-14 dating present the most promise for very old ground water. This conclusion was based largely on the expected geochemistry of these elements, and particularly on the fact that dissolved chlorine is not expected to exchange rapidly with surrounding soil. The most immediate application of chlorine-36 dating is for the determination of the hydrological isolation of potential storage sites for nuclear wastes. Carbon-14 dating has already proved to be very important in studies of the circulation times of deep ocean water. Other radioisotopes however may be better matched to the overall circulation time of 10^3 years; these include Si^{32} (650 yr) and Ar^{39} (269 yr).

Limitations

After such an optimistic discussion of the glories of future accelerator dating, it is appropriate to recall the limitations of the technique. For the immediate future, the following general rule will undoubtedly apply:

Any object that can be dated using the standard decay technique *should* be dated in that way. Any isotope that can be detected using an ordinary mass spectrometer *should* be detected with that method.

"Standard" radioisotope dating and mass spectrometry are highly developed arts; accelerator dating is a new technique, and we are only about to learn the problems associated with it. The main applications of accelerator dating in the next few years will be to obtain approximate answers in areas where approximate answers are adequate and where no answer is obtainable otherwise.

Because mass spectrometry can detect trace elements at concentrations of 10^{-6} to 10^{-9} , it is unlikely that accelerators will replace them for stable isotopes. Virtually all elements appear at this level as traces in virtually all other substances. Except for exotic molecules such as $C^{13}D_4$ (see references 8 and 26), the only isotopes at sufficiently low level to require an accelerator for direct detection are the radioactive ones.

The ultimate usefulness of several of the radioisotopes, including Be^{10} and Cl^{36} , will depend on their geochemistry, and presently this is poorly known. Questions to be answered include: What path does the radioisotope take from the upper at-

mosphere to the Earth's surface? In what chemical and physical forms does it arrive? Is it ingested by living organisms? What is the appropriate stable element to use for normalization? How uniformly is the radioisotope distributed over the surface of the Earth? Fortunately, the same technique that makes these questions interesting also makes them experimentally tractable. Much of the work to be done with accelerators in the next few years will be devoted to answering these questions:

One limitation to dating samples that are many half-lives old is the background of spurious isotopes introduced by recent contamination of the old material. For a sample t half-lives old, contamination by modern material in an amount 2^{-t} will cause a systematic error in the age determination by one half-life. For example, a contamination of a carbon sample 100 thousand years old by $2^{-(100/5.73)} = 6$ parts per million of modern carbon will cause the calculated age to be underestimated by 5730 years. It is too early to know whether one can in practice maintain the extreme level of purity required to measure such great ages. It is equally important to determine whether at the low levels encountered for the older dates, there might be a process other than cosmic radiation (such as radioactivity in the Earth) which can produce the radioisotope even after the sample "died."

Accelerator dating is still a young field, and it is, as yet, impossible to predict what the most important applications will be. I suspect we also don't yet know which radioisotopes and which experimental techniques will prove the most fruitful. As a physicist, what I have enjoyed most about accelerator dating has been talking to scientists in many other fields and learning about their unsolved problems. I hope that my enjoyment in the future will come from helping them solve some of these problems.

* * *

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References

1. W. F. Libby, Phys. Rev. **69**, 671 (1946); E. C. Anderson, W. F. Libby. S. Weinhouse, A. F. Reid, A. D. Kurshenbaum, A. V. Groose, Phys. Rev. **72**, 931 (1947). See also W. F. Libby, *Radiocarbon Dating*, U. of Chicago Press, Chicago (1955).
2. For a recent review see P. E. Damon, J. C. Lerman, A. Long, Ann. Rev. Earth and Planet. Sci. **6**, 457 (1978).
3. Reviews of cosmogenic nuclides can be found in *Handbuch der Physik* **46/2**, Springer, Berlin (1967): D. Lal, B. Peters, page 551; M. Honda, J. R. Arnold, page 613.
4. M. Anbar, Proceedings of the 22nd Conference on Mass Spectrometry, (Philadelphia Pa., 1974).
5. L. W. Alvarez, R. Cornog, Phys. Rev. **56**, 379 (1939).
6. K. H. Purser, US Patent 4037100, filed March 1976, issued July 1977.
7. R. A. Muller, L. W. Alvarez, W. R. Holley, E. J. Stephenson, Lawrence Berkeley Laboratory Report LBL-5399, 1976; Science **196**, 521 (1977).
8. R. A. Muller, LBL-5510 (1976); Science **196**, 489 (1977). Most of the ideas appeared in an internal memo, Physics Note 319 (July 1976).
9. D. E. Nelson, R. G. Korteling, W. R. Stott, Science **198**, 507 (1977).
10. E. J. Stephenson, L. W. Alvarez, D. J. Clark, R. A. Gough, W. R. Holley, A. Jain, R. A. Muller, Bull. Am. Phys. Soc. **22**, 579 (1977).
11. K. H. Purser, R. B. Liebert, A. E. Litherland, R. P. Beukens, H. E. Gove, C. L. Bennett, M. R. Clover, W. E. Sondheim, 2nd Int. Conf. Electrostatic Accel. Tech., Strasbourg, France, 1487 (1977); C. L. Bennett, R. P. Beukens, M. R. Clover, H. E. Gove, R. B. Liebert, A. E. Litherland, K. H. Purser, W. E. Sondheim, Science **198**, 508 (1977).
12. C. L. Bennett, R. P. Beukens, M. R. Clover, D. Elmore, H. E. Gove, L. Kilius, A. E. Litherland, K. H. Purser, Science **201**, 346 (1978); see also ref. 13, page 70.
13. Proceedings of the First Conference on Radiocarbon Dating with Accelerators, (H. E. Gove, ed.), University of Rochester, 20, 21 April 1978.
14. R. A. Muller, E. J. Stephenson, T. S. Mast, Science **201**, 347 (1978); see also ref. 13, pages 33-37, 239-244, 197-195, and LBL-7585.
15. D. E. Nelson, R. G. Korteling, D. G. Burke, J. W. McKay, W. R. Stott, ref. 13, page 47.
16. G. M. Raisbeck, F. Yiou, M. Fruneau, M. Lieuvain, J. M. Loiseau, ref. 13, page 38.
17. E. T. Hall, R. E. M. Hedges, N. R. White, H. R. McK. Hyder, D. Sinclair, ref. 13, page 257.
18. H. R. Andrews, G. C. Ball, R. M. Brown, N. Burn, W. G. Davies, Y. Imahori, J. C. D. Milton, ref. 13, page 114.
19. D. Elmore, B. R. Fulton, M. R. Clover, J. R. Marsden, H. E. Gove, H. Naylor, K. H. Purser, L. R. Kilius, R. P. Beukens, A. E. Litherland, to be published in Nature.
20. G. M. Raisbeck, R. Yiou, M. Fruneau, J. M. Loiseau, Science **202**, 215 (1978); G. M. Raisbeck, F. Yiou, M. Fruneau, M. Lieuvain, J. M. Loiseau, Laboratoire Rene Bernas preprint LRB-78-10 (Orsay, to be published) 1978.
21. E. J. Stephenson, T. S. Mast, R. A. Muller, LBL-7579 (June 1978), to be published in Nucl. Inst. Methods.
22. R. A. Muller, ref. 13, page 34.
23. The contributors to the applications discussion in ref. 13 include C. V. Haynes, L. A. Currie, J. R. Arnold, W. S. Broecker and T. Peng.
24. J. C. Higdon, R. E. Lingenfelter, Nature **246**, 403 (1973).
25. Workshop on Dating Old Ground Water (S. N. Davis, ed.) U. of Arizona, Tucson (1978).
26. G. Cowan, D. Ott, A. Turkevich, L. Machta, G. Ferber, N. Daly, Science **191**, 1048 (1974). □

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