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Radioisotope Dating with a Cyclotron

The sensitivity of radioisotope dating is improved by counting atoms rather than decays.

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The sensitivity of radioisotope dating is frequently limited by the need to destroy a relatively large sample of what may be irreplaceable material in order to yield a low count rate of difficult to detect radiation. The dating problem is seen in a new perspective when one realizes that for each decay per minute, there may be 10^9 to 10^{12} or more radioactive atoms in the sample. Waiting around for the decay of these atoms is clearly an inefficient way to count them. If a technique could be found for detecting them with even a modest efficiency ($>10^{-6}$), the size of the sample could be reduced and the age that can be measured could be pushed back by many half-lives.

Although the cyclotron has been used primarily as a source of energetic particles, it can also be used as an extremely sensitive mass spectrometer: only particles in the ion source with the proper charge-to-mass ratio (given by the cyclotron resonance equation) will be accelerated. The cyclotron was first used in this mode by Alvarez and Cornog (*1*) in their discovery of the true nuclear natures of ^{3}He and tritium. More recently, the 88-inch sector-focused cyclotron at Berkeley was used as a mass spectrometer by our group in a search for integrally charged quarks in terrestrial material (*2*). Although the ion source in the cyclotron was not specifically designed for high efficiency, the value of 3×10^{-5} obtained for typical beams is sufficiently high to make the cyclotron an extremely attractive tool for dating purposes.

Radioisotope dating with the cyclotron is a special example of trace element analysis. In our search for quarks (which was, in effect, a search for new isotopes of hydrogen), a few seconds of counting were sufficient to detect isotopes present in hydrogen or deuterium at the 10^{-14} level. With a few minutes of counting, a sensitivity of 10^{-16} was obtained. Although the sensitivity that can be reached varies from element to element, the latter number is a useful figure of merit: any radioisotopes present at the 10^{-16} level or more might be used to determine the age of the sample.

Other approaches to radioisotope dating by trace element analysis might be possible. It is conceivable that one could detect the radioisotopes by resonance fluorescence, using a laser to detect an isotope-shifted atomic line. Or it might be possible to use a linear accelerator in place of a cyclotron. Unfortunately, an ordinary mass spectrometer (*3*) cannot be used because of the difficulty of distinguishing the radioisotopes from stable ions with similar charge-to-mass ratios. For example, radioactive $^{14}C^{6+}$ could not be distinguished from stable $^{14}N^{6+}$, and radioactive $^{10}Be^{5+}$ could not be distinguished from stable $^{10}B^{5+}$. The stable contaminants are inevitably present in much greater numbers than are the radioisotopes. The cyclotron makes the separation possible by accelerating the particles to a high energy (several million electron volts, rather than the several thousand obtained with an ordinary mass spectrometer), at which it is possible to distinguish the chemically different atoms (such as ^{14}C and ^{14}N) by measuring their different ionization rates dE/dx. The only serious limitation to the technique comes from the requirements that the count rate be low enough to avoid saturation and radiation damage effects in the dE/dx detector, and that the sample be small enough to process through the cyclotron in a reasonable time. As a high-energy mass spectrometer, the cyclotron is characterized both by high mass (m) resolution ($\Delta m/m < 3 \times 10^{-4}$) and by extremely low background rates (< 1 count per hour during the quark search).

For radioisotope dating, the cyclotron is tuned to accelerate the isotope of interest and the sample is introduced into the ion source, preferably as a gas. The accelerated ions with the proper signature in the dE/dx detector are counted. Coincidence with a total energy (E) detector which follows the dE/dx detector helps keep backgrounds low. During the run, the cyclotron frequency is switched periodically to that of a stable isotope, for normalization purposes. For tritium dating, for example, one switches between ^{3}H and ^{2}H, and the quantity measured is their ratio. During switching to the abundant stable isotope, it is necessary to replace the sensitive particle detectors with a Faraday cup in order to handle the large current. Most of the running time is spent on the radioisotope.

The potential applications of the cyclotron as a high-energy mass spectrometer are many, in trace-element analysis as well as in radioisotope dating. The technique is most powerful for elements at the low end of the periodic table, for which relatively large beam currents can be obtained. For radioisotope dating, the greatest gains over radioactive counting techniques come for the longer-lived species, which have lower decay rates. For example, we will show that by using a cyclotron for ^{10}Be dating one can date back more than 20 half-lives rather than the

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one or two that are now typical. In this realm we have a new advantage: reduction of the tyranny of Poisson statistics. Fluctuations in the number of detected atoms can be a severe limitation when one is going back only one half-life: a factor of 2 error in the count rate results in a factor of 2 error in the age. However, for a sample 20 half-lives old, the same factor of 2 error results in a misestimation of the age by only 5 percent. In both cases the absolute error in the age measurement was the same: one half-life.

It is easiest to demonstrate the potential advantages of the cyclotron by developing several examples in detail. The radioactive isotopes that lend themselves most readily to cyclotron dating are ^{14}C, ^{10}Be, and ^{3}H, although in principle the cyclotron could be used to detect heavier isotopes such as ^{26}Al, ^{53}Mn, ^{81}Kr, and even ^{205}Pb. As of this writing, the only isotope that we have used to obtain a date has been ^{3}H; this work is described later in this article. An experimental program is now under way at Berkeley to date samples by accelerating ^{14}C and ^{10}Be and to improve the accuracy of our ^{3}H dating technique. Although any cyclotron might be used for dating, we assume in our examples the properties of the 88-inch sector-focused cyclotron at Berkeley, which produces particles with energies of many millions of electron volts and can be switched from the resonant state for one ion to that for another in minutes. The beam intensities we assume for each ion species are those that have already been achieved on this cyclotron.

Radiocarbon Dating

The technique of ^{14}C dating developed by Libby and co-workers (*4*) depends on the fact that cosmic-ray neutrons are continuously producing ^{14}C in the atmosphere through the reaction $^{14}N\ (n, p)^{14}C$ (*5*). Approximately 13.5 atoms of ^{14}C are produced each minute for each gram of carbon on the surface of the earth; thus each gram of carbon in equilibrium with the atmosphere will have 13.5 decays per minute. The half-life of ^{14}C is 5730 ± 40 years (*6*). A sample containing m grams of carbon, which was taken out of equilibrium with the atmosphere t years ago, will have a decay rate (per minute) of

$$\frac{dn_0}{dt} = 13.5\ m\ 2^{-t/5730} = 13.5\ m\ e^{-t/8270}$$

where n_0 is the number of ^{14}C atoms in the sample. Because of background counts, typically 10,000 disintegrations must be observed for 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.

Converting this equation to decays per year and integrating, we calculate the number of ^{14}C atoms in the sample

$$n_0 = 5.8 \times 10^{10}\ m\ e^{-t/8270}$$

Thus a fresh gram of carbon that contains 5×10^{22} atoms of ^{12}C will contain 5.8×10^{10} atoms of ^{14}C. The ratio as a function of time will be

$$\frac{^{14}C}{^{12}C} = 1.2 \times 10^{-12}\ e^{-t/8270}$$

A 20-microampere beam of $^{12}C^{2+}$ ions would require 2.5 milligrams of carbon per minute, assuming an efficiency of 3×10^{-5} (typical for carbon beams). The number of detected ^{14}C atoms would be

$$n = 1.7 \times 10^{6}\ m\ e^{-t/8270} \qquad (1)$$

This equation is plotted in Fig. 1. For new carbon, 440 atoms of ^{14}C would be detected per minute. For one count per minute, the sample age would be $8270 \cdot \ln(4400) = 69{,}000$ years. If we see no ^{14}C atoms in 10 minutes of counting, it is easy to show that the age of the sample $t \geq 79{,}000$ years (95 percent confidence level). No counts in 1 hour of counting (requiring 150 mg of carbon) would imply $t \geq 94{,}000$ years. For the older samples, care would have to be taken to avoid contamination with young carbon. For a sample α mean lives old, a contamination fraction of $e^{-\alpha}$ would double the count rate and introduce a systematic error in the measured age of one half-life.

As mentioned in the introduction, for samples many mean lives old the fractional error in the measured age is relatively insensitive to fluctuations in the number of detected atoms. Even "one count" should not be dismissed as too low a number to yield a useful age determination: we show in the next section that the *observation of one atom determines the age of the sample to ± one mean life*, irrespective of the age of the sample. For example, the observation of one ^{14}C atom in a 150-mg sample yields an age measurement of $t = 103{,}000 \pm 8{,}000$ years. In Fig. 1 we have plotted the 1–standard deviation (S.D.) statistical errors associated with the detection of 1, 10, 100, and 1000 atoms.

If we accelerate carbon ions, the major source of background is going to be ^{14}N from residual nitrogen in the sample and in the ion source of the cyclotron. At the 88-inch cyclotron at Berkeley, the residual nitrogen beam from the latter source amounts to approximately 10 nanoamperes (3×10^{10} ion/sec for a beam of $^{14}N^{2+}$). This rate would have to be reduced by a factor of at least 10^6 in order to introduce such a beam safely into dE/dx counters.

A brute-force way to reduce the nitrogen beam would be to introduce stripping foils, followed by magnetic separation. Unfortunately, at cyclotron energies (several million electron volts per nucleon) the emerging nitrogen atoms will not be fully stripped; we can expect about 10 percent of them to come out of the foil in the $Z = 6$ charge state (*7*) and to be indistinguishable from $^{14}C^{6+}$. Nevertheless, six stages of separation (perhaps all accomplished in the same magnet) could do the job.

A much simpler way to reduce the nitrogen beam is to send it into a foil sufficiently thick to stop ^{14}N but not ^{14}C. At 56 Mev (4 Mev/A, where A is the atomic mass number) the ranges in a gold foil are 17 micrometers for ^{14}N and 22 μm for ^{14}C (*8*). Straggling should be approximately 1 to 2 percent for the ^{14}N beam, so a foil 18 μm thick should be sufficient to stop the nitrogen ions. The emerging ^{14}C atoms have a range in silicon of about 10 μm, so a very thin dE/dx detector has to be used in order to pass the ions into a total E detector. Spurious production of ^{14}C through the reaction

$$^{14}N + Au \rightarrow {}^{14}C + Hg$$

is avoided by keeping the beam energy well below 62 Mev, the estimated Coulomb barrier energy for N and Au.

Another possible way to eliminate the ^{14}N background is to operate away from the region of 14 atomic mass units (amu), by accelerating molecular ions such as $^{14}CH_4^+$ or $^{14}CD_4^+$. The most serious potential background ion is NH_4^+, and it is unlikely that this ion will be present at a high enough level to cause trouble. (Both ^{18}O and H_2O differ in mass from $^{14}CH_4$ by a few tenths of a percent, and they should be resolved by the cyclotron.) But a CH_4^+ beam is not trouble-free. The low value of the charge-to-mass ratio requires operation of the Berkeley cyclotron in the fifth harmonic, which results in a relatively low energy beam (0.4 Mev/A) with which particle identification is difficult. And we may not be able to achieve more than a few hundred nanoamperes of beam current, so that the maximum detectable age would be several mean lives shorter than that obtainable with a 20-μa C^{2+} beam.

Yet another way to reduce the ^{14}N

background is to eliminate the nitrogen from the ion source of the cyclotron. At present this does not appear feasible for the *internal* ion source at Berkeley; however one could construct an *external* ion source specifically designed to have low nitrogen contamination. Although constructing such a source is undoubtedly the most expensive way to eliminate ^{14}N, it may be worth it if ^{14}C dating is to be done regularly.

Thus many techniques are available to separate ^{14}N from ^{14}C. The easiest and perhaps the best makes use of their range difference in a gold foil. We have some experience with this technique from our tritium-dating experiment, in which we used an aluminum foil to stop ^{3}He while passing ^{3}H. But a wealth of possible separation techniques exist, and we cannot be certain which will be the best until further experimental work is done.

In summary, it appears likely that ^{14}C dating can be accomplished by using the cyclotron, with a potential of reaching back 40,000 to 100,000 years, with carbon samples 1 to 100 mg in mass.

Accuracy of the Age Determination

There are well-documented differences between the ages of materials determined by dating with radioisotopes and the ages determined by other means, such as tree-ring counting (*4, 5*). In addition to systematic effects, there are statistical errors due to the limited number of atoms observed. Both types of errors can be considered to be fluctuations in n, the number of atoms observed. We next derive a relationship between the magnitude of these fluctuations and the resulting error in the estimation of the age of the sample.

We assume the general form

$$n = k\, e^{-t/\tau}$$
$$t = \tau \ln(k/n) \qquad (2)$$

Here τ is the mean life of the isotope, t is the age of the sample, and k is the initial number of radioactive atoms in the sample multiplied by the efficiency for detecting them. If n has errors associated with it of $+\delta n_1$ and $-\delta n_2$, then the corresponding values of t will be

$$t = \tau \ln \frac{k}{n^{+\delta n_1}_{-\delta n_2}}$$
$$= \tau \ln(k/n) \,^{+\,|\tau \ln(1\,-\,\delta n_2/n)|}_{-\,|\tau \ln(1\,+\,\delta n_1/n)|} \qquad (3)$$

For $n = 1$, inverse Poisson statistics (*9*) gives $n_1 = 1.36$ and $n_2 = 0.62$. Putting these values into Eq. 3 gives

$$t = \tau \ln(k)\, ^{+0.96\tau}_{-0.86\tau}$$

It will usually be sufficient to use the appropriate values

$$n = 1^{+1.4}_{-0.6}$$
$$t = \tau \ln(k) \pm \tau$$

Thus the observation of one event determines the age of the sample to within one mean life.

Another useful approximation, which is valid when $\delta n_1 = \delta n_2 \equiv \delta n \ll n$, is

$$\delta t = -(\delta n/n)\tau \qquad (4)$$

Equation 4 is easily derived, either by expanding the logarithm in Eq. 3 or by differentiating Eq. 2. Its important feature is the appearance of τ on the right side, rather than t. Thus, for example, a 10 percent error in the measurement of n results in an error in the estimate of t, not to 10 percent, but to 10 percent of a mean life. For a sample many mean lives old, such an error is often negligible.

Equations 3 and 4 are general results, true whether the error in n is due to Poisson statistics or fluctuations in either the cosmic-ray flux or the sedimentation rate. Thus, although it is necessary to know these quantities, it is often not necessary to know them accurately.

Beryllium-10 Detection

Beryllium-10 is produced in the atmosphere at the rate of 1.5×10^{-2} atom cm^{-2} sec^{-1} by cosmic rays that break up oxygen and nitrogen nuclei (*10*). We shall assume that in a period much less than its half-life of 1.5×10^{6} years (*11*) it becomes mixed with the atmosphere and the oceans, and that at equilibrium it settles out on the ocean floor at the same rate at which it is produced. The number of atoms of ^{10}Be in a volume v cm^3 of ocean sediments is therefore

$$n_0 = 1.5 \times 10^{-2}\, \frac{v}{s}\, e^{-t/2.2\times10^6}$$
$$= 1.6 \times 10^{10}\, v\, (s_0/s)\, e^{-t/2.2\times10^6}$$

where s is the sedimentation rate, t is the age of the sediment in years, and $s_0 = 3 \times 10^{-5}$ cm/year (a typical deep-sea value for s). The number of decays per minute from a sample of rock is

$$\frac{dn_0}{dt} = 0.014\, v\, (s_0/s)\, e^{-t/2.2\times10^6}$$

Despite such extremely low decay rates, ^{10}Be has been used in studies of both sea-floor spreading (*12*) and manganese nodule formation (*13*). Its usefulness derives partially from the extreme rarity of ordinary beryllium in sediment, approximately 3×10^{-6} by weight (*14*); by chemically extracting the beryllium from the sediment, the activity per gram of material is increased by a factor of 3×10^{5}. Even so, measurement back more than a few half-lives is very difficult.

To use the cyclotron for ^{10}Be dating, we would mix the beryllium with the metal cathode and use sputtering to create the ions. (Once again, an external ion source would be very useful, this time to facilitate changing samples.) The efficiency for accelerating these ions is probably similar to that for other heavy ion beams, 3×10^{-5}, although the beam current will be less than those obtainable from gases. Beam currents of 5 μa have been achieved at Berkeley for doubly charged ions, corresponding to 9×10^{14} per minute. Taking a rock density of 2.7 g/cm^2 and a beryllium content of 3 parts per million we calculate the ratio of ^{10}Be to ordinary ^{9}Be to be

$$\frac{^{10}Be}{^{9}Be} = 3 \times 10^{-8}\, (s_0/s)\, e^{-t/2.2\times10^6}$$

For a 5-μa beam, $s = s_0$, and $t \ll \tau$, we would observe 3×10^{7} ions of $^{10}Be^{2+}$ per minute. We would get one count per minute for a sample $\ln(3 \times 10^{7})$ mean lives = 38 million years old. One count in an hour would indicate an age of 47 million years. The total number of atoms that would be detected from a rock sample of volume v is

$$n = 4.8 \times 10^{5}\, v\, (s_0/s)\, e^{-t/2.2\times10^6} \qquad (5)$$

This equation, with 1-S.D. errors, is plotted in Fig. 2. The oldest dates (> 35

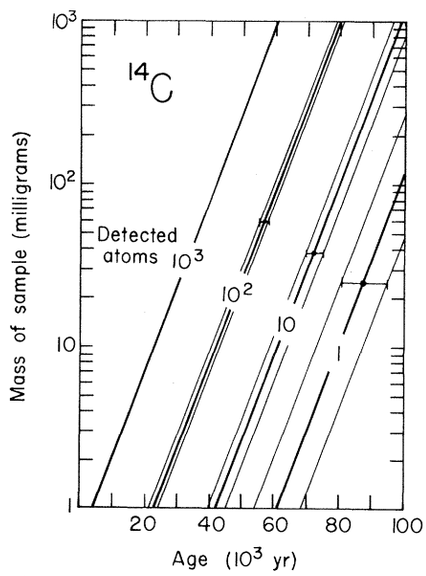

Fig. 1. Number of ^{14}C ions detected in the beam of the cyclotron, as a function of the age and mass of the carbon sample, based on Eq. 1. Statistical errors are indicated with error bars.

million years) can be reached only by using large samples of rock, 10 to 100 cm^3 or more.

As with ^{14}C dating, the main problem is expected to be interference from other ions with the same charge-to-mass ratio as the radioisotope. A cyclotron tuned to accelerate $^{10}Be^{2+}$ will also accelerate $^{10}Be^{2+}$ and $^{15}N^{3+}$. These particles can be removed from the beam by stopping them in an ^{27}Al foil. For a 6 Mev/A beam the ranges are approximately (*8*) ^{10}Be : 171 μm, ^{10}B : 112 μm, and ^{15}N : 92 μm. A 140-μm foil will stop all the background ions; straggling for ^{10}B is approximately 1 μm, with a Gaussian tail on the long-range end. The ^{10}Be emerges with about 32 percent of its original energy, sufficient to send it through a 10-μm silicon dE/dx detector and into a total E detector.

Aluminum was chosen as the foil material because of the large $-Q$ of 5.4 Mev required for the reaction

$$^{10}B + {}^{27}Al \rightarrow {}^{10}Be + {}^{27}Si$$

Thus any ^{10}Be produced in the foil from an incident ^{10}B will have at most an energy of 60 − 5.4 = 54.6 Mev. The ^{10}Be produced with this energy will have a range of 132 μm, and it will stop within the foil. Beryllium-10 produced deeper in the foil will have less energy (because of the ionization loss of the parent ^{10}B), and in fact none of the secondary ^{10}Be ions will emerge. The only particles counted by the silicon detectors should be ^{10}Be ions accelerated from the ion source.

We conclude that ^{10}Be dating with the cyclotron should be practical for ages of 5 to 35 million years or more, requiring rock samples ranging in volume from less than 1 mm^3 for the younger samples to 100 cm^3 for the older ones.

Double Dating

Whenever there are two radioisotopes with different mean lives that can be used to date the sample, we can deduce its age without having to know either the cosmic-ray flux that produced the isotopes or the sedimentation rate. The ratio of the two isotopes will be given by

$$r(t) = r(0) \exp[-t(1/\tau_1 - 1/\tau_2)] \quad (6)$$

where $r(0)$ is the ratio at $t = 0$ (that is, the ratio of the rates at which they are produced), and τ_1 and τ_2 are their mean lives. Once the age has been determined in this way, the absolute density of an isotope in the sample can be used to calculate the ratio of the cosmic-ray flux that produced the isotope to the rate of sedimentation that diluted it in the rock. If either of these is known, or assumed constant, the other can be calculated. This approach was used by Higdon and Lingenfelter (*15*) with measurements of the decays of ^{10}Be and ^{26}Al ($\tau = 1.1 \times 10^6$ years) to study the variations in the cosmic-ray intensity over the past 4 million years. Unfortunately, ^{26}Al is difficult to measure by the cyclotron technique because of the high natural abundance of ordinary ^{27}Al and the difficulty of separating ^{26}Al from ^{26}Mg. Still, it might be possible to double date with ^{10}Be and ^{26}Al to 5 or 10 million years.

Double dating ^{10}Be and ^{53}Mn looks more attractive. The mean life of ^{53}Mn is 2.9×10^6 years. Manganese-53 is not produced by cosmic-ray interactions in the atmosphere; it is produced by cosmic-ray interactions with the iron in meteors, which then rain down on the earth. The ^{53}Mn could be detected with the cyclotron (the major background would be ^{53}Cr), or it could be detected by using neutron-activation analysis (*16*).

However, there are other phenomena besides age that can affect the $^{10}Be/^{53}Mn$ ratio; these are variations in the meteor impact rate and variations in the earth's magnetic field (which shields the atmosphere from low-energy cosmic rays that create ^{10}Be). Triple dating, using ^{10}Be, ^{53}Mn, and ^{26}Al, might help to untangle these effects. And, of course, the existence of more than one interesting interpretation of an observed variation does not necessarily reduce the importance of looking for such a variation.

Trace Element Detection

Given its sensitivity of $\sim 10^{-16}$, the cyclotron has numerous potential applications to trace element analysis. Virtually any element or simple molecule that can be detected with an ordinary mass spectrograph can be detected with greater sensitivity by a cyclotron, because of its extremely low background count rate. Present-day cyclotrons are not particularly well suited to the detection of complex molecules, because most cyclotrons are designed to operate with low mass-to-charge values and because of the possibility of molecules breaking up during acceleration.

As an example of trace element detection we consider methane-21 ($^{13}CD_4$), whose usefulness as an atmospheric tracer has been recently demonstrated by Cowan *et al.* (*17*). These authors released up to 84 g of this compound into the atmosphere and detected it downwind by using a cryogenic air trap to remove methane from the air and a mass spectrometer to separate methane-21 from methane-16. They were able to detect ratios of these two compounds as low as 10^{-11}.

We briefly mentioned the acceleration of methane beams in the section on ^{14}C dating. Although we do not know yet what intensity of beams can be achieved on a cyclotron, it is safe to assume that we can obtain at least 100 na. Even this low current, running for 10 minutes, would give one count of methane-21 if it were at the level of 3×10^{-15}, more than three orders of magnitude better than the level detectable with an ordinary mass spectrometer. If we can increase the current to 10 μa, we would be able to detect the natural methane-21 that is expected to be present in the atmosphere. The dE/dx detector would have to be made sufficiently thin (< 3 μm) that the ^{13}C atom would emerge and give a coincident signal in the total E detector. We might wish to use a thin-foil scintillator in place of a silicon dE/dx detector.

Tritium Dating: Principles and Experimental Results

Despite the short mean life of tritium (17.8 years), tritium dating has important applications not only in cosmic-ray physics, but in hydrology, meterology, and oceanography (*18*). If one is tapping an underground reservoir of water, for example, and wishes to estimate how long it will take for the reservoir to refill, the age of the water as measured by tritium dating can often supply a valuable clue.

Before the early 1950's, tritium in the atmosphere was produced from cosmic rays by (n,t) reactions and by spallation of oxygen and nitrogen nuclei; most of the tritium in the atmosphere since then is left over from atmospheric testing of thermonuclear bombs. Both the cosmic ray–produced tritium and the "spikes" introduced by the bombs have been useful for dating water (*19–21*). We will be concerned primarily with ^3H in older water samples, which was cosmic ray–produced. Because the half-life of tritium is short, mixing over the surface of the earth is incomplete, leading to geographical variations in the tritium content of rainwater of factors of 4; however these variations can often be compensated for in analyzing data by looking at fresh rainwater from the same region as the sample being dated.

Measurements of the tritium content of rainwater (*19*) give an average value of $^3H/^1H = 5 \times 10^{-18}$, beyond the limit of detectability by the cyclotron technique. Fortunately tritium is easily concentrated

electrolytically by factors of several thousand or more; this enrichment is also essential for radioactive dating. One potential complication comes from the fact that tritium is enriched in such samples even more than deuterium. Leventhal and Libby (*20*) determined that with electrolytic concentration nearly 100 percent of the tritium in the original sample is retained.

To test the cyclotron dating technique, W. R. Holley, E. J. Stephenson, and I performed an experiment to measure the $^3H/^2H$ ratio in a deuterium sample 24 years old. The sample had been collected before the thermonuclear bomb testing period, so the original $^3H/^1H$ ratio should be close to the value measured for rainwater in the early 1950's (*20, 21*): 5×10^{-18}. Dividing this by the known deuterium content of water, $^2H/^1H = 1.5 \times 10^{-4}$, we get $^3H/^2H = 3.3 \times 10^{-14}$ for the original water at $t = 0$. Deuterium had been separated from the water at the Savannah River Heavy Water Plant, using the GS process followed by vacuum distillation and electrolysis (*22*). Approximately 20 percent of the deuterium in the processed water, and nearly 100 percent of the tritium was recovered; thus the $^3H/^2H$ ratio was increased by a factor of 5. Combining all these numbers, we find the predicted ratio as a function of age

$$\frac{^3H}{^2H} = 1.7 \times 10^{-13}\, e^{-t/17.8} \qquad (7)$$

where 17.8 is the mean life of tritium in years.

The major source of background, as expected, was $^3He^+$; H_3^+ and HD^+ molecules differ in mass from $^3H^+$ by 0.2 percent (approximately eight resolution widths). The ^3He and the residual tails from the molecular beams were removed by passing the beam through a 25 mg/cm^2 ($\simeq$ 95 μm) aluminum foil. Aluminum was chosen for the foil material because of the large $-Q$ of 4.8 Mev required to produce spurious tritium atoms in the reaction

$$^3He + {}^{27}Al \rightarrow {}^3H + {}^{27}Si$$

In our experiment, the tritium beam energy was 6 Mev; the tritium produced by ^3He interactions was too low in energy to emerge from the foil. Particles that did emerge were identified and counted by a 15-μm silicon dE/dx detector in coincidence with a 500-μm silicon total E detector. We counted 136 ^3H atoms in 4 minutes of observation, or 0.57 atom per second; when we tuned off the ^3H resonance we observed no counts in several minutes, confirming that our background was essentially zero. The ^2H beam was measured with a Faraday cup, preceded by collimators to simulate the acceptance geometry of the silicon detectors; we observed an average current of 3.4 μa, indicating 2.1×10^{13} ion/sec. Thus the observed ratio was 2.7×10^{-14}. Using Eq. 7 we calculate $t = 33$ years, to be compared to the "known" age of 24 years.

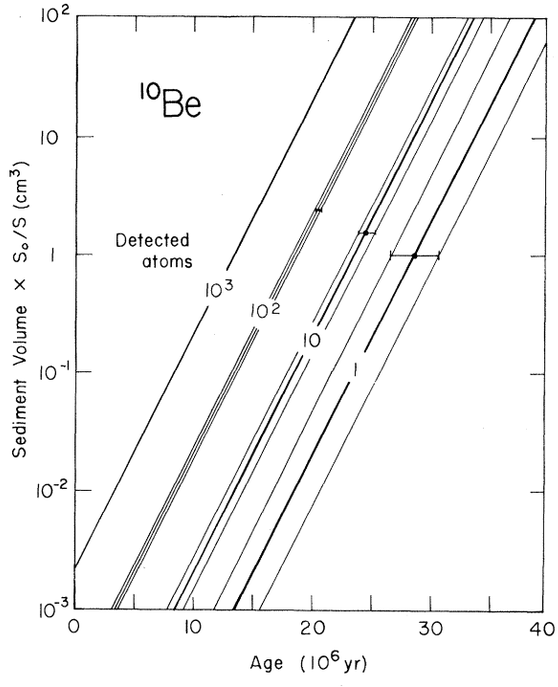

Fig. 2. Number of ^{10}Be ions detected in the beam of the cyclotron, as a function of the age and volume of the sedimentary rock from which the beryllium was extracted, based on Eq. 5. Statistical errors are indicated with error bars. The sedimentation rate is s; $s_0 = 3 \times 10^{-5}$ cm/year; and for deep-sea samples $s_0/s \simeq 1$.

It is premature to try to assign an error to the measured age, or to interpret the result as a verification that the assumed $^3H/^1H$ value at $t = 0$ was correct. The greatest source of error was undoubtedly the assumption that the efficiency of the cyclotron was the same for the two beams. Although we have determined that the efficiency does not change by more than a few percent for small changes in cyclotron frequency, it is likely that the efficiency changed by 50 percent or more for the very large frequency shift required to switch from ^2H to ^3H. For future measurements the efficiency ratio will be measured to a few percent by accelerating samples of known ^3H and ^2H content before introducing samples of unknown age. Dated samples are readily available in the form of vintage wine.

On the basis of this experiment, we can calculate the potential sensitivity of the cyclotron technique for tritium dating. Had we observed one count in our 4 minutes of observation, we would have calculated that the sample age was 120 years; one count per hour would have implied 160 years. Previous tritium-dating measurements using decay counting have been limited to a maximum age of about 25 years. For the older samples even an error of a factor of 2 in the efficiency calibration would have been tolerable; it would have led to a misestimation of the age by one half-life (12 years), an error of only 10 percent for a sample 120 years old.

The ability to detect tritium in older samples should enable us to look at one of the unsettled questions of cosmic-ray physics: whether the prenuclear-testing tritium levels are consistent with the calculated rate of production by cosmic rays, or whether another much more powerful source must be postulated (*23*). New measurements of dated samples will allow us to determine what the original tritium concentrations were.

Summary

By considering radioisotope dating as a problem in trace element detection, and by using the cyclotron as a high-energy mass spectrometer for this purpose, we have shown that one can greatly increase the maximum age that can be determined while simultaneously reducing the size of the sample required. The cyclotron can be used to detect atoms or simple molecules that are present at the 10^{-16} level or greater. For ^{14}C dating one should be able to go back 40,000 to 100,000 years with 1- to 100-mg carbon samples; for ^{10}Be dating, 10 to 30 million years with 1-mm^3 to 10-cm^3 rock samples; for tritium dating, 160 years with a 1-liter water sample. The feasibility of the technique has been demonstrated experimentally by measuring the tritium/

deuterium ratio in a sample 24 years old. For samples many half-lives old, the fractional error in the age is small even if rates of production or deposition of the isotopes.

Although cyclotrons are expensive to build, their operating costs are relatively low. If several samples are dated per hour the cost per date may not be substantially higher than it is today for decay dating. There are already more than 50 cyclotrons in operation which have the potential to do radioisotope dating, and their application to important problems of dating and trace element analysis should prove very fruitful.

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Local Mate Competition and Parental Investment in Social Insects

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Kinship theory (*1*) and sex ratio theory (*2*) were used by Trivers and Hare (*3*) to predict the relative investments in reproductive males and females by various eusocial insects and their nonsocial relatives. They suggested that in eusocial species with haplodiploid sex determination, queens gain by a 1:1 (male: female) investment in reproductive offspring, while their sterile worker offspring gain by a 1:3 investment among reproductive siblings, and that (*3*, p. 250) ". . . a measurement of the ratio of investment is a measure of the relative power of the two parties . . ." From their measurements of investment patterns in various species, Trivers and Hare concluded that in single-queen (monogynous) ants, the investment pattern is "near 1:3," while in nonsocial bees and wasps, which lack sterile castes, the investment pattern "approximates 1:1." Their interpretation is that the interests of the workers are more nearly realized than are those of the queen. In support of this interpretation they also cite investment ratios from multiple-queen (polygynous) ants, slave-making ants, termites, and bumblebees. Their conclusions have been multiply cited (*4*).

We argue here that, on the contrary, (i) Trivers and Hare's predictions of 1:1 and 1:3 investment patterns are inappropriate for the insect groups they analyzed, (ii) they did not demonstrate such patterns, (iii) their data are not explained by their hypothesis, and (iv) their data for the most part conform to an alternative hypothesis, that is, Hamilton's (*5*) hypothesis of "local mate competition" (mating rivalry among close relatives), which they mention (*3*, footnotes 9, 53, and 96 and p. 251) but do not apply.

Trivers and Hare's predictions depend upon (i) monogamy or effective monogamy among laying females, (ii) inability of workers to lay eggs, and (iii) outbreeding without effects from local mate competition (LMC) (*6*). However, multiple matings by females, worker oviposition, and local mate competition may actually be typical of haplodiploid insects rather than rare or absent among them, as Trivers and Hare may have assumed in drawing their conclusions (*3*, p. 261).

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