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RADIOISOTOPE DATING WITH A CYCLOTRON

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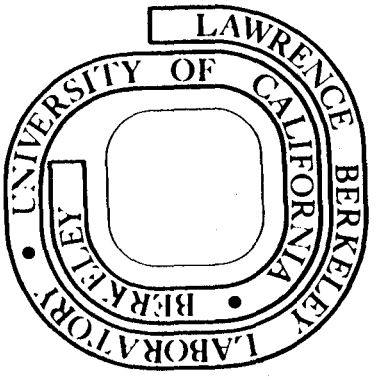

DISCLAIMER

RADIOISOTOPE DATING WITH A CYCLOTRON

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

by

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ABSTRACT

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 show that one can greatly increase the maximum age that can be dated while simultaneously reducing the size of the sample required. The cyclotron can be used to detect atoms or mulecules which are present at the 10^{-18} level or greater. For ^{10}Be dating one can go back 34 million years with a sample of rock 10 cm^3 in volume; for ^{14}C dating: 88 thousand years with a 25 mg carbon sample; for ^{53}Mn dating: 35 million years with a 10 cm^3 rock sample; for tritium dating: 153 years with a half-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 $\delta t/t$ in the age is small even if there are large uncertainties in the rates of production or of deposition of the isotopes.

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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 one could find a technique to detect these atoms with even a modest efficiency ($>10^{-6}$) one could reduce the size of the sample and still push back the age that can be measured 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 those 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" 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 quark search (which was, in effect, a search for new isotopes of hydrogen), a few seconds of counting were sufficient to

detect isotopes present in ordinary hydrogen at the 10^{-18} level. Although the sensitivity that can be reached varies from element to element, this number will be a useful figure of merit: any radioisotope present at the 10^{-18} 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 multiple photon scattering, 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 cannot be used because of the impossibility of distinguishing the radioisotopes from stable atoms with similar charge-to-mass ratios. For example, radioactive ^{14}C could not be distinguished from stable ^{14}N; the radioactive ^{10}Be could not be distinguished from stable ^{10}B. 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 MeV, rather than the several KeV obtained with an ordinary mass spectrometer) where it is possible to distinguish the chemically different atoms (such as ^{14}C and ^{14}N) by measuring their differing 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 resolution ($\Delta m/m < 3 \times 10^{-4}$) and by extremely low background rates (< 1 count/hr 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 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. When switched to the abundance 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 for ^{10}Be dating one can date back more than twenty half-lives rather than the one or two which is 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 two error in the count rate results in a factor of two error in the age. However for a sample twenty half-lives old, that same factor of two error results in a misestimation of the age by only 5%. 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. Although any cyclotron might be used, we will assume in our examples the properties of the 88" sector-focused cyclotron at Berkeley, which produces particles of multi-MeV energy, and can be switched from the resonant state for one ion to that of another in a matter of minutes. Except as noted, the beam intensities we shall assume for each ion species are those that have already been achieved on this cyclotron. For the case of tritium we have used the cyclotron to make an experimental measurement of the age of a deuterium sample. For the other radioisotopes, the claimed sensitivities are projections based on measurements of backgrounds made during the quark search.

BERYLLIUM-10 DATING

^{10}Be is produced in the atmosphere at the rate of 4.5×10^{-3} atoms/cm^2·sec, by cosmic rays which break up oxygen and nitrogen nuclei (4,5). In a period much less than its half-life of 1.5×10^6 years (6), it becomes mixed with the atmosphere and the oceans, and at equilibrium it settles out in 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:

$$n_o = 1.6 \times 10^{10} \, v \, (s_o/s) \, 2^{-t/1.5\times10^6}$$

$$= 1.6 \times 10^{10} \, v \, (s_o/s) \, e^{-t/2.2\times10^6} \qquad (1)$$

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

$$\frac{dn_o}{dt} = 0.014 \, v \, (s_o/s) \, e^{-t/2.2\times10^6} \qquad (2)$$

Despite this extremely low decay rate, ^{10}Be has been used in studies both of sea-floor spreading (7) and of manganese-nodule formation (8). Its usefulness derives partially from the extreme rarity of ordinary beryllium in sediment, approximately 3×10^{-6} by weight (9); 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 calculate the effectiveness of using the cyclotron for ^{10}Be dating, we start by calculating the ratio of ^{10}Be to ordinary ^{9}Be. Taking a density for sedimentary rock of 2.7 g/cm^3, we find:

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

Taking $s = s_o$, and t small, the ratio is 3×10^{-8}. For the current of accelerated ^{9}Be ions obtainable from the cyclotron, we will assume the modest value which has already been achieved: 5 μA of doubly-charged ions (100 μA may be obtainable). Of course, the cyclotron would be set to accelerate only the ^{10}Be ions; we would count 3×10^{7} per minute in our detectors. We would get 1 count/min for a sample $\ell n(3 \times 10^{7})$ mean-lives = 38 million years old. Counting for an hour (vs. one minute) would increase the sensitivity by $\ell n(60)$ mean-lives, to a value of 47 million years. Increasing the beam current to 50 μA would give us an additional 5 million years.

Before one dismisses "one count" as being too small to yield a useful age determination, one must work through the error calculation. We shall do this in the next section, where we show 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 if the ion source gives 5 μA of $^{9}Be^{2+}$, and we observe one count in ten minutes, the age of the sample is 43 ± 2 million years.

To use the cyclotron for ^{10}Be dating, we could introduce the beryllium which was extracted from the sediment into the ion source either as a gas ($BeCl_2$) or as a metal (using sputtering to create the ions). We will assume that we will achieve an efficiency of 3×10^{-5} a typical value at the Berkeley 88" cyclotron for heavy ion beams. Then the number of atoms that will be detected from a rock of volume v will be

$$n = 4.8 \times 10^5 \; v \; (s_o/s) \; e^{-t/2.2 \times 10^6} \qquad (4)$$

This number of detected ^{10}Be atoms, as a function of sample age and volume, is plotted in Fig. 1. As can be seen from the figure, the oldest dates (> 35 million years) can be reached only by using large samples of rock, 10-100 cm^3 or more.

A cyclotron tuned to accelerate $^{10}Be^{2+}$ will also accelerate $^{10}B^{2+}$ and $^{15}N^{3+}$. These particles are easily removed from the beam by stopping them in a ^{27}Al foil. For a 6 MeV/A beam the ranges are (10):

^{10}Be	171 μ
^{10}B	112 μ
^{15}N	92 μ

A 140 μ foil would stop all the background ions; straggling for ^{10}B is approximately 1 μ, with a Gaussian tail on the long range end. The ^{10}Be emerges with about 32% of its original energy, sufficient to send it through a 10 μ silicon dE/dx detector and into a total E detector.

Aluminum was chosen as the foil material because of the large negative Q required for the reaction:

$$^{10}B + ^{27}Al \longrightarrow ^{10}Be + ^{27}Si - 5.4 \text{ MeV}$$

Thus any ^{10}Be produced in the foil from an incident ^{10}B will have <u>at most</u> an energy of 60 - 5.4 = 54.6 MeV. The range of ^{10}Be produced with this

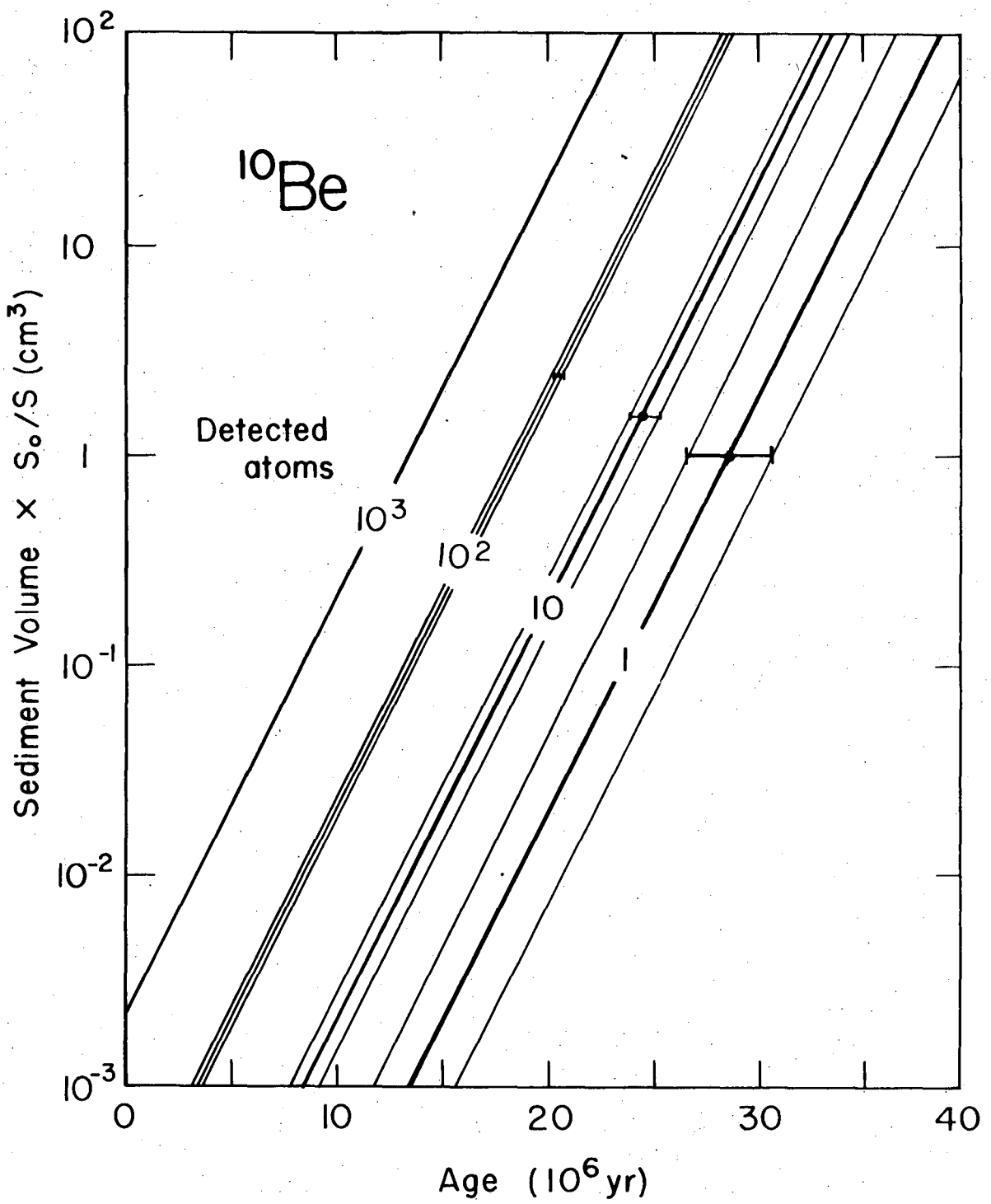

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Fig. 1. The number of ^{10}Be ions detected in the beam of the cyclotron, as a function of the age and volume of sedimentary rock from which the Beryllium was extracted; based on Eq. 4. The statistical errors associated with each number are indicated with error bars. s is the sedimentation rate, $s_o = 3 \times 10^{-5}$ cm/yr, and for deep-sea samples $(s_o/s) \approx 1$.

energy is 132 μ, and it will stop within the foil. ^{10}Be ions 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 a cubic millimeter for the younger samples to 100 cm^3 for the older ones.

ACCURACY OF THE AGE DETERMINATION

There are well-documented differences between the ages of materials dated with radioisotopes, and the ages as determined by other means, e.g. tree ring counting (11). In addition to these systematic effects, there are statistical errors due to the limited number of atoms observed. Both of these errors can be considered fluctuations in n, the number of observed atoms. We shall derive here the relationship between the magnitude of these fluctuations and the resulting error in the estimation of the age of the sample.

Let us assume the general form:

$$n = k\, e^{-t/\tau} \quad ; \quad t = \tau\, \ell n(k/n) \tag{5}$$

If n has errors associated with it of $+\delta n_1$, $-\delta n_2$, then the corresponding values of t will be

$$t = \tau\, \ell n \frac{k}{n \begin{matrix} +\delta n_1 \\ -\delta n_2 \end{matrix}}$$

$$= \tau\, \ell n(k/n) \begin{matrix} + \left| \tau\, \ell n(1-\delta n_2/n) \right| \\ - \left| \tau\, \ell n(1+\delta n_1/n) \right| \end{matrix} \tag{6}$$

For n = 1, inverse-Poisson statistics (12) gives $\delta n_1 = 1.36$, $\delta n_2 = 0.62$. Putting these values into Eq. 6 gives:

$$t = \tau \ln(k) \begin{matrix} +0.96\tau \\ -0.86\tau \end{matrix}$$

It will usually be sufficient to use the approximate values:

$$n = 1 \begin{matrix} +1.4 \\ -0.6 \end{matrix} \qquad t = \tau \ln(k) \pm 1 \tag{7}$$

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

Another useful approximation of Eq. 6, valid when $\delta n_1 = \delta n_2 \equiv \delta n \ll n$, is:

$$\delta t = -(\delta n/n) \cdot \tau \tag{8}$$

This equation is easily derived, either by expanding the logarithm in Eq. 6, or by differentiating Eq. 5. The important feature of this equation is the appearance of τ on the right side, rather than t. Thus, for example, a 10% error in the measurement of n results in an error in the estimate of t, not to 10%, but to 10% of a mean-life. For a sample many mean-lives old, such an error is often negligible.

Equations 6 and 8 are general results, true whether the error in n is due to Poisson statistics, or fluctuations in either the cosmic-ray flux or sedimentation rate. Thus although it is necessary to know these quantities, it is not necessary to know them accurately.

RADIOCARBON DATING

The technique of ^{14}C (radiocarbon) dating developed by Libby (11) depends on the fact that cosmic ray neutrons are continuously producing ^{14}C in the atmosphere through the reaction $^{14}N(n,p)^{14}C$. 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. 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:

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

Because of background counts, typically 10,000 disintegrations must be observed for ages in the range 5-10,000 years. This requires 1-10 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:

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

Thus a fresh gram of carbon, containing 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 μA beam of $^{12}C^{2+}$ ions would require 2.5 mg of carbon per minute, assuming an efficiency of 3×10^{-5} (typical for carbon beams). For new carbon, 4400 atoms of ^{14}C would be detected per minute. For one count per minute, the sample age would be $\ell n(4400) \cdot \tau$ = 69,000 years. With ten minutes of counting (assuming we can achieve the same "zero background" levels we had in the quark search) we could go back 88,000 years. An hour of counting (requiring 150 mg of carbon) could go back 103,000 years.

For a sample 88,000 years old, the ratio $^{14}C/^{12}C = 3 \times 10^{-17}$. Extraordinary care would have to be taken to avoid contamination with young carbon; 24 parts per million would double the count rate. Fortunately the sample size is small (25 mg) so it could be carefully selected. The number of detected ^{14}C atoms is:

$$n = 1.7 \times 10^{6} \, m \, e^{-t/8270}$$

This equation is plotted in Fig. 2.

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" cyclotron at Berkeley, the residual nitrogen beam from the latter source amounts to approximately 10 nA (3×10^{10} ions/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 MeV per nucleon), the emerging nitrogen atoms will not be fully stripped; we can expect about 10% of them to come out of the foil in the q = +6 charge state (13), 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 would be to send it into a foil sufficiently thick to stop ^{14}N but not ^{14}C. At 56 MeV (4 MeV/A) the ranges in a gold foil are 17 μ for ^{14}N and 22 μ for ^{14}C. Straggling should be approximately 1-2% for the ^{14}N beam (10), so a foil 18 μ in thickness should be sufficient to stop the nitrogen ions. The emerging ^{14}C atoms will have a range in silicon of about 10 μ, so a very thin dE/dx

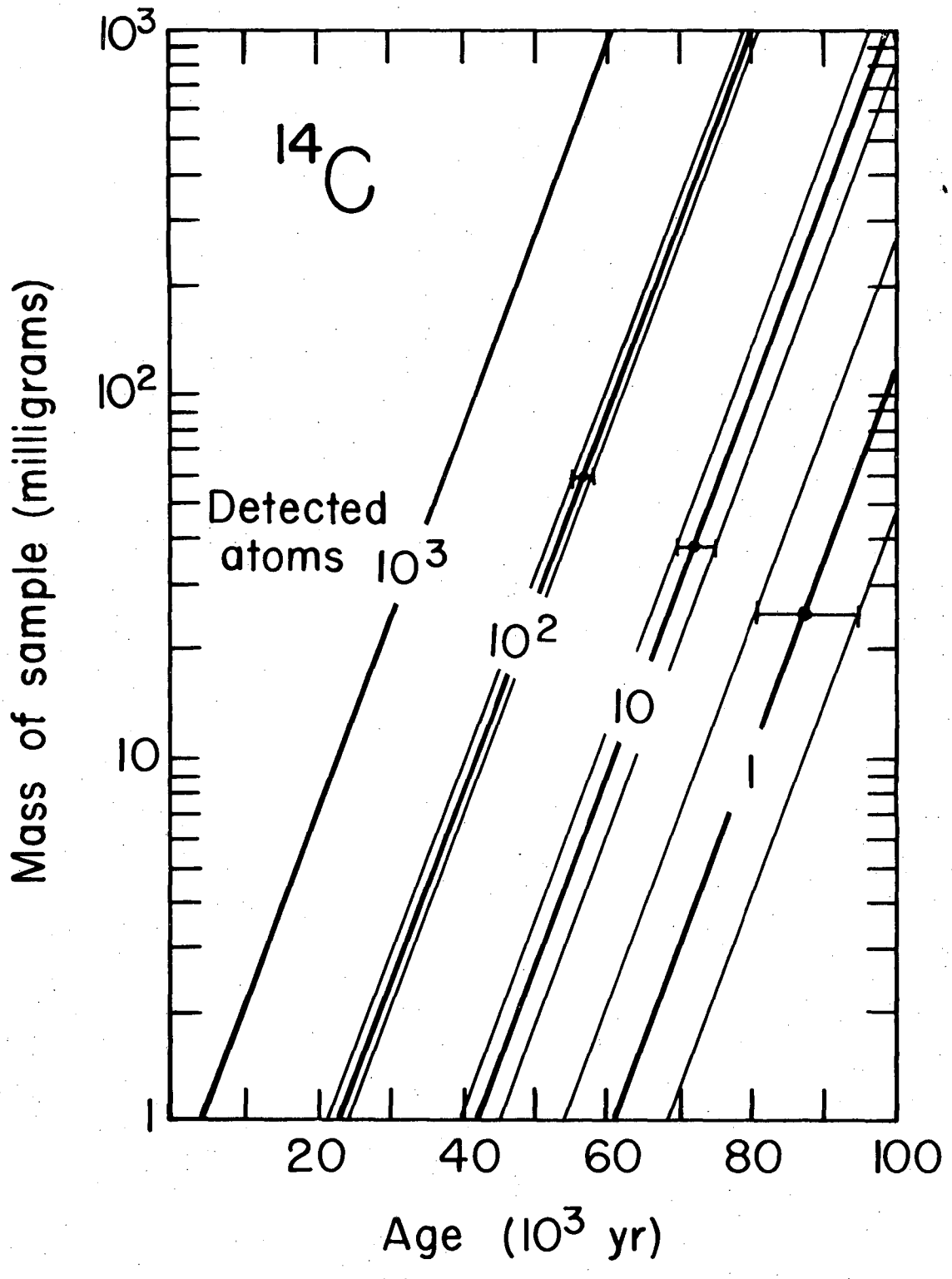

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Fig. 2. The number of ^{14}C atoms detected in the beam of the cyclotron, as a function of the age and mass of the carbon sample; based on Eq. 9. Statistical errors are indicated with error bars.

detector would have to be used in order to pass the ions into a total E detector. Secondary production of ^{14}C through the reaction

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

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

Another possible way to eliminate the ^{14}N background, is to accelerate a molecular ion such as $^{14}CH_4^+$ or $^{14}CD_4^+$. The most serious potential background is NH_4^+, and it is unlikely that this ion will be present at a high enough level to cause trouble. (^{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 would require operation of the Berkeley cyclotron in the 5^{th} harmonic, resulting in a relatively low energy beam (0.4 MeV/A) on which particle identification would be difficult. And we may not be able to achieve more than a few hundred nanoamps of beam current, resulting in a maximum detectable age four 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 the construction of 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.

It appears likely that ^{14}C dating can be accomplished using the cyclotron, with a potential of reaching back 40-100 thousand years with carbon samples 1-100 milligrams in weight. But because of the natural abundance

of ^{14}N, the difficulty of identifying the natural ^{14}C in the sample is more severe than for the other radioisotopes discussed in this paper, and a final evaluation of the sensitivity of ^{14}C dating with the cyclotron awaits additional experimental development.

ALUMINUM-26 DATING

Rather than attempt to calculate the ^{26}Al content of ocean sediments from cosmic ray data directly, let us take the experimental result (5) that its ratio in decays per minute for young rock, compared to ^{10}Be, is ≈ 1%. Modifying Eq. 2, we find the number of decays per minute from a sample of rock is

$$\frac{dn_o}{dt} = 1.4 \times 10^{-3} \; v \; (s_o/s) \; e^{-t/1.1x10^6} \qquad (10)$$

where 1.1×10^6 is the mean-life of ^{26}Al in years. Given the smallness of the coefficient in Eq. 10, it may seem surprising that ^{26}Al decays have been detected in sediment. However unlike the previously discussed radioisotopes, which emit low energy electrons, ^{26}Al emits positrons, whose annihilation radiation is very easy to detect. Converting Eq. 10 to decays per year, and integrating to find n_o, gives:

$$n_o = 8.1 \times 10^8 \; v \; (s_o/s) \; e^{-t/1.1x10^6}$$

Unfortunately (for our purposes) ordinary ^{27}Al is very common in sedimentary rocks: 10% by weight, on the average (9). Using a density of 2.7 g/cm^3, this implies a number density of 2×10^{22} per cm^3. The ratio of $^{26}Al/^{27}Al$ is 1.3×10^{-13} (for $s = s_o$ and $t = 0$). A 2 μA beam of $^{27}Al^{4+}$ would have 25 counts per min for young rock. A ten minute run would yield one count for a sample which was 6.1 million years old. We could date back further for rock samples (such as pure limestone) which had significantly lower

aluminum content, provided that the sedimentation rate were no greater than we assumed. If, for example, the aluminum content of the rock were 0.1% instead of 10%, then we could date back an additional ℓn(100) mean-lives = 5 million years, to samples which were over 11 million years old.

The only background which would cause serious trouble is ^{26}Mg, which differs in mass from ^{26}Al by 0.01%. The ionization rates in thin silicon detectors for the two elements differ by 12% (10); a particle identifier might handle 10^5 particles per second. In order to reduce the ^{26}Mg to this level for a 2 μA beam of ^{27}Al, the aluminum would have to be purged of magnesium to better than 0.1 ppm unless additional separation were attempted in the beam. As was the case for ^{14}C, special care would have to be taken to avoid the production of ^{26}Al in stripping foils or in the dE/dx detector through a charge exchange reaction.

MANGANESE-53 DATING

^{53}Mn is not produced in the atmosphere by cosmic-rays; there are almost no nuclei in the atmosphere heavy enough to spallate into manganese. It is produced in iron meteorites, however. For meteors more than a few million years old, the ^{53}Mn contained in them is at equilibrium with the cosmic rays which are producing it, and just as for radioisotopes produced in the atmosphere, the density of ^{53}Mn in them will depend only on the spallation cross-section and the flux of cosmic rays. The collision of such meteors with the earth results in a constant rain of this isotope. ^{53}Mn has a half-life of about 2×10^6 years. It decays via electron capture; the resulting 5 keV x-ray is exceedingly difficult to detect because of self-absorption in the manganese. As a result, ^{53}Mn has never been detected in sedimentary rocks.

We can estimate the expected ^{53}Mn concentration in sedimentary rocks as follows: in meteorites, ^{53}Mn has been observed to yield between 360-515 decays per minute per kilogram of meteor (14). We shall assume an average value of 400 dpm/kg. Meteoric dust falls on the 5×10^{18} cm^2 surface of the earth at the rate of 4×10^8 g/day (15). From these numbers we can calculate the number of ^{53}Mn atoms in a volume of v cm^3 of sedimentary rock:

$$n_o = 6 \times 10^8 \, (s_o/s) \, v \, e^{-t/2.9x10^6} \qquad (10)$$

where s is the sedimentation rate, s_o again is 3×10^{-5} cm/yr, and t is the age of the sample. A typical value for the amount of ordinary manganese (^{55}Mn) found in sedimentary rocks is 6.7×10^{-4} by weight (9). Assuming a rock density of 2.7 g/cm^2, this implies that there are 2×10^{19} atoms of ^{55}Mn per cm^3 of rock. The ratio $^{53}Mn/^{55}Mn$ of 3×10^{-11} is large enough to make cyclotron dating look attractive.

The number of ^{53}Mn atoms detected with the cyclotron will be

$$n = 1.8 \times 10^4 \, (s_o/s) \, v \, e^{-t/2.9x10^6} \qquad (11)$$

where we have again assumed an efficiency for the cyclotron of 3×10^{-5}. This equation is plotted in Fig. 3. In contrast, the number of decays per minute from the sample will be:

$$\frac{dn_o}{dt} = 4 \times 10^{-4} \, (s_o/s) \, v \, e^{-t/2.9x10^6} \qquad (12)$$

a radioactive decay rate virtually impossible to detect.

We would introduce the manganese into the ion source as a metal on the electrodes, and use sputtering to form the beam. Beams of 2 μA may be possible. Assuming a charge state q = +4, we would have 5.6×10^3 counts/min for young manganese. One count per minute would indicate an age of

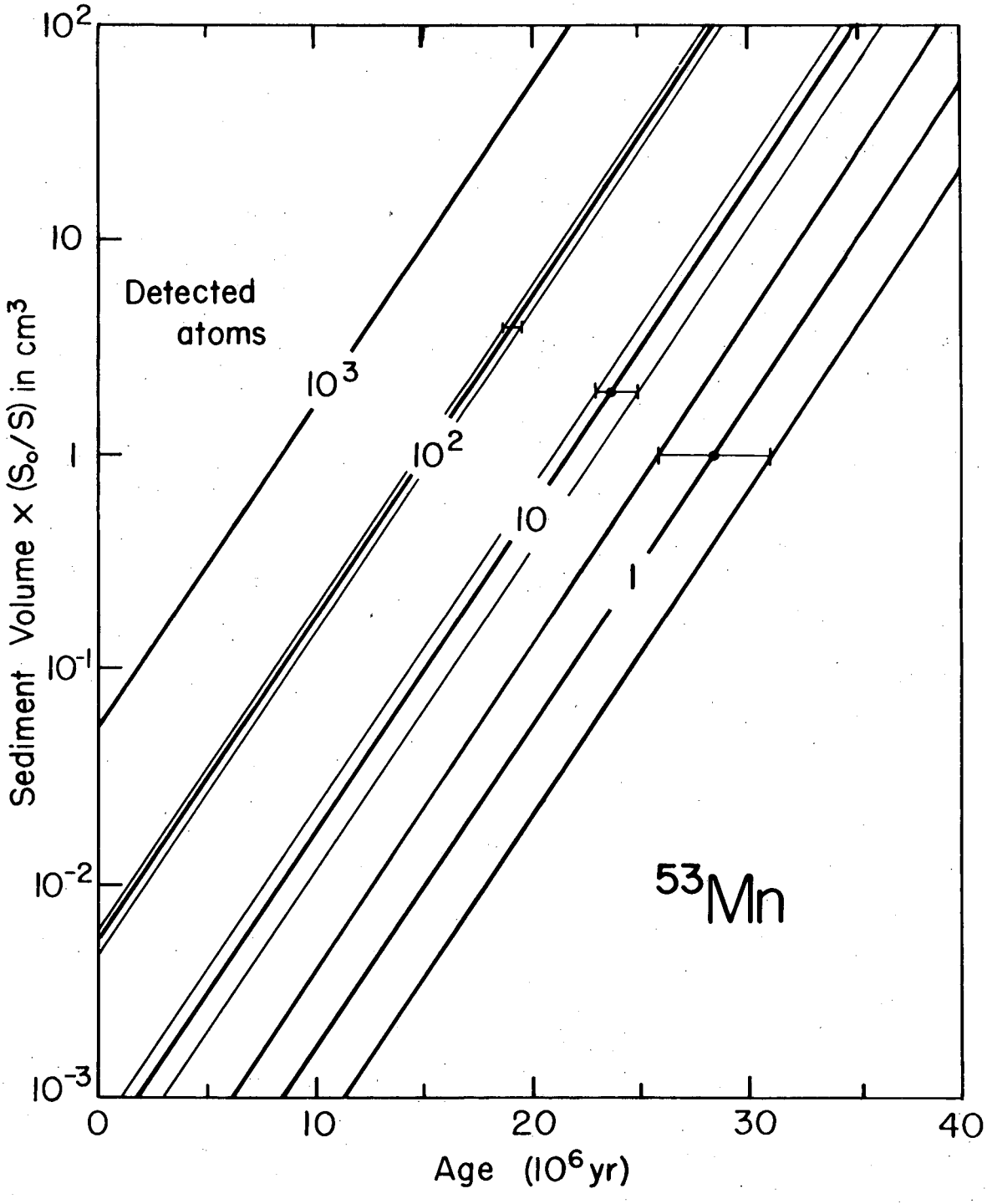

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Fig. 3. The number of ^{53}Mn ions detected in the beam of the cyclotron, as a function of the age and volume of the sedimentary rock from which the manganese was extracted; based on Eq. 11. For deep-sea samples, $(s_o/s) \approx 1$.

25 million years; one count in ten minutes an age of 32 million years. A 50 μA beam would lead to a ten-minute sensitivity of 41 million years.

The only serious background is ^{53}Cr, which is found in sedimentary rock at an average level of 15 ppm (9). It is difficult to estimate what the chromium level of the separated manganese would be; it would have to be less than 0.1 ppm in order to introduce the beam safely into a silicon dE/dx detector. Several options are open: one could chose to measure only those samples which are already low in chromium; one could attempt to reduce the chromium levels chemically; or one could reduce the chromium in the beam using one of the techniques we discussed for carbon: stripping followed by magnetic separation.

DOUBLE DATING

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

$$r(t) = r(0)\, e^{-t(1/\tau_1 - 1/\tau_2)} \qquad (13)$$

where r(0) is the ratio at t = 0 (i.e. it is the ratio of the rates of which they are produced), and τ_1 and τ_2 are the mean-lives of the two isotopes. Once the age has been determined in this way, the absolute density of the isotope in the sample can be used to calculate the ratio of the cosmic ray flux which produced the isotope to the sedimentation rate which diluted it in the rock. If either of these is known, or assumed constant, then the other can be calculated. This approach was used by Higdon and Lingenfelter (16) with measurements of the decays of ^{10}Be

and ^{26}Al to study the variations in the cosmic ray intensity back 4 million years. Using the cyclotron technique to measure the ^{26}Al, we could perhaps stretch this measurement back to 5 or 10 million years.

Double dating ^{10}Be and ^{53}Mn looks more attractive since they cover the same range in age: 0-35 million years. The situation is a bit more complicated than for $^{26}Al/^{10}Be$ double dating, since ^{10}Be was produced in the atmosphere whereas the ^{53}Mn was produced in meteors. This distinction is not as great as it first appears, however. The average residence time for any particular radioactive atom in the meteor is one mean-life τ. Thus the ^{53}Mn in the meteor was nearly all produced in the period just before it struck the earth. Since most of the meteoric material orbits the sun with low eccentricity, it will have been exposed to the same cosmic ray flux as the earth. Thus one can think of the meteors in orbit with us around the sun almost as an extended atmosphere. However there are two phenomena besides age which can affect the $^{10}Be/^{53}Mn$ ratio: variations in the meteor impact rate, and variations in the earth's magnetic field (which shields the atmosphere from low energy cosmic rays which 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 ~ 10^{-18}, the potential applications of the cyclotron to trace element analysis are numerous. Virtually any element or simple compound that can be detected with an ordinary mass spectrograph can be detected with greater sensitivity by a cyclotron, due to its extremely low background count rate. Present-day cyclotrons are not particularly well suited to the detection of complex molecules, both because most cyclotrons are designed to operate with low values of mass-to-charge, and because of the possibility of molecules breaking up during acceleration.

As a particular example of trace element detection, we consider methane-21 ($^{13}C\ D_4$) whose usefulness as an atmospheric tracer has been recently demonstrated by Cowan et al. (17). In their study they released up to 84 g of this compound into the atmosphere, and detected it downwind 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 down to 10^{-11}.

We briefly mentioned the acceleration of methane beams in the section on ^{14}C dating. Although we don't know yet what intensity 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 (< 3μ) so 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

Despite its short half-life (12.3 years), tritium dating has important applications not only in cosmic-ray physics, but in hydrology, meteorology and oceanography (18). If one is tapping an underground reservoir of water, for example, and one 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.

Prior to 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 the 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, 20). We will be concerned primarily with older water samples, which were cosmic ray produced. Because the half-life of tritium is so 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 calibrated out 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 $^{3}H/\ ^{1}H = 5 \times 10^{-18}$, right at the limit of detectability by the cyclotron technique. Fortunately tritium is easily concentrated by means of electrolysis by a factor of about 1000; this enrichment is also essential for radioactive dating. A 50 μA beam of ions from enriched fresh water would have 94 tritium atoms per minute accelerated. The oldest

date that could be measured, in ten minutes of counting, would be ℓn(940) mean-lives = 121 years. Counting for an hour could extend this back to 153 years. Previous measurements have been limited to about 25 years. Dated samples are readily available in the form of vintage wine. A 50 μA beam, even if run for a full hour, would require an original sample of liquid only a half-liter in volume (21).

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 pre-nuclear-testing tritium levels are consistent with the calculated rate of production by cosmic rays, or whether another much more powerful source must be postulated (22, 23). New measurements of dated samples will allow us to determine what the original tritium concentrations were.

Potential backgrounds are $^{3}He^{+}$, H_3^{+}, and HD^{+}. The masses of the latter two molecules differ from that of $^{3}H^{+}$ by 0.2% (approximately 8 resolution widths) so they can be separated by the cyclotron. ^{3}He and residual molecular ions from the tails of the HD^{+} and H_3^{+} beams can be eliminated by sending the beam into a foil thick enough to stop them but thin enough to pass the ^{3}H beam. The ion that gets the furthest is the D^{+} fragment of the HD molecule; it will have the same energy per nucleon as the $^{3}H^{+}$, and 2/3 of the range. Again, we choose aluminum for the foil material because of the large Q of 4.8 MeV required to produce spurious tritium atoms in the reaction

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

Thus the produced tritium will be distinguished by its lower energy; it can be eliminted completely by keeping the beam energy below the 4.8 MeV threshold.

TRITIUM DATING: EXPERIMENTAL RESULTS

In order to test the cyclotron 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 undergone special processing, so we begin by making an estimate of the expected $^3H/^2H$ ratio as a function of age.

The sample had been collected prior to the thermonuclear bomb testing period, so the original $^3H/^1H$ ratio should be close to value measured for rainwater in the early 1950's (20): 5×10^{-18}. Multiplying 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 (23). Approximately 20% of the deuterium in the processed water, and nearly 100% of the tritium was recovered (20); thus the $^3H/^2H$ ratio was increased by a factor of 5. Combining all these numbers, we find the ratio as a function of age.

$$\frac{^3H}{^2H} = 1.7 \times 10^{-13} \, e^{-t/17.8} \qquad (14)$$

where 17.8 is the mean-life of tritium in years.

In our experiment we were able to switch the cyclotron between the resonant frequencies for 6 MeV ^3H and 9 MeV ^2H in a matter of minutes; the magnetic field was left unchanged. The ^3H beam was sent through a 25 mg/cm^2 ($\simeq$95 μ) aluminum foil, and identified and counted by a 15 μ silicon dE/dx detector in coincidence with a 500 μ silicon total E detector. We counted 136 ^3H atoms in 4 minutes of observation, or about 0.57/sec. (Most of the time spent at the cyclotron was used performing various tests to convince ourselves that we really <u>were</u> observing tritium, and that the background counts really were zero in number.) 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} ions/sec. Thus the observed $^3H/^2H$ ratio is 2.7×10^{-14}; using Eq. 14, we calculate t = 33 years, remarkably close to the known age of 24 years.

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 is not statistical but systematic: the uncertainty of the implicit assumption that the efficiency of the cyclotron was the same for the two beams. The two efficiencies may differ by 50% or more; in future experiments they will be measured directly by accelerating samples of known tritium and deuterium content before introducing samples of unknown age. Even without such a calibration, however, the present experiment does demonstrate the feasibility of using the cyclotron for radioisotope dating.

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 which can be dated while simultaneously reducing the size of the sample required. The cyclotron can be used to detect atoms or simple molecules which are present at the 10^{-18} level or greater. For ^{10}Be dating, one can go back 34 million years with a sample of rock 10 cm^3 in volume; for ^{14}C dating: 88 thousand years with a 25 mg carbon sample; for ^{53}Mn dating: 35 million years with a 10 cm^3 rock sample; for tritium dating: 153 years with a half-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 $\delta t/t$ in the age is small even if there are large uncertainties in the rates of production or of deposition of the isotopes.

Needless to say, a cyclotron is more expensive to build and to operate than an ordinary mass spectrometer. But over 50 cyclotrons with the potential to do radioisotope dating already exist, and their application to important problems of dating and trace-element analysis should prove very fruitful.

REFERENCES AND FOOTNOTES

1. L.W. Alvarez and R. Cornog, Phys. Rev. 56, 379 (1939); Phys. Rev. 56, 613 (1939).

2. R.A. Muller, L.W. Alvarez, W. Holley, E. Stephenson, Lawrence Berkeley Laboratory Report LBL-5399 (to be published).

3. The technology of the "standard" mass spectrometer is reviewed by T. Alvager and J. Uhler, in Progress in Nuclear Techniques and Instrumentation, F. Farley ed. (North-Holland, 1968).

4. A general review of cosmic-ray produced radioactivity on the earth is given by D. Lal and B. Peters in Handbuch der Physik, Vol. XLVI/2, 551 (Springer-Verlag, 1967).

5. New data, along with a review of the theoretical and experimental situation for ^{10}Be and ^{26}Al appears in J.L. Reyss, Y. Yokogama, S. Tanaka, Science 193, 1119 (1976).

6. The half-life of ^{10}Be is 1.5 x 10^6 years, and not 2.5 x 10^6 years as has been frequently quoted in the literature. See F. Yiou, G. Raisbeck, Phys. Rev. Lett. 29, 372 (1972), and E.M. McMillan, Phys. Rev. C 6, 2296 (1972). The other half-lives as well as isotopic masses used in this report are taken from the compilation Table of Isotopes by C.M. Lederer, J.M. Hollander, and I. Perlman (Wiley, 1967).

7. B.S. Amin, D.P. Kharkar, D. Lal, Deep-Sea Res. 13, 805 (1966).

8. S. Krishnaswami, B.L.K. Somayajulu, W.S. Moore, in Proceedings of the Conference on Ferromanganese Deposits on the Ocean Floor, 117 (Lamont-Doherty Geological Observatory, 1972).

9. A.P.V. Vinogradov, as cited in V. Valkovic, Trace Element Analysis Wiley, 1975).

10. The range and ionization rate differences can be calculated from the tables and formulas appearing in L. Northcliffe and R.F. Schilling, Nuclear Data Tables 7A, (1970). Straggling is difficult to estimate, because it serves not only from fluctuations in the energy lost to electrons, but also from fluctuations in the net charge of the ion as seen by the electrons. Recent data relevant to this question appeared in K.H. Schmidt, H. Wohfarth, H.G. Clerc, W. Land, H. Schrader, and K.E. Pferdekamper, Nucl. Inst. Meth. 134, 157 (1976).

11. W.F. Libby, Phys. Rev. 69, 671 (1946); E.C. Anderson, W.F. Libby, S. Weinhouse, A.F. Reid, A.D. Kurshenbaum, and A.V. Groose, Phys. Rev. 72 931 (1947). See also W.F. Libby, Radiocarbon Dating (U. Chicago Press, 1955), and Radiocarbon Variations and Absolute Chronology, Ingrid U. Olsson, ed. (Wiley, 1970).

12. We use here the anti-Bayesian approach to estimation of parameters. Thus the errors for a detection of one event are derived from the observations that if the true rate were 1 + 1.36 = 2.36 then the probability of detecting one count or less is 32% (corresponding to one standard deviation), and that if the true rate were 1 - 0.62 = 0.38, the probability of one count or more is 32%. See, for example, F.T. Solmitz, Annual Reviews of Nuclear Science 14, 375 (1964).

13. J. Marion and F. Young, Nuclear Reaction Analysis (Wiley, 1968).

14. J. Arnold, Ann. Rev. Nucl. Sci. 11, 349 (1961); M. Honda and J.R. Arnold, Handbuch der Physik, Vol. XLVI/2, 613 (1967).

15. C.W. Allen, Astrophysical Quantities (Univ. of London, 1973).

16. J.C. Higdon and R.E. Lingenfelter, Nature 246, 403 (1973).

17. G. Cowan, D. Ott, A. Turkevich, L. Machta, G. Ferber, N. Daly, Science 191, 1048 (1974).

18. W.F. Libby, Proc. Nat. Acad. Sci. 39, 245 (1953).

19. S. Kaufman and W.F. Libby, Phys. Rev. 93, 1337 (1954).

20. J.S. Leventhal and W.F. Libby, J. Geophys. Res. 75, 7628 (1970); R.L. Michel and H.E. Suess, J. Geophys. Res. 80, 4139 (1975); R.L. Michel, Nature 263, 103 (1976).

21. If the sample is purchased in standard one-liter containers, then care should be taken to see that the remaining 0.5 liter is disposed of properly.

22. D. Lal and B. Peters, Prog. Elem. Part. Cosmic Ray Phys. 6, 1 (1962).

23. The literature on the tritium question includes: H. Craig, Phys. Rev. 105, 1125 (1957); F. Begemann, Z. Naturforsch 14a, 334 (1959); and J.A. Simpson, J. Geoph. Res. 65, 1615 (1960).

24. See for example the Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., vol. 6, p. 815-918 (Wiley, 1968).

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