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RADIOCARBON DATING WITH A CYCLOTRON

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ABSTRACT

A technique is described for detecting and measuring the high energy ^{14}C beam from a natural sample ionized in the Berkeley 88-inch cyclotron. An intense nitrogen background was removed using its shorter range in a xenon gas cell immediately ahead of the detector. Beams from several samples were compared by rapidly switching the CO_2 gas source feed. The ^{14}C concentration in an unknown sample was measured relative to that of a sample 465 years old to obtain an age of 5900 $\pm$ 800 years.

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1. Introduction

The use of a cyclotron and its associated particle detectors to separate and count the ^{14}C atoms in a natural carbon sample was recently proposed by Muller[1]. Within one year, we had measured the age (or the ^{14}C concentration) of an unknown sample and compared our answer with the age obtained using standard beta-decay counting techniques[2]. For this measurement, it was possible to count ^{14}C atoms at a level of less than 1 part in 10^{12} of the original carbon sample, or below the level at which ^{14}C appears in the atmosphere. In this paper, we describe the methods used to obtain that age. A range separation technique was developed to remove the intense ^{14}N background from the cyclotron beam and a rapid switching technique was developed to compare the ^{14}C concentration among several samples. These methods are not specific to ^{14}C, and with some variation have been applied to ^{3}H (ref. 1), ^{10}Be (ref. 3-5), and ^{36}Cl.

Concurrent work with tandem Van de Graaff accelerators has also shown the feasibility of detecting ^{14}C from natural carbon samples[6,7], and ages measured with the tandem accelerator have been compared to standard beta-decay ages[8]. With tandem accelerators, the instability of the $^{14}N^{-}$ in the injected beam provides an alternative to the range-separation technique for nitrogen removal. Recent work[9] has also been reported on the detection of ^{36}Cl.

Samples to be analyzed were introduced in the form of CO_2 gas in to the ion source and their constituent atoms ionized, extracted, and accelerated as beam. The cyclotron was tuned to accelerate mass-14,

and the ^{14}C atoms were detected by charged particle counters placed in an external beam line.

The attractiveness of this technique lies in its sensitivity[1]. Under conditions similar to the acceleration of ^{14}C, ^{12}C from the ion source produces 2-4 x 10^{13} particles/sec of external beam. Thus, only a few minutes of integration time are required to obtain a measurement of ^{14}C concentrations near the natural level (1.2 x 10^{-12} of ^{12}C). Since little source gas is used in the process, it is possible to use samples 100 times smaller than the 1 to 10 grams usually required for standard beta-decay counting. If contamination can be kept to a minimum, one should also be able to extend the useful range of ^{14}C-dating by many half-lives.

The cyclotron not only accelerates the beam, but simultaneously acts as a high-resolution mass spectrometer with exceedingly low tails in its mass spectrum[10]. Consequently nitrogen ions, which appear in the beam with a charge-to-mass ratio unresolved from that of ^{14}C, are the only background. Molecular ions are not present in the charge 3^+ beam. The nitrogen comes from air leaks which contaminate the gas in the cyclotron's internal ion source. Typically 1-10 nA of ^{14}N are accelerated, too high a level to be sorted in charged-particle counters. To remove the ^{14}N from the beam we made use of the fact that its range is approximately 30% less than that of ^{14}C. The nitrogen was stopped in a xenon gas cell (discussed in section 2.) with thin windows to isolate it from the cyclotron vacuum. The ^{14}C ions were detected in an ionization chamber/silicon detector telescope[11] behind the gas cell.

In order to obtain an age from an accelerated sample, it is necessary to know the $^{14}C/^{12}C$ ratio. This was measured by comparing the ^{14}C beams in rapid succession from three samples: the unknown, a sample containing a known ^{14}C concentration previously measured by decay counting, and a sample (blank) containing no ^{14}C. The use of a blank was required because of ^{14}C contamination from the cyclotron interior. The CO_2 manifold design used in the rapid sample cycling is discussed in section 3.

2. ^{14}N absorption and ^{14}C detection

The most serious problem impeding ^{14}C detection was the removal of the nitrogen from the beam. Of the solutions suggested in ref. 1, we chose the range-absorption technique because of its simplicity and low cost. Although the range difference between ^{14}C and ^{14}N is about 30%, not all of this difference is available because of nitrogen straggling beyond the nominal range. The difference in ranges can be increased somewhat by going to higher beam energies. The absorbing material must be sufficiently uniform so that the straggling is not dominated by imperfections or voids in the material. Crystalline materials are unsuitable because of their anisotropic stopping power due to channeling. It is also necessary to choose a material with high Z and a beam energy so that the Coulomb barrier for nitrogen is sufficiently high to prevent reactions that produce ^{14}C. The need to avoid nuclear interactions puts an upper limit of approximately 60 - 70 MeV on the particle energy; the need to have sufficient energy in the emerging beam for accurate particle identification prescribes a lower limit to the beam energy of about 30 MeV.

Both gold foils and silicon crystals were tried as the stopping material with only limited success, due to excessive straggling. For the silicon crystal there was evidence that the straggling was due to channeling; for the gold foils it was due to non-uniformities in the thickness of the foil. The requirements for the experiment were finally met by using xenon gas as the absorbing material, with thin platinum/gold foils forming the window between the gas and the cyclotron vacuum (see figure 1). The xenon chamber was 9.7 cm long, and pressures between 0.2 and 0.5 atm were sufficient to stop nitrogen ions in the range of 40-60 MeV. The xenon pressure was adjusted remotely by operating solenoid valves connected to a xenon gas bottle and a vacuum pump. Each solenoid valve was in series with a needle valve to regulate flow.

Care was taken in the design of the gas cell to assure that all materials exposed to the nitrogen beam were of sufficiently high atomic number Z that the Coulomb barrier would inhibit the nuclear reactions converting ^{14}N into spurious carbon. The foils for the gas cell consisted of a layer of platinum 670 $\mu g/cm^2$ thick and one or more layers of gold 620 $\mu g/cm^2$ thick supported on chemically-etched tungsten grids[12] (see fig. 2). The layers of gold sealed pinhole leaks in the platinum. At 60 MeV, the nitrogen ions lose 1.3 MeV in the entrance foil, and a pinhole would add only 2.7% to the nominal range. The large-mesh grid was 0.1 mm thick and provided the strength to hold the pressure; the small mesh grid resting on the first was 0.03 mm thick and supported the platinum foil. The combined clear aperture was 65%.

Platinum was used for the window material because of its ability to hold an atmosphere of pressure across the 0.3 mm apertures of the fine-mesh grid even when exposed to 10-100 nA of ^{14}N. For lower nitrogen currents, gold alone was used. For other applications (e.g. ^{36}Cl detection and dating) where the high-Z requirement is eased and only picoampere currents encountered, polypropylene windows have been used instead of gold.

The transmission of nitrogen ions through the gas cell was measured as a function of xenon pressure for 40 MeV incident ions. To be detected in our ionization chamber, the ions emerging from the gas cell had to have a residual energy greater than 0.8 MeV. The incident nitrogen flux was adjusted to keep the ionization chamber count rate in the range 500-50,000 min^{-1}; measurements were repeated after each flux adjustment to preserve the normalization. The results, covering a range of nearly 10^9, are shown in fig. 3. These measurements were not corrected for the time variation in the ion source output, which is typically less than a factor of two in the half hour required to measure this curve. These measurements fall gradually at first due to losses from multiple Coulomb scattering in the absorber. At the endpoint of the nitrogen range, the curve falls steeply with a shape dependent on the straggling of nitrogen ions.

The transmission losses due to multiple scattering were calculated from the rms scattering angle for the absorber as given by eq. (2) of ref. 13. The range-energy relations of Northcliffe and Schilling[14)] were used to scale the straggling with xenon gas pressure. To obtain the observed nitrogen range, we found it necessary to multiply the

energy scale of ref. 14 by a factor of 0.84. This transmission curve was convolved with a gaussian to simulate the range straggling. The theoretical curve is shown in fig. 3. Factors multiplying the rms scattering angle and the width of the gaussian were adjusted to obtain qualitative agreement with the transmission requirements.

Using this model, a similar curve (see fig. 3) was calculated for ^{14}C. For values of the ^{14}N transmission less than 10^{-9}, the ^{14}C curve is still high, indicating that the ^{14}C ions are well separated from the nitrogen and have sufficient energy to be detected and identified. Because of multiple scattering, the efficiency of the particular absorber-detector combination used here appears to be about 10%.

The ^{14}C ions were detected by the ionization chamber and a heavy ion silicon detector[15] operated as a telescope[11]. A comparison of the charge deposited in the two detectors served to confirm the Z of the carbon ion. A coincidence requirement between the two detectors eliminated background from stray radiation. A typical two-dimensional plot taken at 40 MeV is shown in fig. 4, along with the experimentally-determined loci for nitrogen and carbon ions of various energies. The region around ^{14}C is free of counts. During several hours of running, no nitrogen penetrated the gas cell to be detected in the ionization chamber. This corresponds to a rejection factor against nitrogen greater than 10^{14}. If the nitrogen current into the absorber is increased by a factor of 100, carbon reaction products begin to appear. These can be distinguished from the ^{14}C signal by their energy spectrum (shown in projection in fig. 4). The width of the ^{14}C signal in energy (fig. 4) is due to straggling. This width is larger than

the predictions of ref. 16 by a factor of 1.4. The energy spread of the cyclotron beam contributes less than 5% to this width.

The absorber and detector system were most effective in the 40-60 MeV range. To obtain this energy, the ^{14}C ions were accelerated in the 3+ charge state. Since 14 and 3 are relatively prime, this choice has the additional advantage that no lighter ions (with their longer range in the absorber) are accelerated simultaneously. The CO_2 was ionized in a Penning Ion Gauge source[17], which gave good production coupled with reasonable source lifetime.

These tests have shown that ^{14}N can be eliminated from the cyclotron beam by absorption, and that the ^{14}C emerging from the absorber can be detected unambiguously. The sensitivity of the absorber and detector is limited by the carbon generated in nitrogen-induced reactions, most likely on impurities in the gas cell materials. We measured the reaction rate by increasing the nitrogen current; with the present nitrogen current and gas cell such reaction products form less than 1% of the carbon events from a modern sample.

3. Gas manifold

A useful measurement of the ^{14}C concentration in a sample must determine the ratio of ^{14}C to ^{12}C. A direct comparison cannot be made since the cyclotron will not simultaneously accelerate these two isotopes. In principle the beams could be compared by rapidly changing the resonance frequency to accelerate mass-14 and mass-12, or even mass-13. At the Berkeley 88-inch cyclotron, a resonance change takes about 1 minute. However, the efficiency for beam production is mass dependent, and must be calibrated by a known sample under

similar conditions in the ion source and accelerator. We took an alternative approach and constructed a sample changing system that switched from one gas bottle to another rapidly. When the perturbations caused by switching were made sufficiently small, we could compare directly the ^{14}C beams from a known and unknown sample without reference to another carbon isotope.

Even when samples containing no ^{14}C were used in the ion source, a ^{14}C signal was registered in the detectors. Extensive measurements and checks were made of this background. It appears to consist of ^{14}C contamination of the ion source discharge by highly enriched carbon from the interior of the cyclotron. The carbon may originate in graphite shielding blocks that have been exposed to the beam for long periods of time. It was necessary to include a "blank" CO_2 sample known to be free of ^{14}C in the switching routine to measure this background. It is likely that this background will be eliminated by using an external ion source where the source environment can be rigidly controlled. The design and installation of such a source is in progress. Until it is installed, the precision of our ^{14}C experiments is limited by this background subtraction. For measurements we have made with ^{10}Be and ^{36}Cl no similar background exists.

The gas manifold was constructed both to switch rapidly among at least three samples and to regulate the gas pressure for the ion source. Internal volumes were kept small to reduce the amount of possibly precious sample gas filling the manifold lines, and to reduce the switching times. Dead spaces not swept clean by the gas flow were deliberately avoided. A schematic of the manifold is shown

in fig. 5. Valves used during an experiment were operated with solenoids or motors.

The CO_2 gas samples were kept in 300 ml stainless steel bottles, each equipped with a pressure gauge and valve which was easily attached to the system. Pressure out of the bottle was regulated to about 2/3 atm before entering the junction with other bottles. To eliminate small pressure differences from different bottles, the gas passed through a final regulator which delivered a pressure of about 1/3 atm. A motor driven needle valve dropped the pressure to about 6 Torr before sending it to the gas line to the source. Impedance in the gas line further reduced the pressure to less than 10^{-2} Torr at the ion source.

Changing samples was accomplished in several seconds with only small changes in the gas pressure at the ion source and without extinguishing the arc. To reduce cross sample contamination, the junction among the bottles was evacuated for a few seconds between the time one bottle was closed and the next opened. In addition, the space between the last regulator and the needle valve was evacuated briefly (less than 1 s). With early designs of the manifold system, we observed the residual count rate left over from a previous sample gradually disappear over a period of several minutes. This residual was traced to gas trapped within excess volume in the manifold. By reducing this volume and by flushing the manifold from one to three times at each gas change, we reduced the residual gas to a point where the residual count rate from a previous sample decays with a time constant of less than 0.5 minutes. The manifold used for the blind measurement

consumed about 50 cc at 1 atm of CO_2 for each change. The flow rate into the ion source was less than 1 cc/min. A total of about 150 mg of carbon was used to obtain the age. This is already about two orders of magnitude less than the 10 grams typically required for the beta-decay counting technique. Subsequent improvements in the manifold have further reduced the gas consumed in flushing by a factor of ten.

Although the brief switching vacuum did affect the ion source pressure, a thermocouple gauge at the manifold output indicated that the gas pressure stabilized in a few seconds to within 3% of its original value. Beam from the ion source depends crucially on pressure[18] and this beam was stable only to within 10%. Some of this switching effect was removed by monitoring the nitrogen current.

The present efficiency for ^{14}C detection is about 10^{-5}. About a factor of 10 is lost in multiple scattering from the absorber and in the beam transport from the cyclotron exit to the detector. Rebuilding the absorber-detector system with improved geometry can substantially reduce this loss. During data collection the ion source gas feed was run deliberately high to suppress ^{14}C from the cyclotron interior. An external ion source could be operated more efficiently.

4. Normalization and data collection

In spite of the ability to switch gas samples rapidly, comparison of the ^{14}C count rate with different samples was complicated by changes in the cyclotron beam current. These changes are due mainly to fluctuations in the source output with time, and some additional interruptions result from sparks and discharges around the cyclotron dee. To improve

the accuracy of the comparison among samples, it was necessary to measure the cyclotron output simultaneously with data collection to correct for these instabilities. In part, the additional accuracy was needed because of the large ^{14}C background.

The cyclotron output was monitored by integrating the external ^{14}N beam during the collection of ^{14}C events. For this experiment, the ^{14}N current was taken from the jaws of the collimator at the exit of the cyclotron some distance upstream of the detector. Normalization of the ^{14}C count rate with this nitrogen current successfully removed the effects of short term (less than 5 minutes) variations in the source output. Over a longer time period, however, the nitrogen and carbon signals do not remain correlated, as they have different origins and their distribution within the beam at the collimator may change. Some of this variation will be removed in the future by monitoring the nitrogen current at the absorber. In addition, with an external ion source the ^{12}C or ^{13}C could be monitored.

For each sample, ^{14}C events were accumulated and the nitrogen current integrated for 1 minute. After repeating the measurement on one sample several times to verify reproducibility, the gas sample was changed and data collection continued. Measurements comparing a blank, an unknown, and a sample of known age (465 yr) are shown as a function of time in fig. 6. The ion source output falls slowly with time. The nitrogen points vary smoothly, unaffected by gas sample changes. This confirms that the manifold is keeping the pressure of the gas feed properly regulated. The variation of ^{14}C count rate

from sample to sample is clear. The errors plotted for each ^{14}C measurement are statistical.

Figure 7 shows the same measurements, now displayed as the ratio of ^{14}C count rate to integrated nitrogen current. Most of the time variation is gone. To extract an age, these measurements were fit to a single third order polynomial with an overall factor for the unknown and known count rates relative to the background. This model assumes that the background is always a constant fraction of the real ^{14}C count rate, and that the time variation in fig. 7 is due entirely to changes in the ratio of carbon events to nitrogen integrated current.

The ratio of unknown to known count rates after background subtraction is 0.51 ± 0.05. The error was estimated by varying the fitting parameters until the chi square of the fit had increased by 1. Using a radiocarbon halflife of 5570 yr, the age of the unknown is calculated to be 5900 ± 800 yr, with the error dominated by the statistical uncertainty in the background subtraction. The age measured by beta-decay counting was 5080 ± 60 yr (ref. 19), differing from our value by about one standard deviation.

In each small group of measurements on one sample, there is no systematic deviation of the first point in the direction of the ^{14}C count rate for the previous sample. This is consistent with a clearing time constant in the gas manifold of less than 0.5 minutes. Contamination from ^{14}C that remains in the gas handling system for a much longer time becomes part of the ^{14}C background from the cyclotron and is removed by subtraction.

5. Conclusions

We have shown that one can use a cyclotron to detect and count ^{14}C atoms in a natural carbon sample. The major source of background expected, ^{14}N accelerated with the ^{14}C, was eliminated by using a xenon absorber. In spite of a ^{14}C background from radioactive carbon inside the cyclotron, rapid switching of the gas feed between the unknown, a standard, and a blank allowed measurements to be made of the $^{14}C/^{12}C$ concentration in the unknown. Less than 1% of the 1-20 grams that are typically required for the standard decay-dating technique were required to measure the age of an object approximately one half-life old. Since most of the carbon consumed in our measurements was used to flush the gas manifold, improved manifold design should reduce the carbon consumed by another order of magnitude.

The sensitivity and accuracy of the cyclotron technique are presently limited by the existence of the background ^{14}C. The primary source of error is from systematic effects in the subtraction of this background. If the external ion source has the expected effect of eliminating this contamination, then we anticipate that the full predicted[1)] sensitivity of the cyclotron technique will be reached: 40 to 100 thousand years for 1 to 100 mg carbon samples.

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*Work performed under the auspices of the Department of Energy.

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Figure Captions

Fig. 1. Cross-sectional view of xenon gas cell and detector telescope. Gas flow is regulated by a solenoid (S) and needle (N) valve in series. Features of the system are discussed in the text.

Fig. 2. Tungsten supporting grids for gas cell windows. The centers of adjacent large hexagons are 1 mm apart.

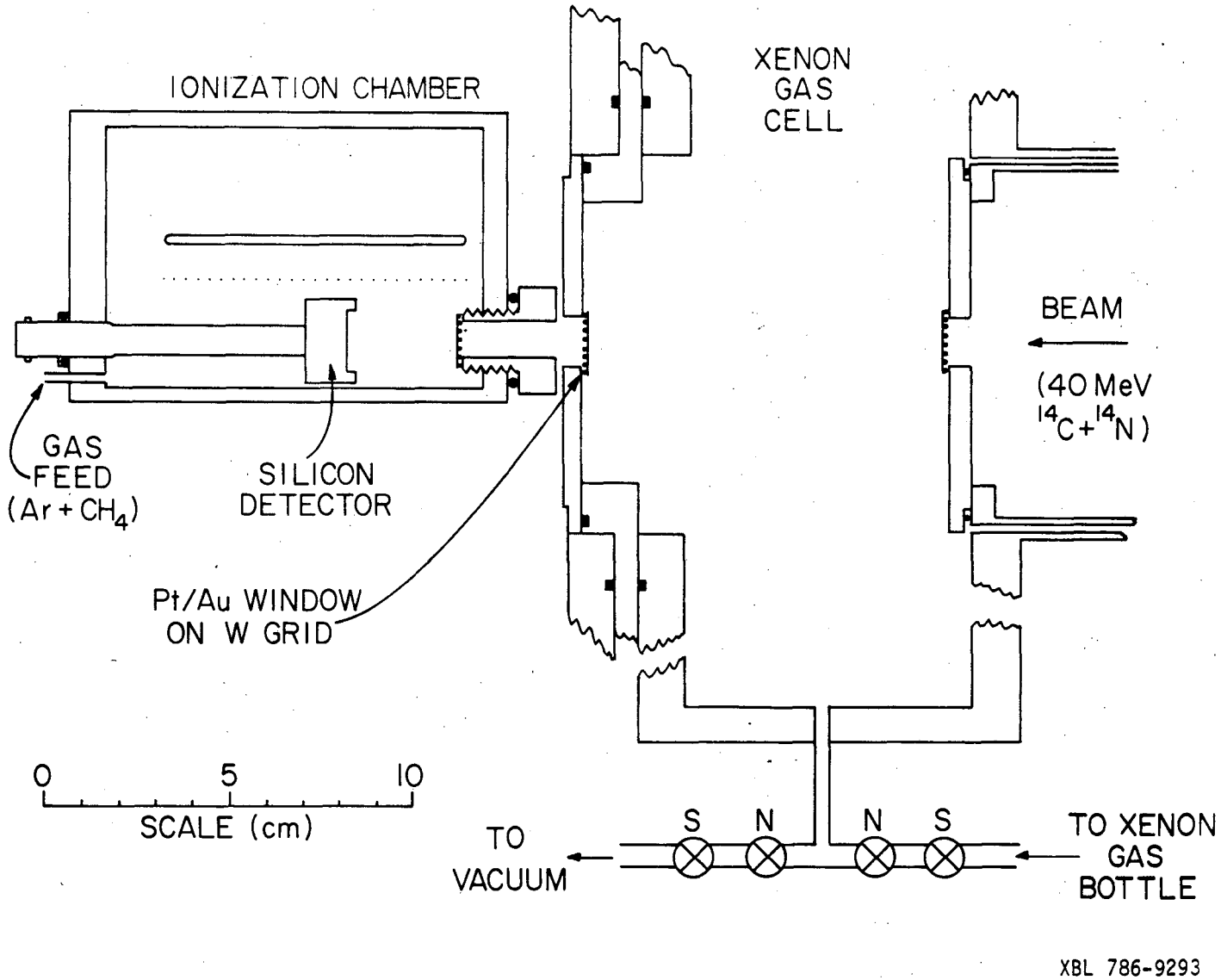
Fig. 3. Transmission of nitrogen through the gas cell as a function of xenon pressure. The fitted curve for nitrogen was used to predict the curve for carbon (see text).

Fig. 4. Events recorded in the detector telescope as a function of energy deposited in the ionization chamber (E) and silicon detector (E). The size of the plotting symbol varies as the logarithm of the number of events. The lines show the loci of carbon and nitrogen events. Projected plots show ^{14}C with low and high nitrogen currents. At high currents, carbon reaction products appear in the spectrum.

Fig. 5. Schematic of CO_2 gas manifold. Features are discussed in the text.

Fig. 6. Beam currents for ^{14}C and ^{14}N for each sample as a function of time (hrs). The normalization of the nitrogen current is arbitrary.

Fig. 7. Ratio of ^{14}C to ^{14}N beam currents (arbitrary units) as a function of time (hrs). Lines represent fits to the ratio for each sample.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S N N S
TO XENON GAS BOTTLE
XBL 786-9293

Fig. 1.

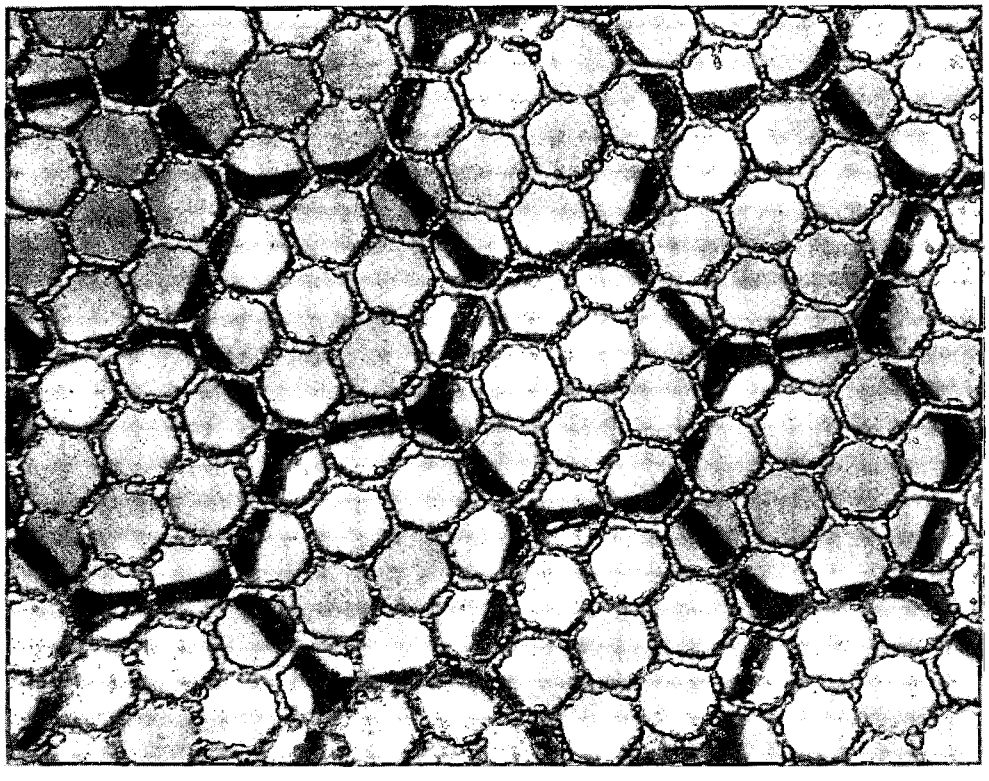

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Fig. 2.

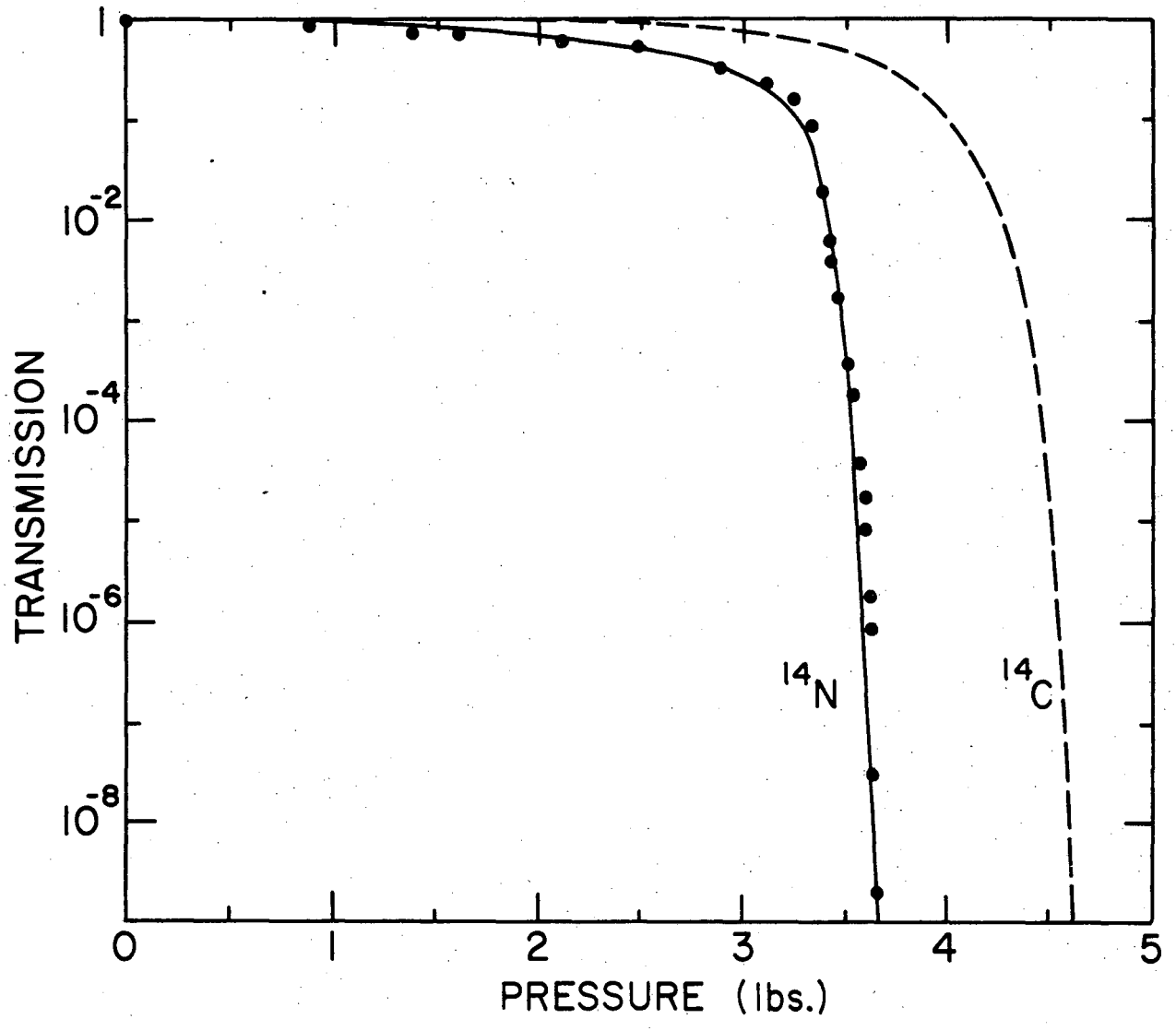

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Fig. 3.

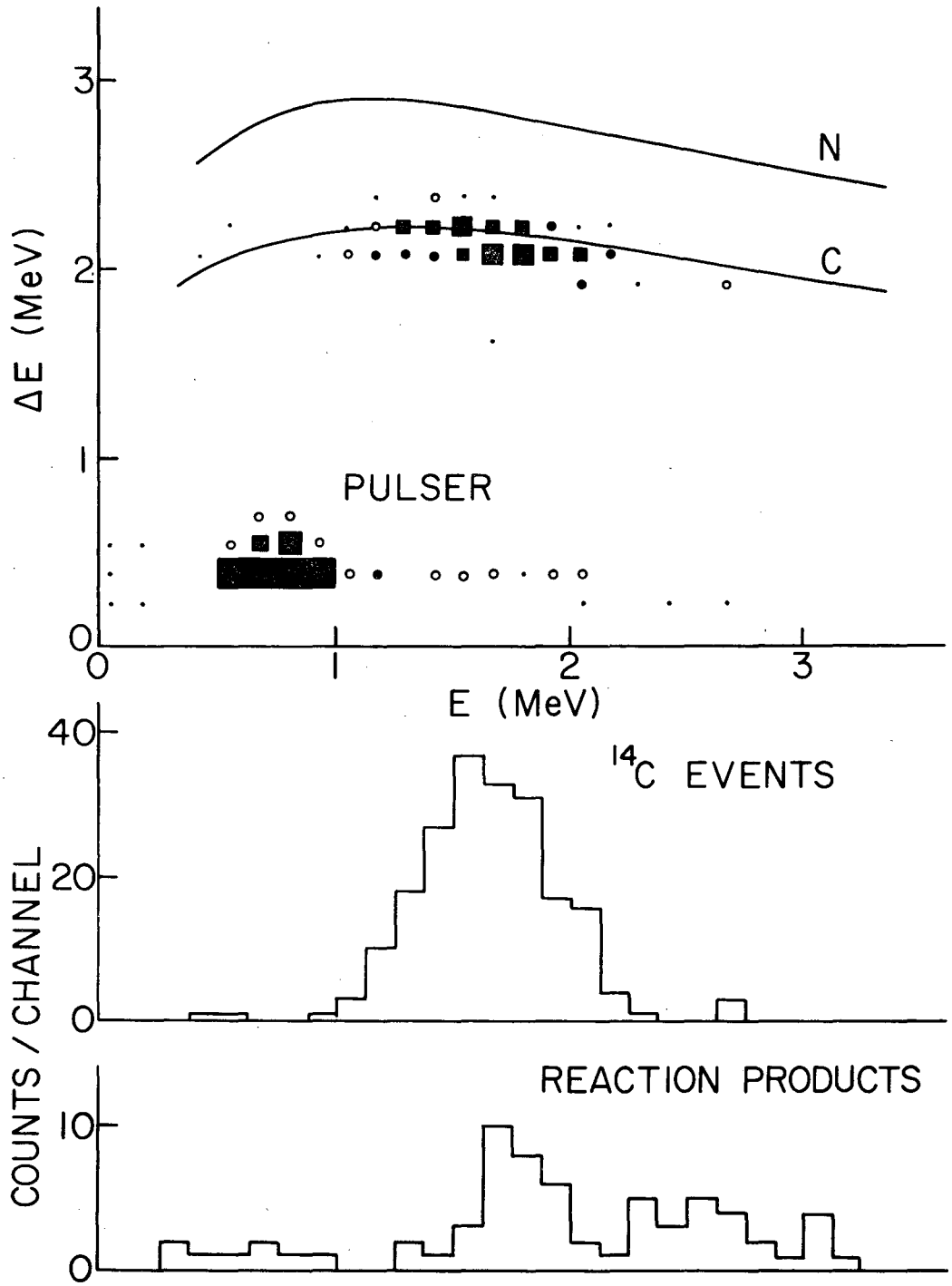

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Fig. 4.

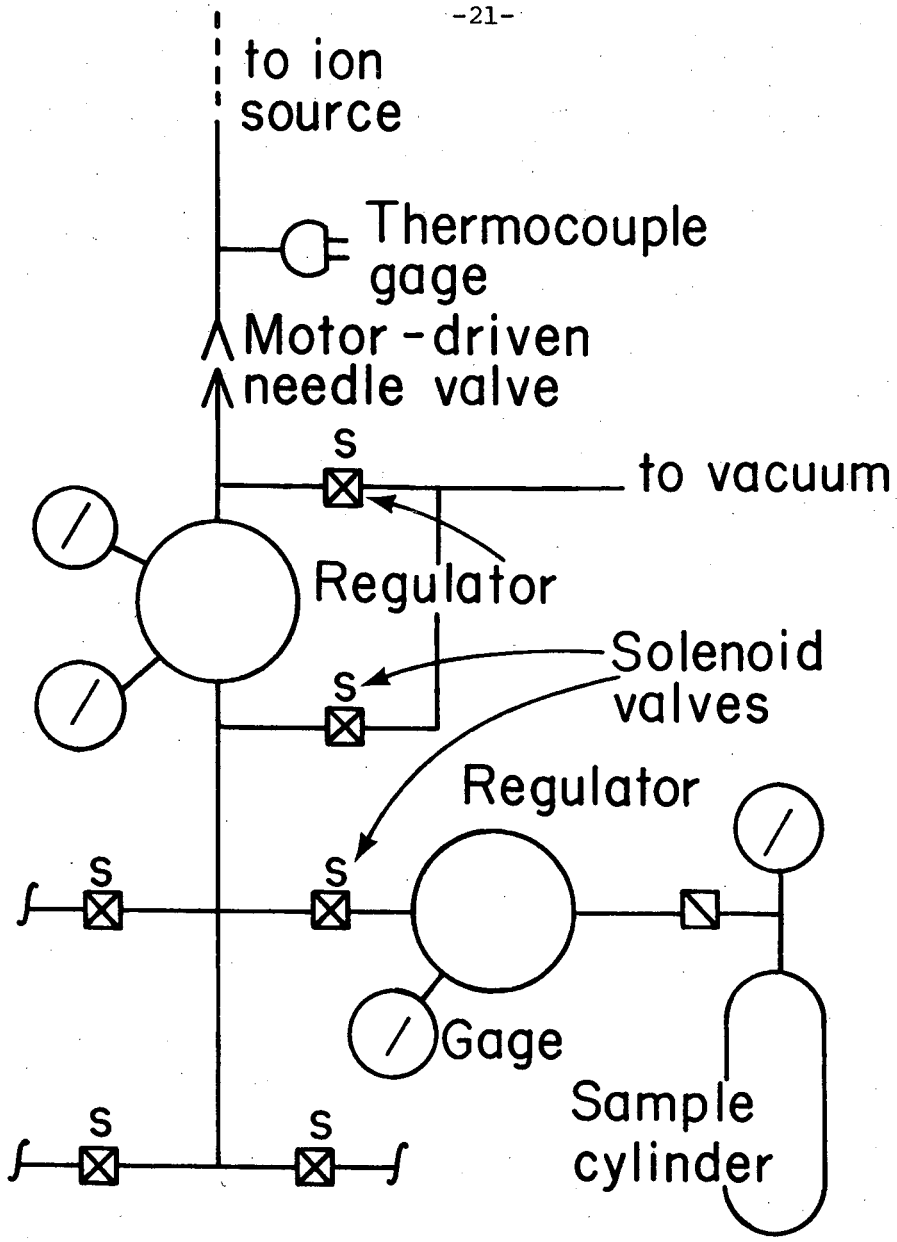

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Fig. 5.

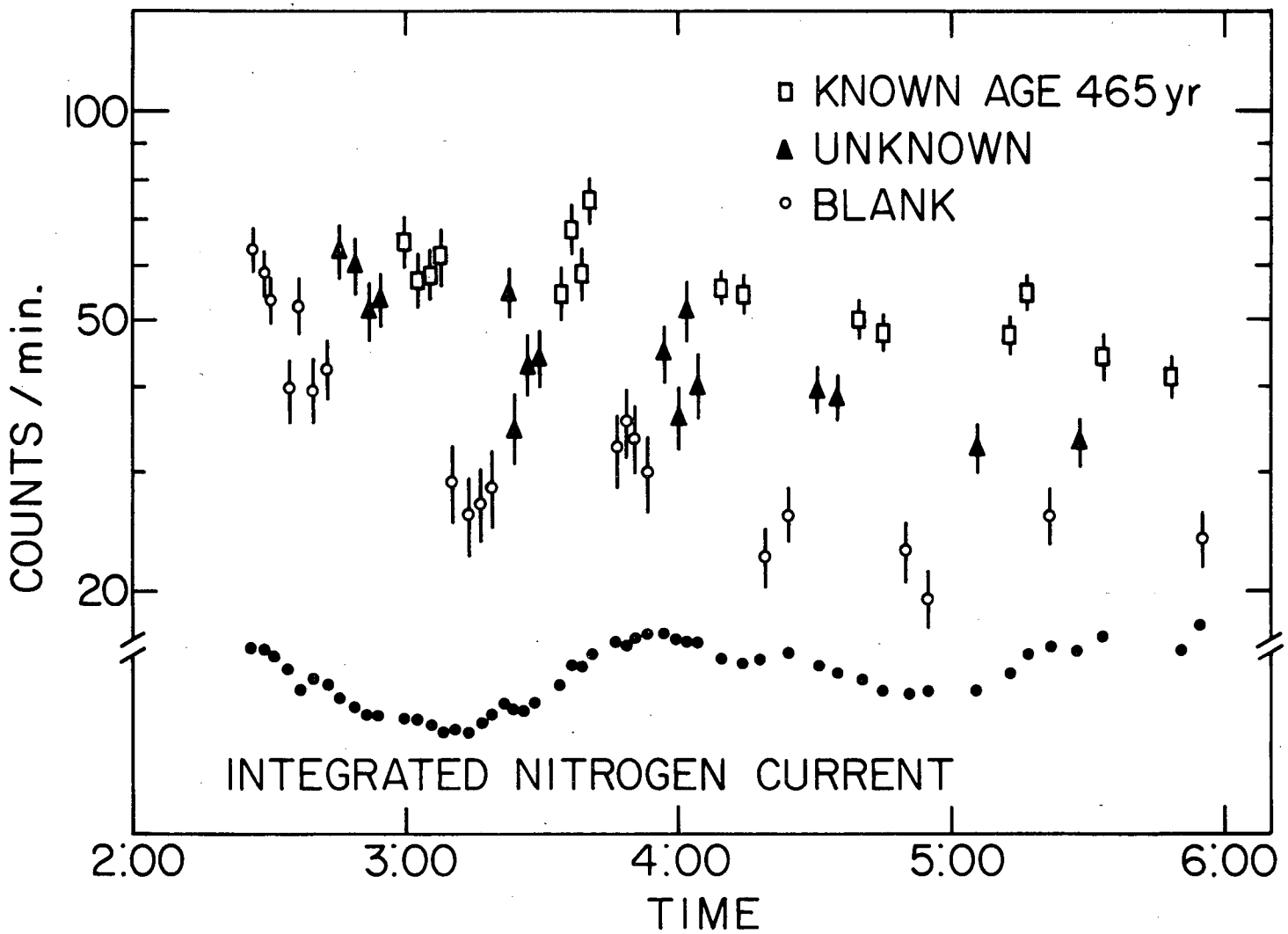

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Fig. 6.

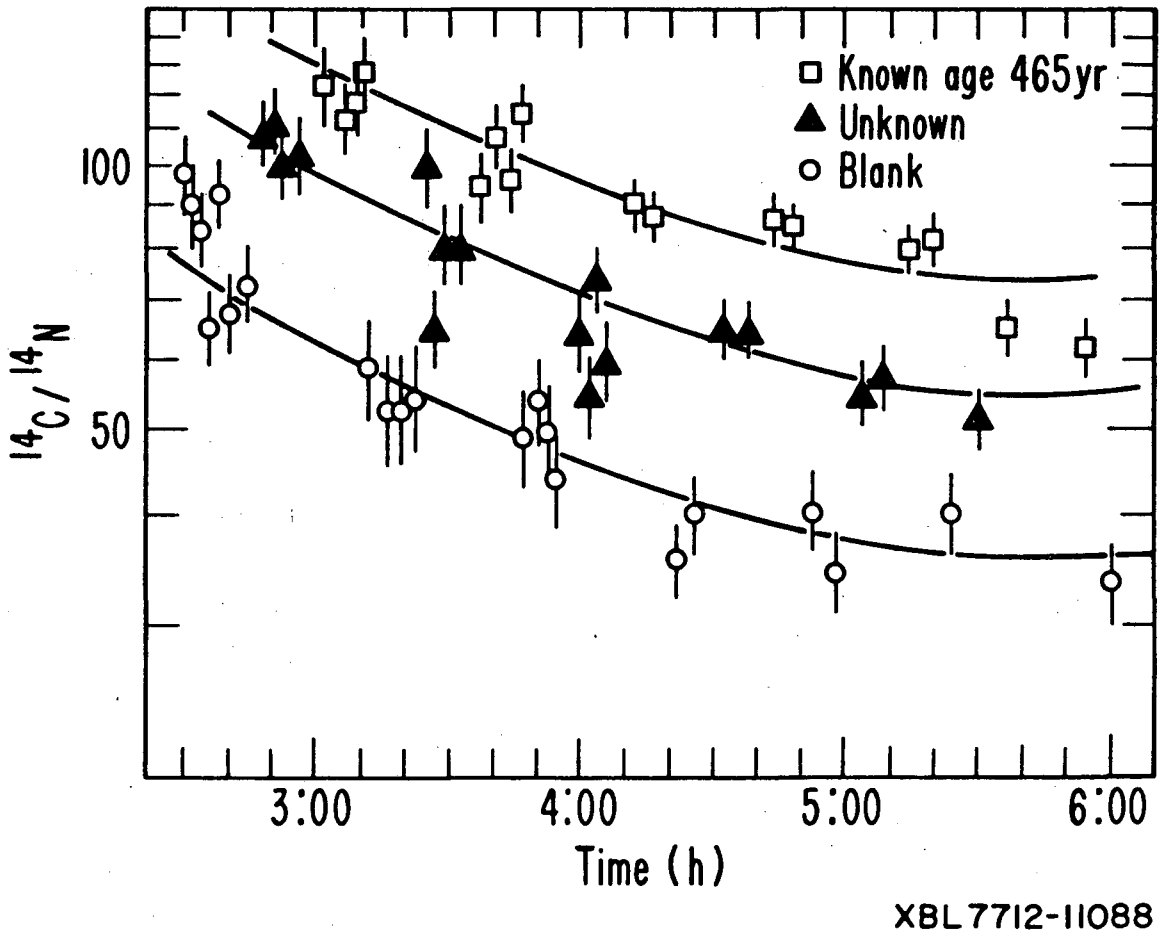
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Fig. 7.

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