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The application of accelerator mass spectrometry for the radiocarbon dating of earthquakes

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Craig, John Michael, M.S.

San Jose State University, 1990

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The Application of
Accelerator Mass Spectrometry
for the Radiocarbon Dating of
Earthquakes

A Thesis

Presented to

The faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree of
Master of Science

By

John Michael Craig

May 1990

Approved for the Department of Physics

Dr. Allen Tucker

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Dr. M. L. Morris

Approved for the University

Abstract

The Application of Accelerator Mass Spectrometry for the Radiocarbon Dating of Earthquakes

by John M. Craig

This thesis demonstrates the use of accelerator mass spectrometry (AMS), to measure the radiocarbon ages of material associated with prehistoric earthquakes. It describes the sample preparation and graphitization, as well as the AMS methods used for obtaining radiocarbon dates. In addition to these methods, a computer program was written to analyze the AMS data and output probable dates.

Using the facilities of the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL), we have obtained radiocarbon ages for 11 samples from an excavation at Salt Creek in the Salton Sea basin in Southern California. These dates indicate possible seismic events occurring between 1530 AD and 1200 AD.

This work is dedicated to my mother and father, who have always loved and supported me, and to Pamela, who has been my inspiration through the most challenging times.

Acknowledgements

I am deeply indebted to a number of people and organizations for their help in making this work possible.

First, I would like to thank Dr. Allen Tucker of San Jose State University for all of his encouragement, advice, and the knowledge that he has shared with me. I would also like to thank Dr. Steve Robinson of the United States Geological Survey in Menlo Park, CA, who has greatly increased my knowledge in the processes of radiocarbon dating.

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I am grateful to Dr. Patrick Williams of Lawrence Berkeley Laboratory for the opportunity to use his samples for earthquake analysis. And I am also grateful to the staff of the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory for allowing me to use their facility to analyze these samples.

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Chapter 1.

Introduction

In order to better understand the methods described in later chapters, the inclusion of some of the many advances in the chemistry, physics, and geology of radiocarbon earthquake analysis is necessary. Chapter 1 briefly discusses the theories and development of radiocarbon dating, accelerator mass spectrometry, and earthquake recurrence analysis.

A. Discovery of Radiocarbon Dating

Dr. Willard F. Libby, of the University of Chicago, first proposed the the idea of radiocarbon dating in the mid 1940's, and

had developed a method for dating by the early 1950's. By 1952, when he published his book on radiocarbon dating, the concept was widely accepted by the archaeology community. In 1960, Dr. Libby won the Nobel Prize for Chemistry for his work on radiocarbon dating.

It had already been discovered that cosmic rays created high energy neutrons in the upper atmosphere. The energetic neutrons cause several different reactions with nitrogen-14, the most abundant constituent of the atmosphere. The most probable reactions were:

For neutrons in the energy range of 0.4-1.6 MeV, the third reaction is dominant. The ^{14}C decays:

with a half-life of 5730 years. The value 5568 years, originally determined by Libby, is still widely used in the radiocarbon literature.

Because of this relatively long half-life, atmospheric circulation distributes ^{14}C uniformly across the surface of the earth. The amount of radiocarbon in the atmosphere is in an equilibrium state, with a balance of production and decay rates. The ^{14}C , in the form of CO_2 , is continuously absorbed by all living

organisms. When an organism dies it no longer absorbs carbon dioxide; thus the ^{14}C concentration in the organism decreases.

Using these facts Libby was able to calculate an age for a sample by measuring the ^{14}C activity of the sample and comparing it with the average modern activity. Libby measured the average modern activity of terrestrial biosphere samples to be 15.3 disintegrations per second per gram of carbon. The elapsed time since the "death" of a sample was calculated using the decay equation:

$$A(t) = 15.3 e^{(-.693t/5568)},$$

where $A(t)$ is the activity of the sample at t years after "death".

The half-life of ^{14}C is relatively large, which means that the decay probability is small. Thus accurate beta decay data requires a large sample of carbon and a long counting time.

Libby was able to measure the activity of natural samples with a screen-wall Geiger tube.

A metal sleeve coated with elementary carbon from the sample was inserted into the Geiger counter. To form the elementary carbon, the sample was combusted with copper oxide to form carbon dioxide. The resulting carbon dioxide was reduced to elementary carbon using magnesium shavings:

Using the methods described above, Dr. Libby was able to evaluate dates for many important archaeological objects, such as one of the Dead Sea scrolls and an Egyptian mummy from the Ptolemaic period. His method allowed dates to be obtained up to about 25,000 years bp (before present). (1)

B. Radiocarbon Dating Progress

Since the discovery of radiocarbon dating, several modifications have been made to the techniques. Many laboratories started to use gas-filled counters to avoid atmospheric sample contamination. These gas counters are still in use today.

Various gases have been used for this method, for example, carbon dioxide, methane, and acetylene. Both methane and acetylene are derivatives of carbon dioxide. So, the conversion from sample to carbon dioxide is the first basic step. The carbon dioxide is formed in a similar manner as mentioned in Section 1.A. For the gas counters, however, a purer form of carbon dioxide is required, so the carbon dioxide is purified by chemically removing other gases formed in the combustion process. Methods for obtaining methane and acetylene are outlined in Taylor. (2)

The sample gas is mixed with argon inside of the ionization chamber. The gas is continuously circulated through the chamber, and the ionization current, I , is measured and used for calculation of the radiocarbon activity. The average ionization current is a function of the activity:

$$I = [(E_{ave})e/W]A, \text{ where}$$

E_{ave} is the average energy deposited in the gas per disintegration (eV)

e is the electronic charge (coulombs)

W is the average energy deposited per ion pair in the gas (eV)

A is the total activity (Bq). (3)

Background from cosmic rays and other natural activity set the upper limit for beta counting between 30,000 to 60,000 years. One to five grams of carbon are required for a radiocarbon age of 40,000 years. Very precise dates, however, require more carbon, about 7-20 grams.

Some laboratories use liquid scintillation techniques for carbon dating. Certain types of organic compounds, called scintillators, emit photons when in an excited state. By combining a beta emitter, such as ^{14}C , with a scintillator, a substance is formed that will produce photons every time the ^{14}C sample emits a beta particle. A photomultiplier tube converts these scintillations into electrical pulses, which are readily counted. (2)

Another modification to the dating method was made to correct the age of a sample for the small fluctuations in the ^{14}C concentration in the atmosphere. In 1958, H. de Vries observed the variations in the ^{14}C content of wood from the 15th to the 17th centuries. Other experimenters later confirmed that the ^{14}C production rate was varying by measuring the radiocarbon content of tree rings. By using bristlecone pine trees, which live for more

than 1000 years, tree ring sequences were obtained for as far back as 5400 BC. The curve obtained by plotting the change in ^{14}C versus age was approximately a sine curve with an amplitude of about 10% and a period of about 10,000 years (see Figure 1.1). It was also noticed that the "wiggles" in the curve seemed to correspond to the sun-spot cycle. Investigators then concluded that the ^{14}C variations are due to the modulation of primary cosmic ray intensity due to variations in the magnetic field near the earth.

(4)

To more accurately determine the age of a sample, a calibration curve was made of radiocarbon age versus calendric (tree ring) date. Then any age (within the tree ring data base) determined from radiocarbon dating processes could be matched with possible calendric dates. An example of this is the calibration curve of Stuiver & Pearson (5,6) which represents tree ring data from present to approximately 8000 years bp.

C. Development of AMS Dating Process

In 1939, Dr. Luis Alvarez was able to detect the rare isotope helium-3 using a cyclotron and an ionization chamber. Before this experiment, it was thought that helium-3 was radioactive thus not present in natural helium. To make his observation he placed a thin ionization chamber with a pulse amplifier in front of the cyclotron's exit window to see the pulses of the individual accelerated ions. This was the first time that anyone had used an

accelerator to detect individual accelerated ions. He used gas-well helium in the ion-source and detected helium-3. Since gas-well helium was quite old and free of any radioactive isotopes, Alvarez' observation proved that helium-3 was stable. (7)

During World War II, a 37 inch cyclotron was reconfigured as a mass spectrometer to separate uranium-235 from uranium-238 so that the two isotopes could be evaluated for fission and neutron capture capabilities. (8)

Accelerator Mass Spectrometry (AMS) was revived in 1974, by Dr. Alvarez and a colleague Richard Muller. Alvarez mentioned to Muller that he had read a research proposal, by Michael Anbar, an employee of SRI International, which suggested that AMS could be used for radioisotope dating. Muller immediately started work on this project. In July 1976, at a colloquium at the Lawrence Berkeley Laboratory, Muller reported the first date using this new technique. The age of a deuterium sample was obtained by measuring the ratio of tritium to deuterium. He also described methods for dating beryllium-10 and carbon-14 samples. Unlike the beta counting methods, AMS counts isotopic species directly, rather than waiting for some to decay.

Muller's cyclotron technique involved five stages:

- ionization of the sample;
- acceleration of the sample;
- separation of isotope from stable background ions;

- identification of ions;
- normalization of radioisotope with respect to a stable isotope.

The cyclotron has the advantage of requiring no mass spectrometry to separate the initial "junk" ions from the ions of interest. Only the particles with the proper charge to mass ratio will be accelerated through the window. All other ions will be accelerated at a different radius. For carbon-14 dating the main background ions come from nitrogen-14. If the emerging beam current is low enough, the beam can be steered right into a particle identifier. If the current is too large, however, a filter must be added to suppress the background ions.

A disadvantage of using a cyclotron is that the cyclotron's dee is protected from the beam by graphite, which produces copious ^{14}C background.

With slight modification to this process, a tandem Van de Graaff accelerator can be used in place of the cyclotron. The tandem accelerator works on a charge transfer concept. In the first phase of acceleration, negative ions are accelerated towards a high positive potential electrode. When these ions reach the electrode the electrons are stripped away, by a foil or a gas, to form a positively charged ion. This positive ion is then repelled from the electrode by a large coulomb force. This is the second phase of acceleration.

Unlike the cyclotron, the tandem accelerator has no preference as to the mass it accelerates. It will accelerate any negatively charged ion that is introduced, so in order to retrieve the desired ions for counting, magnetic and electric filters are used to select only the ions with the correct momentum to charge ratio. The final beam enters a particle identifier where the energy and atomic number are determined.

One of the advantages to using the tandem is that it only accelerates negative ions. Since nitrogen-14 does not form a stable negative ion, this major background contributor will not be accelerated. Another advantage of this method of radiocarbon dating is that counting parent atoms instead of decays reduces the amount of required sample to less than a milligram. This means that much less of a historically significant sample will be consumed in the dating process. (9)

D. Application to Earthquake Dating

Before an analysis can be done to find earthquake frequency, the geology of the area must be studied. A geologist must know what kind of a fault is present and what effects the fault slippage will have on the surrounding terrain. In short, the geologist must have enough information to be able to associate present features of the area with past seismic events.

In the study of lateral-slip faults, it is often convenient to study areas in which a river passes over or near the fault. In many

areas like this, a seismic event will cause a diversion of the river. By finding the paths on which the river traveled in the past and dating the charcoal sediments that were deposited, dates can be found for the river diversions. (10)

Chapter 2.

Samples

Chapter 2 is a discussion of the selection and handling of samples collected for AMS counting. After a chemical pretreatment, the sample is converted from charcoal to graphite. Graphite is the preferred form of carbon to be used in the tandem's ion source because it produces strong and steady beam currents.

A. Types of Samples Used

Carbon samples collected for geologic dating are usually charcoal, which survive longer in the ground than unburned shards of wood. The reason for this is that charcoal shows resistance to chemical oxidation and decay, whereas the unburned wood will

dissolve into the humic acids of the soil. This charcoal may be in large chunks, or small flakes mixed with other sediments.

B. Pretreatment

A charcoal sample from the field must be chemically pretreated to remove traces of carbonate or humic acids picked up from the surrounding soil. The pretreatment consists of mild HCl and NaOH washes. The procedure is outlined in Appendix A. The pretreatment was performed at one of two laboratories, the Radiocarbon Laboratory at the USGS in Menlo Park, California or at the Nuclear Science Facility at San Jose State University, San Jose, California.

C. Combustion to CO₂

Before graphitization, the carbon sample is converted to carbon dioxide. The reaction used for this conversion is:

For samples containing a great deal of sediment there is a possibility of the release of volatile gases. To keep these gases from contaminating the graphitization apparatus, the sediment samples are combusted in a closed tube. A 7 mm Vycor combustion tube containing the sample and CuO is connected to a vacuum line

and vacuum sealed with a torch. The tube is then placed in a 900°C oven for 1-1.5 hours to oxidize the carbon in the sediment.

For pure charcoal samples, there are not as many volatiles, so the combustion process could be performed on the graphitization apparatus. The sample and some CuO wire are placed inside of a combustion tube which is connected to the graphitization apparatus (see Figure 2.1). The end of the tube is heated with a mild flame to oxidize the carbon. The combustion procedure is outlined in Appendix B.

D. Conversion to Graphite

Once the sample is converted to carbon dioxide, it is ready to be converted to graphite. The apparatus used was similar to the one used by Vogel (11)(see Figure 2.1). The graphitization apparatus is constructed of 1/4 inch o.d. stainless steel tubing, Swagelok junctions, and Nupro valves. There are four reaction vessels, which would make it possible to do eight graphitizations in a day, forty in a week. There is a junction located at the bottom of each reactor arm. This junction can be used to hold either a combustion system, or a bellows for closed tube samples. The bellows is flexible so that a Vycor vessel with a scored line (an etched line running the circumference of the tube) could be broken open inside the graphitization apparatus. In this way, the CO₂ can be injected into the system.

The ovens and the pressure transducers are controlled by the computer. When the carbon dioxide level inside a reactor drops to 1 percent, the computer automatically shuts-off that oven. The pressure transducers are also controlled by the computer. During the Combustion phase, the two combustor transducers are monitored as well as the manifold transducer. And during the Graphitization phase, the four reactor sensors are monitored. The schematic diagrams for the pressure transducer circuit and the oven control circuit are given in Appendix C.

The process for producing graphite from carbon dioxide follows the reaction:

Iron oxide or cobalt serves as a catalyst. The graphite forms on the catalyst surface. Convectional currents inside the assembly are established due to the temperature difference between the cold trap and the catalyst vessel. These currents assist in the flow of reactants to the catalyst. The graphitization procedure is outlined in Appendix B.

Finally, the catalyst and graphite conglomerate are pressed into an aluminum target sample holder with 1/16 inch drill stock.

Many graphitizations were run at different temperatures and using different catalysts. The results were that the temperature of the oven did not seem to affect the speed of the reaction in between 500° C and 700° C. The reaction seemed to run faster, however, when the cold trap was maintained below 0° C than at

room temperature. The cobalt seemed to be the better of the two catalysts.

The fractionation of several graphitizations using the iron oxide catalyst was measured by a gas chromatograph at the USGS in Menlo Park. Fractionation is a depletion of the natural abundance of ^{13}C in a sample. Fractionation can occur in both the combustion process and the graphitization process. The average fractionation of these samples was found to be 11 parts per thousand.

Combustion and graphitization of the sample were done at the Radiocarbon Laboratory at the USGS in Menlo Park.

E. Calibration and Background Standards

Preparation of calibration and background samples would be the same as listed above for the unknown sample.

Three different calibration standards can be used. These consist of two oxalic acid standards, OXI and OXII, and the ANU sugar standard. These standards represent samples with precisely known ^{14}C activity.

Anthracite coal obtained from deep Pennsylvania coal mines, is used for background standards. Since anthracite is very old, it is presumed that it has virtually no ^{14}C left. This makes anthracite very useful for examining the amount of ^{14}C background introduced in the graphitization process and the accelerator system.

Chapter 3.

Radiocarbon Counting

Chapter 3 describes the components of the accelerator mass spectrometer system.

A. Description of Accelerator Mass Spectrometer

The new Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL) was used for counting the samples. CAMS uses a tandem Van de Graaff accelerator for its mass spectrometry. The steps involved in the process are similar to the technique used by Muller (see section 1.C).

- 1) ionization of the sample;
- 2) acceleration of the ions to an energy of several MeV;
- 3) separation of ^{12}C , ^{13}C , and ^{14}C beams;
- 4) identification and counting of ^{14}C ;
- 5) evaluation of the ^{14}C to ^{13}C ratio.

The graphite samples are pressed into aluminum target holders as mentioned in section 2.D. These "targets" are loaded into a 60 sample carousel. The carousel allows for single target selection.

The basic components of the system are shown on Figure 3.1.

1) In the ion source a beam of 20 keV Cesium ions is focused onto the graphite target, sputtering carbon atoms from the surface. Many carbon atoms are released as negative ions, acquiring an electron from the highly electronegative Cesium deposited on the target. ^{13}C and ^{14}C beams are injected into the accelerator by a 90° magnet. The potential difference between the ion source and the magnet is switched to select either mass 13 or mass 14 beams for acceleration and analysis.

2) The negative ions are accelerated due to a highly attractive force established by a 5 MV positive terminal (phase 1). Inside the high voltage terminal the beam passes through a thin foil stripping several electrons from each atom in the beam and breaking apart any molecules. The positive ions are accelerated away from the high voltage terminal (phase 2).

3) The beam of positive ions emerging from the tandem is focused using a 10 cm aperture magnetic quadrupole lens. The focused beam is then sent through a magnet which deflects all

particles with a momentum to charge ratio equal to that of $^{14}\text{C}^{4+}$, to an angle of 90° . The ^{13}C ions, deflected slightly less than 90° , are stripped in a Faraday cup and their current recorded. The ^{14}C beam is sent through another 90° deflection magnet to further separate ^{14}C from stray background ions. The beam is then refocused with another quadrupole, and sent into a Wien filter before being analysed by the particle detector. The Wien filter is used to remove background ions from the ^{14}C beam. By applying a specific magnetic and electric fields, the Wien filter will only allow particles with a velocity ($v = E/B$) equal to that of ^{14}C at the selected energy to pass.

4) ^{14}C ions are counted by a $dE/dx - E$ particle detector. The amplitude of the signal produced in the dE/dx ("stopping power") portion is proportional to the square of the nuclear charge, thus can be used to discriminate background ^{14}N particles which could pass all the other barriers. Ions found within the boundaries set by previous ^{14}C ions are counted. The ^{14}C to ^{13}C ratio in the sample is proportional to the ^{14}C count rate divided by the ^{13}C beam current. ^{13}C is used instead of ^{12}C because the natural abundance of ^{13}C is 1% that of ^{12}C and accelerator stability is easier to maintain during switches between isotopes with lower currents.

Control of all beam transporting systems is handled by a system of Hewlett-Packard 9000 computers. Beam transport characteristics are recorded on the computer, so that these characteristics can be repeated on future AMS runs. With the computer automation of the beamline, CAMS has the capabilities for operating on a 24 hour-a-day basis. (12)

The analysis for section 5 is performed in Chapter 4.

B. AMS Counting Data for 'Typical' Samples

The raw counting data received from CAMS were the ^{14}C counts, the ^{14}C to ^{13}C ratios, the integrated ^{13}C beam current, and the counting time. The ^{14}C to ^{13}C ratio gives the radiocarbon age of a sample; statistical uncertainty in the total ^{14}C counts is the dominant factor in the precision of this result. The run times are typically between 100 and 300 seconds. The older samples are run for longer times so that a larger ^{14}C count may be obtained. The modern standards, however, are run for 100 seconds so as not to pass the AMS computer's ^{14}C counting limit of 10,000. Figure 3.2 is an example of the raw data from the mass spectrometer.

The AMS cycles through the set of samples three or four times to check system stability and reproducibility. Calibration standards are run approximately every fifth sample in order to keep track of the variation in the standard. Figure 3.3 shows a typical calibration standard variance. Figure 3.4 shows a typical variance in an unknown sample.

Chapter 4.

Data Analysis

Chapter 4 is a discussion on the data analysis used to obtain sample ages and uncertainties.

A. Radiocarbon Age

It is convenient to use a computer to do the calculations necessary in obtaining a calendric date for an unknown sample. The Basic program RadioCarbon Dating Program (RCDP) was written to perform these calculations. The code for this program is listed in Appendix D. RCDP uses the ^{14}C to ^{13}C ratios of the unknown sample, a calibration standard, and a background sample to calculate the radiocarbon age of the unknown. These ratios along

with the uncertainties in each sample are the data required to make the date calculations.

Since there are several AMS runs for each sample, the ^{14}C to ^{13}C ratios must be averaged. The best value for the ^{14}C to ^{13}C ratio is found by weighting each ratio according to the number of ^{14}C counts obtained for that run; i.e., a run with a large number of ^{14}C counts would be weighted more heavily than a run with a smaller number of counts.

$\langle R_x \rangle$ will be defined as the average ^{14}C to ^{13}C ratio for the sample x .

$\langle R_u \rangle$ = average ^{14}C to ^{13}C ratio of the unknown

$\langle R_{st} \rangle$ = average ^{14}C to ^{13}C ratio of the calibration standard

$\langle R_b \rangle$ = average ^{14}C to ^{13}C ratio of the background sample

$\langle R_x \rangle$ is obtained by the following equation:

$\langle R_x \rangle = \sum a_j R_j$, where a_j is the weighting factor for each R_j .

a_j is found by:

$a_j = C_j / \sum C_i$, where C_j is the number of ^{14}C counts for run j , and $\sum C_i$ is the total number of ^{14}C counts for all of the runs of that sample.

These average ratios are entered into RCDP. These ratios, however, are uncorrected for background ^{14}C . The program then calculates the corrected ^{14}C to ^{13}C ratios. These "corrected" ratios are found by subtracting the background ratio from the unknown and the standard ratios. (Treatment of background is a controversial issue in AMS. As our understanding of the origin of these ^{14}C counts from "dead" samples improves, more accurate corrections will develop. For samples measured in this study, background was not significant compared to uncertainty from counting statistics.)

CR_x will be defined as the corrected ^{14}C to ^{13}C ratio for the sample x .

$\text{CR}_u = \langle R_u \rangle - \langle R_b \rangle$: the corrected ^{14}C to ^{13}C ratio of the unknown

$\text{CR}_{st} = \langle R_{st} \rangle - \langle R_b \rangle$: the corrected ^{14}C to ^{13}C ratio of the
standard

At this time, the calibration standard ratio is corrected to the modern activity and for fractionation. OXI ratios are multiplied by .95. OXII ratios are multiplied by .7368. The oxalic standards are normalized to -19 parts per thousand fractionation. ANU ratios are multiplied by $975/1.529(1000+\delta^{13}\text{C})$, where $\delta^{13}\text{C}$ is the fractionation in the sample.

By using the decay equation: $N=N_0e^{-\lambda t}$, where N is the number of atoms left after a time t , N_0 is the number of atoms at time $t=0$, and λ is the time constant, a radiocarbon age can be found by solving

for t. By dividing the corrected unknown ratio by the corrected standard ratio yields the ratio N/N_0 .

$$N/N_0 = CR_u/CR_{st}: \text{ ratio of unknown to standard}$$

Thus the radiocarbon age is given by:

$$\text{radiocarbon age} = -\ln(N/N_0)/\lambda; \text{ where } \lambda = \ln(2)/5568, \text{ and the half-life of } ^{14}\text{C} \text{ is } 5568 \text{ years.}$$

B. Precision

The precision of each calculated age is limited by the number of ^{14}C counts for each sample. The precision calculations were performed using methods obtained from Knoll. The uncertainty in each sample ratio is entered into RCDP at the same time the average ^{14}C to ^{13}C ratio is entered. The uncertainty in each sample is dependent upon ΣC_i . The uncertainty is found from

$$\sigma_x = \langle R_x \rangle / [(\Sigma C_i)_x]^{1/2}, \text{ where}$$

$$\sigma_u = \text{standard deviation in } \langle R_u \rangle,$$

$$\sigma_{st} = \text{standard deviation in } \langle R_{st} \rangle,$$

$$\sigma_b = \text{standard deviation in } \langle R_b \rangle.$$

The precision of the radiocarbon age is calculated by RCDP as follows.

After the ^{14}C to ^{13}C ratios are corrected for background measurements, the background corrected standard deviations must be found. $C\sigma_x$ will be defined as the corrected standard deviation of sample count x . The equation for the corrected standard deviations is given by:

$$C\sigma_x = [(\sigma_x)^2 + (\sigma_b)^2]^{1/2}.$$

$C\sigma_u = [(\sigma_u)^2 + (\sigma_b)^2]^{1/2}$: the corrected standard deviation of the unknown ratio

$C\sigma_{st} = [(\sigma_{st})^2 + (\sigma_b)^2]^{1/2}$: the corrected standard deviation of the standard ratio (3).

The standard deviation of the ratio of unknown to standard can be found using the following equation:

$$\sigma_{N/N_0} = N/N_0 [(C\sigma_u/CR_u)^2 + (C\sigma_{st}/CR_{st})^2]^{1/2} :$$

standard deviation of the ratio of the unknown to standard (3).

This last standard deviation can be used to find the accuracy of the calculated radiocarbon age. The accuracy limits are found by adding or subtracting σ_{N/N_0} to or from N/N_0 , and using these values in the age equation.

$$\text{radiocarbon young limit} = -\ln[N/N_0 + \sigma_{N/N_0}]/\lambda$$

$$\text{radiocarbon old limit} = -\ln[N/N_0 - \sigma_{N/N_0}]/\lambda$$

After the calculations listed above are complete, the radiocarbon age and accuracy limits are printed at the bottom of Screen 1. Figure 4.1 is a sample of what Screen 1 may look like.

C. Conversion to Calendric Date

To convert the data obtained from Section 4.A and 4.B to the most probable calendric date requires the use of graphical analysis and probability statistics. The first step is to locate the portion of the calibration curve of Stuiver and Pearson (see Section 1.B) which lies between the accuracy limits obtained above. A range of calendric dates can be found by finding the first and last intersections of the accuracy limits with the calibration curve. These dates are possible calendric dates for the unknown sample. RCDP illustrates this process on Screen 2. (see Figure 4.2)

To find the most probable calendric date from this range of dates requires the use of probability statistics. First, it is assumed that the probability distribution between the accuracy limits on the radiocarbon age axis is a Gaussian distribution, the most probable radiocarbon age being the calculated radiocarbon age from Section 4.A. If the calibration curve were a straight line (i.e. a constant ^{14}C concentration at $t=0$) then the most probable calendric date could be found at the midpoint of the range of calendric dates found above. However, the calibration curve is not

a straight line, so finding the most probable calendric date is a little more complicated. The probability of each data point on the calibration curve in the range of dates of interest can be found using the following equation:

$$P(T) = \exp\left[-(T - T_C)^2 / 2(T_C - T_L)^2\right], \text{ where}$$

$P(T)$ is the unnormalized probability of a particular calendric date corresponding to its unique radiocarbon age

T is the radiocarbon age parameter

T_C is the calculated radiocarbon age from Section 4.A

T_L is the calculated accuracy limit from Section 4.B.

The general expression for this equation was found in Knoll. (3)

To find the normalized probabilities, all of the unnormalized probabilities for the range of calendric dates must be found. By summing these unnormalized probabilities and obtaining the the inverse of this quantity, the normalization factor can be found:

$$Fac = 1/\sum P(T), \text{ where } Fac \text{ is the normalization factor.}$$

Then the normalized probabilities can be found by multiplying this factor by each unnormalized probability. Screen 3 is a plot of probability versus calendric date (see Figure 4.3). The most probable calendric date can be interpreted from this graph.

Since the probability curve of each sample is quite different from the next, it is very hard to compose a subroutine to conduct a

general analysis of the curve. What may work for one curve may not work for the next. A few simple things may be determined, however. For instance, the largest probability can be found, and the range of possible dates has already been obtained. For a very sharp and tall curve, these quantities may mean a great deal, so these values are given on Screen 3. But for a very round and shallow curve, these values may not mean very much at all. For this reason, a subroutine was not attempted. Instead, visual analysis of the individual probability curves is performed by the experimenter.

Chapter 5.

Salt Creek AMS Results

Chapter 5 is a discussion of how AMS was used for a specific example of earthquake study. Results for this study are also presented.

A. Description of Samples Counted

A study of earthquake geology and seismotectonics was conducted on the southern portion of the San Andreas Fault, in Southern California, by Dr. Patrick Williams, of the Lawrence Berkeley Laboratory.(13) From this study, it was determined that there were periodic diversions of the Colorado River due to seismic

events along the San Andreas Fault, and that these diversions cause flooding events in the Salton Sea Basin. Charcoal sediments deposited during these events can provide a stratigraphical record of seismic activity along the fault.

A total of 30 charcoal samples were extracted from two stratigraphically separated flood plains adjacent to Salt Creek which runs through the Salton Basin. Fifteen samples were taken from the older of the two flood plains which is called Lake 1. Another fifteen samples were taken from the other flood plain, Lake 2.

These samples were pretreated at the Nuclear Science Facility at San Jose State University. The combustion and graphitization procedures for the Lake 1 samples were performed at the Radiocarbon Laboratory at the USGS in Menlo Park, CA. The accelerator mass spectrometry for eleven of these samples was done at the CAMS facility at the Lawrence Livermore National Laboratory. Dates were calculated for these samples using RCDP as described above.

B. Summary of Results

Results were obtained for 11 of the samples taken from the Salt Creek site Lake 1. The radiocarbon age and an estimated calendric date for each sample is given in Figure 5.1.

A graph of this data (Figure 5.2) suggests three possible events regions occurring at 1530 AD + or - 100 years,

1350 AD + or - 150 years, and 1200 AD + or - 100 years. The close grouping of these dates shows a consistency in the Lake 1 site.

Chapter 6.

Conclusions

It has been shown that accelerator mass spectrometry holds a distinct advantage over the gas counting method in that AMS can produce accurate dates from milligram-sized samples of carbon. This eliminates the need to find large carbon samples. A geologist needs only to find a few small flecks of carbon to acquire dates for the site.

The combustion and graphitization processes described in this work are slight variations of the well proven methods of other experimenters. The RCDP program is also a slight variation of the well proven method used by other laboratories. The agreement of the RCDP dates with the CAMS dates gives evidence that the methods described in this effort have worked effectively.

Some effort could be made in the future to analyze the probability curve, described in Section 4.C, for better accuracy in determining calendric dates. A suggestion for better accuracy in the radiocarbon age is to modify RCDP so that it takes a localized average of the calibration standard rather than an average over the entire number of calibration standard runs. This would take into account any long term variations in the ^{14}C to ^{13}C ratios of the standard. These changes would increase the effectiveness of the RCDP program.

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Figure 1.1. Long and short term variations in the ^{14}C concentration in Bristlecone pine trees. (4)

Figure 2.1. Diagram of the Graphitization line at the USGS in Menlo Park, CA.

Figure 3.1. Diagram of the AMS system at the CAMS facility at LLNL.

Sample	C14 counts	C13 Current [nA]	C14/C13 Ratio	Run Time [s]
ANU	10375	1064.7	0.21843	93
USGSA82	965	158.2	0.13569	134
USGSA83	10243	1682.2	0.13611	160
USGSA84	8739	1419.3	0.13716	200
USGSA86	129	1457.9	0.00197	200
USGSA86	162	1667.1	0.00216	200
USGSA86	186	1720.1	0.00240	200
ANU	9851	992.6	0.22673	100
USGSA87	8065	1370.1	0.13123	200
USGSA88	10142	1373.0	0.16472	196
USGSA89	9130	1489.4	0.13688	200
USGSA90	9920	1615.4	0.13701	200
ANU	10277	1046.9	0.21996	97
USGSA91	7241	1166.6	0.13834	200
USGSA92	9498	1468.3	0.14489	200
USGSA93	9837	1505.8	0.14586	200
USGSA94	10166	1710.2	0.13278	188
ANU	9675	1005.8	0.21556	100
ANU	10043	1012.7	0.22272	100

Figure 3.2. An example of typical raw data from the CAMS facility.

Figure 3.3. Typical variance in the ^{14}C to ^{12}C ratio in a calibration standard.

Figure 3.4. Typical variance in the ^{14}C to ^{13}C ratio in an unknown sample.

Make sure that CAPS LOCK is on

Sample Name? SC28
Delta C-13? -11

Standard Used? OXI, OXII, ANU ANU

Sample Run	
Ratio C-14/C-13 .13556	
Standard Deviation 7.6968E-4	Background Run
	Ratio C-14/C-13 background 2.2022E-3
ANU Standard	Standard Deviation 1.0088E-4
Ratio C-14/C-13 Standard .2245703	
Standard Deviation 5.3296E-4	

Age: 581.805 + 32.62201 or -32.75525 years bp

C to continue
Q to quit
?

Figure 4.1. RCDP Screen 1

Figure 4.2. RCDP Screen 2

Figure 4.3. RCDP Screen 3

Sample	C14/C13 Ratio	Standard Deviation	Radiocarbon Age	Calendar Year
SC2A	.13569	4.3685×10^{-3}	570+/-175	1350+/-200
SC2B	.13556	7.6968×10^{-4}	580+/-40	1350+/-80
SC2C	.13710	8.2288×10^{-4}	490+/-45	1420+/-80
SC2D	.13104	7.0427×10^{-4}	860+/-40	1190+/-100
SC2E	.15757	7.8241×10^{-4}	modern	modern
SC2F	.13407	9.6503×10^{-4}	670+/-45	1330+/-80
SC2G	.13135	6.8776×10^{-4}	840+/-40	1200+/-80
SC2H	.13914	8.7216×10^{-4}	370+/-40	1530+/-100
SC2I	.13642	6.9601×10^{-4}	530+/-40	1380+/-100
SC2J	.14174	8.1607×10^{-4}	modern	modern
SC2L	.13309	7.6432×10^{-4}	730+/-40	1270+/-80
Calibration and Background Standards				
Sample	C14/C13 Ratio	Standard Deviation		
ANU	.22457	1.0088×10^{-4}		
Anthr.	.00220	5.3296×10^{-4}		

Figure 5.1. Summary of results for the Salt Creek Lake 1 site.

Figure 5.2. Graph of results from Salt Creek Lake 1.

Figure C.1. Typical voltage regulator used for pressure transducer and oven control systems.

Figure C.2. Schematic diagram of the pressure transducer system.

Figure C.3. Schematic diagram of the oven control system.

Appendix A:

Chemical Pretreatment Procedure

Many samples may be pretreated at the same time, but caution must be used to prevent cross-contamination amongst these samples.

1. If sample is embedded in a large lump of sediment, then break-up the lump and separate the charcoal from the sediment using a microscope if necessary.
2. Pick out any loose roots or other organic materials which may affect the accuracy of the dating of the sample.
3. Mark a centrifuge tube with the sample number, and place the sample in the tube.
4. Add .25N HCl to the tube with a volume of about 3-4 times the volume of the sample. If more than one sample is being pretreated, fill all of the tubes to the same height. This will help to balance the centrifuge.
5. Place tubes in a Sonic bath for about 30 minutes. This helps to break-up the larger chunks of sediment, and to bring more of the sample into contact with the HCl.
6. Separate the sample from the solution with the centrifuge.

Using a dropper, remove the solution from the tube. If more than one sample is being pretreated, use a different dropper for each sample.

7. Repeat steps 4, 5 and 6 using .5N NaOH instead of HCl.
8. Repeat steps 4, 5 and 6 using distilled H₂O. This is done to rinse the sample.
9. Repeat steps 4, 5 and 6 using .25N HCl.
10. Repeat step 8 twice.
11. Loosely cover tubes with Al foil and place tubes in a drying oven until the samples are dry. The samples are then ready for combustion in the graphitization line.

Appendix B:

Combustion and Graphitization Procedures

Combustion Procedure (on-line combustions)

1. 10-30 mm³ of sterilized CuO is placed in a 7 inch Vycor combustion vessel. (The Vycor combustion vessel is a 7 inch section of 6mm o.d. Vycor tubing with a test tube end. The vessel was then sterilized for 45 minutes in a 900° C oven.)
2. .5-1.5 mg of pretreated charcoal is placed on top of the CuO.
3. The combustion vessel is connected to the graphitization line and evacuated.
4. The vessel is outgassed using a hand-held propane torch, with a mild flame, while being evacuated (being careful not to combust any of the sample).
5. Then, the valve to the vacuum is closed.
6. The torch is then employed to combust the sample for 4 minutes (being careful not to soften the Vycor vessel).

Combustion Procedure (closed-tube combustions)

1. 10-30 mm³ of sterilized CuO is placed in a 7 inch Vycor combustion vessel. (The Vycor combustion vessel is a 7 inch section of 7mm o.d. Vycor tubing with a test tube end. The vessel was then sterilized for 45 minutes in a 900° C oven.)
2. .5-1.5 mg of pretreated charcoal is placed on top of the CuO.
3. The combustion vessel is connected to a vacuum line and evacuated.
4. The vessel is outgassed using a hand-held propane torch, with a mild flame, while being evacuated (being careful not to combust any of the sample).
5. Then, the tube is vacuum sealed with a torch to a length of about 6 inches.
6. The tube is then placed in a 900° C oven for about 1-1.5 hours.

Graphitization Procedure

1. 1-2 mm³ of cobalt catalyst is placed in a 4 inch Vycor reaction vessel (the 4 inch vessel is constructed in a similar manner as the 7 inch vessel), and the vessel is attached to the bottom of the reaction assembly (see Figure 2.1).
2. The graphitization line is pumped to better than 5 microns to remove miscellaneous molecules.
3. 1 atm of H₂ is added to the reaction chamber. The pressure is measured with a solid state pressure transducer.
4. The catalyst vessel is heated to 550° C with a small oven for

several hours. Steps 4 and 5 are added to reduce any cobalt oxide to elemental cobalt.

5. The H_2 and H_2O is then pumped away.
6. At this point, the combustion process would occur according to the method outlined above.
7. For the closed tube combustion, the combustion tube is scored and inserted into the bellows. The bellows is then evacuated, then the bellows valve is closed. The tube can then be snapped to release the combustion gases.
8. To obtain pure carbon dioxide from the gaseous mixture produced from the combustion process, liquid nitrogen (LN_2) is placed at the tip of the combustion tube to freeze the gas for about 4-8 minutes. Then pump away the O_2 . About five minutes later, a dry ice slush (isopropyl alcohol and dry ice) replaces the LN_2 to allow the carbon dioxide to escape.
9. LN_2 is placed at the tip of the catalyst vessel to draw the CO_2 into the reaction assembly.
10. The line to the reaction chamber is then opened.
11. The reactor valve to the assembly is then closed and the CO_2 is unfrozen by placing tap water at the tip of the catalyst vessel.
12. The pressure of CO_2 is measured and recorded.
13. The CO_2 is then frozen again with LN_2 .
14. H_2 is added to the reactor (approximately 3 times the CO_2 pressure).
15. Unfreeze the CO_2 , record the total pressure, and start reaction program on the computer.
16. The small oven is placed around the catalyst vessel. The oven

temperature is approximately 550° C. An aluminum rod with a dimple drilled into it is placed in a dry ice slush. This cooling device is placed on the vessel adjacent to the catalyst vessel (this is the cold trap).

17. The ensuing reaction has a duration of about 5 to 7 hours.

Appendix C:

Pressure Transducer and Oven Control Diagrams

The pressure transducer system is designed to monitor the various pressure transducers on an individual basis. The circuit uses a 4053 multiplexer to read all seven transducers into four computer input channels. The +8 vdc and +5 vdc voltages are supplied by 7808 and 7805 voltage regulators respectively. These regulators are combined with 20 μ f capacitors which act as filters (see Figure C.1). Figure C.2 is the schematic diagram for the pressure transducer circuit.

The oven control system is designed to shut-off individual ovens upon request by the computer. The +12 vdc and +5 vdc voltages are supplied in the same way as mentioned above. The oven control system is illustrated in Figure C.3.

Appendix D:

Radiocarbon Dating Program Code

This program runs on an IBM AT with graphics capabilities using GWBasic.

```
10 REM*** C-14 Dating Program
20 '
30 OXI$="OXI": OXII$="OXII": ANU$="ANU": Q$="Q": C$="C"
40 DIM
   CALEN(700),RADCRB(700),DEV(700),P(200),CA(200),RA(200),PG(200)
50 '
60 CLS: KEY OFF: SCREEN 0
70 '
80 LOCATE 4,12: PRINT "Make sure that CAPS LOCK is on"
85 LOCATE 6,12: INPUT "Sample Name? ",SAMPNAME$
86 LOCATE 7,12: INPUT "Delta C-13? ",DELTA
90 LOCATE 9,12
100 INPUT "Standard Used? OXI, OXII, ANU  ",STAN$
110 IF STAN$=OXI$ THEN GOTO 160
120 IF STAN$=OXII$ THEN GOTO 160
130 IF STAN$=ANU$ THEN GOTO 160
```

```

140 GOTO 60
150 '
160 LOCATE 11,1
170 PRINT "Sample Run"
180 INPUT "Ratio C-14/C-13 ",CC          'gathered from AMS
190 INPUT "Standard deviation ",SDCT      'gathered from AMS
200 '
210 LOCATE 15,1
220 PRINT STAN$;" Standard"
230 INPUT "Ratio C-14/C-13 Standard ",CCS  'gathered from AMS
240 INPUT "Standard deviation ",SDSTCT     'gathered from
AMS
250 '
260 LOCATE 13,40
270 PRINT "Background Run "
280 LOCATE 14,40
290 INPUT "Ratio C-14/C-13 background ",CCB 'gathered from
AMS
300 LOCATE 15,40
310 INPUT "Standard deviation ",SDBKGCT    'gathered from
AMS
320 '
390 CCT=CC-CCB                             'true sample ratio
400 SDTCT=SQR((SDCT)^2+(SDBKGCT)^2)        'standard deviation true
sample
410 '
420 CCTS=CCS-CCB                           'true standard ratio

```

```

430 SDTST=SQR((SDSTCT)^2+(SDBKGCT)^2)  'standard deviation true
standard
440 '
450 IF STAN$=OXI$ THEN MODERN=CCTS*.95      'corrected standard
460 IF STAN$=OXII$ THEN MODERN=(CCTS/1.28935)*.95  'corrected
standard
470 IF STAN$=ANU$ THEN
MODERN=(CCTS/1.529)*(975/(1000+DELTA))  'corrected standard
480 '
490 SDRAT=CCT/CCTS*(SQR((SDTCT/CCT)^2+(SDTST/CCTS)^2))  'std
dev  sampl/stdrd
500 '
510 LAMBDA=LOG(2)/5568                      'decay const
520 DATERAT=CCT/MODERN
530 T=-LOG(DATERAT)/LAMBDA                  'date in years bp
540 TP=-LOG((DATERAT)+SDRAT)/LAMBDA  'young date in years bp
550 TM=-LOG((DATERAT)-SDRAT)/LAMBDA  'old date in years bp
560 PRINT ""
570 LOCATE 19,12
580 PRINT "Age: ";T;" + ";T-TP;"or " ;T-TM;" years bp"
590 '
600 BEEP: LOCATE 21,12: PRINT "C to continue"
610 LOCATE 22,12: PRINT "Q to quit"
620 LOCATE 23,12: INPUT OPT$
630 '
640 IF OPT$=Q$ THEN GOTO 1990
650 IF OPT$=C$ THEN GOTO 670

```

```

660 GOTO 620
670 CLS
680 '
690 OPEN "I",#1,"a:SP86.STD"           'opens spuiver & pearson '86
700 FOR K=1 TO 700
710 IF EOF(1) THEN CLOSE#1: GOTO 750
720 INPUT#1, CALEN(K),RADCRB(K),DEV(K) 'reads calendric,C-14
    dates
730 NEXT K
740 '
750 IF T>RADCRB(1)-120 OR T<RADCRB(677)+120 THEN GOTO 1270
760 '
770 '*** Graphics ***
780 CLS: SCREEN 2                     'set screen
    attributes
790 WINDOW(790-T,T-1000)-(2790-T,T+1000) 'opens arbitrary
    window
800 LINE(890-T,T-840)-(2790-T,T-840)    'draws x-axis
805 LINE(890-T,T+1000)-(2790-T,T+1000)
810 LINE(890-T,T-840)-(890-T,T+1000)    'draws y-axis
815 LINE(2790-T,T-840)-(2790-T,T+1000)
820 '
830 FOR L=1 TO K
840 IF CALEN(L)< 890-T THEN XO=CALEN(L): YO=RADCRB(L)
850 IF CALEN(L)>=890-T AND NDAT=0 THEN XI=CALEN(L):
    YI=RADCRB(L): SLOPEO=(YO-YI)/(XO-XI): BO=YO-SLOPEO*(XO-890+T):
    LINE(890-T,BO)-(XI,YI): NDAT=1

```

```

860 IF CALEN(L)>=890-T AND CALEN(L)<=2790-T AND RADCRB(L)>=T-
840 THEN LINE-(CALEN(L),RADCRB(L)) 'boundary of graph
870 IF NDAT=1 THEN X1=DUMX1: DUMX1=CALEN(L): Y1=DUMY1:
DUMY1=RADCRB(L)
880 IF RADCRB(L)<TM AND NDAT=1 THEN XU=CALEN(L): YU=RADCRB(L):
NDAT=2
890 NEXT L
900 IF NDAT=2 AND X1=0 THEN X1=890-T: Y1=BO
910 SLOPE1=(Y1-YU)/(X1-XU): XU1=X1-(Y1-TM)/SLOPE1 'finds cross
point of tm
915 XUS=XU1-20 'correction for uncertainty in cal. curve
920 LINE (XUS,TM)-(XUS,T-840) 'draws old cal boundary
930 '
940 FOR M=K TO 1 STEP -1 'search for new cal bound
950 IF NDAT=2 THEN X2=DUMX2: DUMX2=CALEN(M): Y2=DUMY2:
DUMY2=RADCRB(M)
960 IF RADCRB(M)>TP AND NDAT=2 THEN XL=CALEN(M): YL=RADCRB(M):
NDAT=3
970 NEXT M
980 SLOPE2=(YL-Y2)/(XL-X2): XL2=XL-(YL-TP)/SLOPE2 'finds cross
point of tp
985 XLS=XL2+20 'correction for uncertainty in
cal. curve
990 LINE (XLS,TM)-(XLS,T-840) 'draws new cal boundary
1000 LINE(890-T,TP)-(XLS,TP) 'draws young age bound
1010 LINE(890-T,TM)-(XLS,TM) 'draws old age bound
1020 '

```


1030 LOCATE 2,1: PRINT"BP"	'y-axis label
1040 LOCATE 24,70: PRINT"CALENDAR";	'x-axis label
1050 LINE(910-T,T)-(890-T,T)	'radiocarbon tickmark
1060 LINE(1990-T,T-820)-(1990-T,T-840)	'calendric
tickmark	
1070 LOCATE 3,1: PRINT USING"####";T+800	'c-14 age +800
1080 LOCATE 8,1: PRINT USING"####";T+400	'c-14 age +400
1090 LOCATE 13,1: PRINT USING"####";T	'c-14 age
1100 LOCATE 18,1: PRINT USING"####";T-400	'c-14 age -400
1110 LOCATE 23,1: PRINT USING"####";T-800	'c-14 age -800
1120 LOCATE 24,47: PRINT USING"#####";1990-T;	'uncorr cal
age	
1130 LOCATE 24,31: PRINT USING"#####";1990-T-400;	'cal age -
400	
1140 LOCATE 24,15: PRINT USING"#####";1990-T-800;	'cal age -
800	
1150 LOCATE 24,63: PRINT USING"#####";1990-T+400;	'cal age
+400	
1160 '	
1165 LOCATE 2,50: PRINT SAMPNAME\$	
1170 LOCATE 3,50: PRINT "BP: ";T;"{"T-TP;"}";	
1180 LOCATE 4,48: PRINT "CALENDAR: ";(XLS+XUS)/2;"{"ABS((-	
XLS+XUS)/2;"}";	
1190 BEEP: LOCATE 6,50: PRINT "C to continue"	
1200 LOCATE 7,50: PRINT "Q to quit"	
1210 LOCATE 8,50: INPUT OPT2\$	
1220 '	

```

1230 IF OPT2$=Q$ THEN GOTO 1990
1240 IF OPT2$=C$ THEN GOTO 1280
1250 GOTO 1210
1270 LOCATE 17,12: PRINT "No calendric data for comparison": GOTO
2000
1280 CLS
1290 '
1300 '*** Probability Distribution
1310 '
1320 PI=3.141593 'pi
1330 G=1 'initial conditions
1340 '
1350 FOR J=1 TO 677 'find data in box from graph
1360 IF CALEN(J)>XUS-250 AND CALEN(J)<XLS+250 THEN
CA(G)=CALEN(J):RA(G)=RADCRB(J): G=G+1
1370 NEXT J
1380 '
1390 '
1400 FOR M=1 TO G-1 'find unnormalized distribution
1410 P(M)=EXP((- (RA(M)-T)^2)/(2*(T-TP)^2))
1420 SUMP=SUMP+P(M)
1430 NEXT M
1440 FAC=1/SUMP 'normalization factor
1450 FOR N=1 TO G-1
1460 PG(N)=FAC*P(N) 'normalized distribution
1470 NEXT N
1480 '

```

```

1490 **** Probability graphics
1500 '
1510 WINDOW(XUS-300,-.03)-(XLS+300,.2)
1515 LINE(XUS-260,.2)-(XLS+300,.2)
1520 LINE(XUS-260,0)-(XLS+300,0)           'X-axis
1525 LINE(XLS+300,0)-(XLS+300,.2)
1530 LINE(XUS-260,0)-(XUS-260,.2)         'Y-axis
1540 '
1550 FOR Q=1 TO G-1                       'probability curve
1560 IF Q=1 THEN LINE (XUS-255,0)-(CA(Q),PG(Q)) ELSE LINE -
(CA(Q),PG(Q))
1570 NEXT Q
1580 '
1590 LOCATE 3,1: PRINT ".18"              'y-axis labels
1600 LOCATE 7,1: PRINT ".14"
1610 LOCATE 11,1: PRINT ".10"
1620 LOCATE 15,1: PRINT ".06"
1630 LOCATE 20,1: PRINT ".02"
1640 '
1650 XAV=(XUS+XLS)/2                      'average from prev graph
1660 LINE(XAV,.003)-(XAV,0)               'x-axis tick marks
1670 LINE(XAV+100,.001)-(XAV+100,0)
1680 LINE(XAV-100,.001)-(XAV-100,0)
1690 LINE(XAV+200,.001)-(XAV+200,0)
1700 LINE(XAV-200,.001)-(XAV-200,0)
1710 LINE(XAV+300,.001)-(XAV+300,0)
1720 LINE(XAV-300,.001)-(XAV-300,0)

```

```

1730 LINE(XAV+400,.001)-(XAV+400,0)
1740 LINE(XAV-400,.001)-(XAV-400,0)
1750 LOCATE 23,39: PRINT USING "#####";XAV           'x-axis labels
1760 LOCATE 23,47: PRINT USING "#####";XAV+100
1770 LOCATE 23,31: PRINT USING "#####";XAV-100
1780 LOCATE 23,55: PRINT USING "#####";XAV+200
1790 LOCATE 23,23: PRINT USING "#####";XAV-200
1800 LOCATE 23,63: PRINT USING "#####";XAV+300
1810 LOCATE 23,15: PRINT USING "#####";XAV-300
1820 LOCATE 23,71: PRINT USING "#####";XAV+400
1830 LOCATE 23,7: PRINT USING "#####";XAV-400
1840 '
1850 LOCATE 2,25: PRINT "Probability vs. Calendar Year." 'graph title
1860 '
1870 FOR I=1 TO G-1                                     ' find largest
probability
1880 IF I=1 THEN DUMMY=PG(I): DUMMY2=CA(I): GOTO 1900
1890 IF PG(I)>DUMMY THEN DUMMY=PG(I): DUMMY2=CA(I)
1900 NEXT I
1910 '
1920 CIRCLE(DUMMY2,DUMMY),20      'draw circle around largest
probability
1925 LOCATE 4,50: PRINT SAMPNAME$
1930 LOCATE 5,50: PRINT "Most Probable Date"
1940 LOCATE 6,50: PRINT USING "#####";DUMMY2
1945 LOCATE 7,50: PRINT "+/- ";ABS((-XLS+XUS)/2);" years"
1950 '

```

1960 BEEP

1970 '

1980 IF INKEY\$="" THEN GOTO 1980

1990 CLS

2000 END

Appendix E:

Equipment and Materials

Pretreatment Line Equipment

- IEC clinical centrifuge, Damon/IEC Division.
- sonic bath, Branson 52.
- single wall gravity convection laboratory oven, Blue M: a unit of General Signal.
- 5³/₄" Pasteur disposable pipets, Cat. No. 14672-200, VWR Scientific.
- centrifuge tubes with caps, No. 8142, Pyrex.
- squeeze bottles
- stainless steel spatulas

Pretreatment Line Materials

- .5N sodium hydroxide (NaOH)
- .25N hydrochloric acid (HCl)
- distilled water

Graphite Line Equipment

- Nupro Valves, part number C4B-4BKT, Nupro Company.
- Swagelok union tee, part number 400-3, Swagelok Company.
- Swagelok union cross, part number 400-4, Swagelok Company.
- 1/4" o.d. stainless steel tubing.
- 6 mm o.d. Vycor quartz tubing.
- 8 mm o.d. flexible tubing (for bellows)
- Microswitch pressure sensors, part number PK87639, Honeywell Corp.
- Televac thermocouple vacuum gauge, The Frederick Co.
- Power Stats Type 10B, Superior Electronics Co.
- Airpax 12 vdc relay, part number 28M114BF 341.
- Viton O-rings, size 010
- 8088 XT personal computer
- Data Acquisition and Control Adapter, IBM inc.
- PME hand torch, Bethlehem Apparatus Co.
- Welch Duo-seal vacuum pump, Model 1400, Sargent-Welch Scientific.
- 1/16 inch drill stock

Graphite Line Materials

- cobalt, EMS 300 mesh

- iron oxide (Fe_2O_3), 325 mesh Aesar, Toluman Matthey inc.
- copper oxide wire, J. T. Baker Chemical Co.
- liquid nitrogen
- dry ice
- isopropyl alcohol
- hydrogen, UHP grade, Union Carbide.
- carbon dioxide, 1%, Union Carbide.

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