FALL 1992

AMS Pulse

The National Ocean Sciences Accelerator Mass Spectrometry Facility Newsletter

A Reexamination of the World's First ^{14}C Analysis

A splinter of wood from the third millenium tomb of the Pharaoh Zoser makes its way to the National Ocean Sciences Accelerator Mass Spectrometer in Woods Hole, Massachusetts.

Hot Off The Press

A new, 12-page brochure, which explains the operation and technical capabilities of the NOSAMS facility is now available. For a copy, write to the National Ocean Sciences AMS Facility, McLean Lab, Woods Hole Oceanographic Institution, Woods Hole MA 02543, or call (508) 457-2000, ext. 2585.

It would be something of a historic occasion when the National Ocean Sciences Accelerator Mass Spectrometer went on line in January 1992. This AMS, the world's most sophisticated, deserved to have as its first sample something special, perhaps something historic. But nobody expected to wade into a 45-year old controversy that featured Egyptologists on one side and none other than Willard Libby, the father of radiocarbon dating, on the other. The AMS staff just wanted something special to date, that's all.

But to begin at the beginning. Libby, in 1947, proved the existence of natural ^{14}C, a radioactive isotope produced in the upper atmosphere by cosmic rays. The same year, he and his graduate student Ernie Anderson proved ^{14}C existed in all living things. This was exciting news; it meant that if a method could be devised to precisely measure it, ^{14}C could be used to date any organic material not older than 50,000 years. ^{14}C decays as a function of its half-life, which is 5730 years.

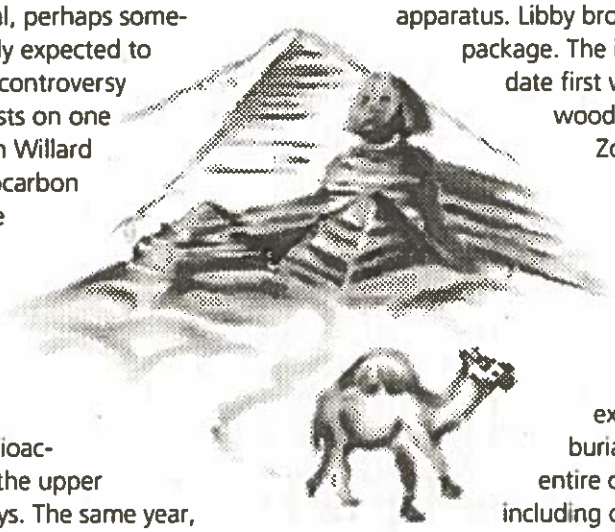
Libby and his team at the Institute for Nuclear Studies, now the Fermi Institute at the University of Chicago, immediately got to work to try to develop a method to measure ^{14}C levels.

Enter Serendipity

It just so happened that the nuclear scientist James R. Arnold was on Libby's team at this time. And Arnold happened to tell his father, an attorney and an amateur archaeologist, about the heady promise of ^{14}C as a dating tool.

A few weeks later, to Arnold's embarassment, a package arrived for Libby from Ambrose Lansing, Curator of Egyptian Archaeology at the Metropolitan Museum of Art in New York City. Lansing sent ten artifacts from ancient Egypt, all dated according to the historical record. "Lansing offered them as a set on which to check the method— a little early," said Arnold, who apologized to Libby for the "over-enthusiasm" of his father and his father's good friend Lansing.

Libby's team made progress and by mid-1948, they were ready to test their new ^{14}C counting apparatus. Libby brought out Lansing's package. The item he chose to date first was a piece of acacia wood from the Pharaoh Zoser's tomb at Saqqara, Egypt.



Zoser's tomb is perhaps best known as the Step Pyramid, the first pyramid known to exist. In fact, Zoser's burial place consists of an entire complex of buildings, including chapels and residences (for the gods and the "dead" Zoser himself); and two underground burial chambers, one called the South Tomb. The ancient wood came from a beam in this tomb. Cecil Firth, the archaeologist who found the wood in 1931, believed it was part of a scaffolding, according to Dorothea Arnold (no relation to the scientist), an Egyptologist and curator at the Metropolitan Museum.

Firth gave the wood to Prentice Dueil, the Field Director of the Saqqara Expedition, and Duell passed it onto Ambrose Lansing in 1933. In his letter accompanying the wood, Duell wrote, "He [Firth] won't be at all offended if you refuse it. In that case, he will make it a paper weight."

As Arnold, the scientist, recalls, it was a hot summer afternoon in Chicago when the ^{14}C device finished counting the radioactive carbon in the wood. He happened to be the one on duty: "For a couple of heady hours," Arnold said, "I was the only person in the world who knew that ^{14}C dating worked. One lives for such moments."

(Continued on page 5)

A view of the Accelerator Mass Spectrometry Lab. A 59-sample target wheel is placed into one of two ion sources and each graphite target is bombarded with a cesium beam. The resulting negative ion beam is then separated into 3 beams having masses 12, 13 and 14. The AMS removes hydrides and moleules leaving the radiocarbon atoms present in a sample to be counted relative to the amount of carbon-12 and carbon-13 atoms.

AMS Pulse

Volume 1,
Numbers 1 & 2
Fall 1992

The *AMS Pulse* is published quarterly by the National Ocean Sciences Accelerator Mass Spectrometry Facility, McLean Laboratory, Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

Telephone:
(508) 457-2000, x2585

Fax:
(508) 457-2183

Internet:
WHAMS@RED.WHOI.EDU.

Omnet:
OCEAN\WHAMS.C14

Direct correspondence to C. Annie Kauffman. Suggestions and feedback are welcomed.
To obtain a free subscription, please call or write the above number or address.

AMS Pulse staff:
Executive Editor
Glenn A. Jones
Managing Editor
C. Annie Kauffman
Designer
Jim Canavan,
WHOI Graphic Services

The NOSAMS facility was made possible through a grant from the National Science Foundation and through the support of the Woods Hole Oceanographic Institution.

News From The Editor

Welcome to the first issue of the *AMS Pulse*, the quarterly newsletter of the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS). Our primary focus is to inform current and potential users of the status of the Facility, how best to interact with the Facility and what services we are capable of performing.

This premier issue is an introduction to the NOSAMS Facility and provides the procedures required to submitt a sample for analysis. The current statistics on sample analysis (i.e., precision, accuracy, sample backlogs, etc.) will be presented for each calendar quarter. For example the Jan.-Feb.-Mar. statistics will be presented in the June issue. However, for this first issue the statistics for the period from January 1 - June 1992 are presented. A regular feature of future issues will be the status of the World Ocean Circulation Experiment (WOCE) radiocarbon sample analysis program. The March issue of the newsletter will serve as our Annual Report. We hope you find *AMS Pulse* to be useful and informative and we welcome your comments and suggestions.

Best Regards,
Glenn A. Jones, Director

Keep Up to Date Electronically

A Special Interest Bulletin Board has been created on SCIENCE.net, the electronic mail box system used by earth science scientists for the exchange of information and ideas with their colleagues throughout the world.

Scientists have access to this mail box system through Omnet, a communications media company. Information is exchanged through postings to bulletin boards and through messages sent to subscribers' mailboxes.

NOSAMS.NEWS is a read-only bulletin board which is updated biweekly. It provides the scientific community with information regarding the status and developments at the National Ocean Sciences AMS Facility. The data provided via this network also enables current and future users of the Facility to evaluate the services that are offered. Schedules for routine maintenance, internal research and development, emergency repair work, machine backlogs and other contingencies that could affect the throughput of samples are examples of the types of information included in the biweekly postings.

To access NOSAMS.NEWS on Omnet enter "check NOSAMS.NEWS" while using your personal mailbox and then (SCAN ALL). The bulletin board announcements are displayed and the subscriber can choose which posting to view by entering the (READ) command and the number of the message to be read. An example of the display screen is in the shaded box.

If you are on E-mail and wish to receive these postings, please contact us and we will place you on our electronic mailing list.

```
check NOSAMS.NEWS

      Now using bulletin board.

Command? scan

      Bulletin Board contains:

No. Delivered  From          Subject                        Lines

1   Aug 19     NOSAMS.NEWS  Bulletin Board Posting #10      59

Read 1
```

Woods Hole NOSAMS Facility Proves Its Capabilities

Radiocarbon dating has become an important tool for the investigation of a wide variety of earth, atmosphere, and ocean processes. To assist in these investigations a National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility has been established and is operated by the Woods Hole Oceanographic Institution (WHOI) in Woods Hole, Mass. The NOSAMS facility began routine analysis of samples in February of 1992. Funded by the National Science Foundation the NOSAMS facility is one of the most technologically advanced radiocarbon-dating facilities in the world. It is dedicated to providing high-precision radiocarbon (carbon-14) analyses primarily to the ocean sciences research community, but selected analyses from the earth and atmospheric sciences are also performed on a case-by-case basis. These analyses are used in the investigations of past climate records, ocean circulation, occurrences and duration of warm periods and ice ages, sea level changes and the atmosphere/ocean exchange processes involved in global climate change.

Scientists began using accelerator mass spectrometry in the 1980's as an ultra-sensitive method for radiocarbon dating. Prior to AMS the radiocarbon measurement process was relatively slow and limited by the need to work with large amounts of sample material, such as a 220 liter drum of seawater for each analysis verses <1 liter for AMS. In AMS, carbon is released from a sample in the form of CO_2 and then catalytically reduced to graphite. This solid sample is then used to count individual atoms of carbon-14 instead of the beta-decay products used in the traditional dating method. The NOSAMS facility's new generation accelerator mass spectrometer enables scientists to date objects >10,000 times smaller; than required by the beta-decay method. It also enables high-precision measurements to be made in less than an hour instead of the two to three days required by older techniques. With this new machine we will analyze 500 samples in 1992 and project the analysis of 4,300 seawater, ocean sediment, and other types of samples per year by 1995.

Accelerator Mass Spectrometer

In order for AMS to be a useful dating tool, a detection sensitivity for ^{14}C of at least one part in 10^{15} is required since the concentration of ^{14}C in modern samples is only one part in 10^{12}. The NOSAMS's accelerator achieves this level of sensitivity and is the first design with dual recombinator-type injectors. This design allows for the simultaneous acceleration and separation of all three carbon isotopes (Figure 1). This accelerator is also one of the first to use the new generation of high intensity ion sources for high precision analyses. The NOSAMS facility's accelerator routinely counts radiocarbon atoms at a rate > 80 cps for samples of modern age. This allows for both the rapid analysis of samples and the simultaneous achievement of high precision. Sample targets of less than 1 mg of carbon can be analyzed with a precision of better than 0.5 % in less than 30 minutes.

Precision and Accuracy

The routine precision of the new machine has improved steadily from approximately 4.0% in July 1991 to < 0.7% in June 1992 (Figure 2). The entire AMS system was designed to meet a

(Continued on page 4)

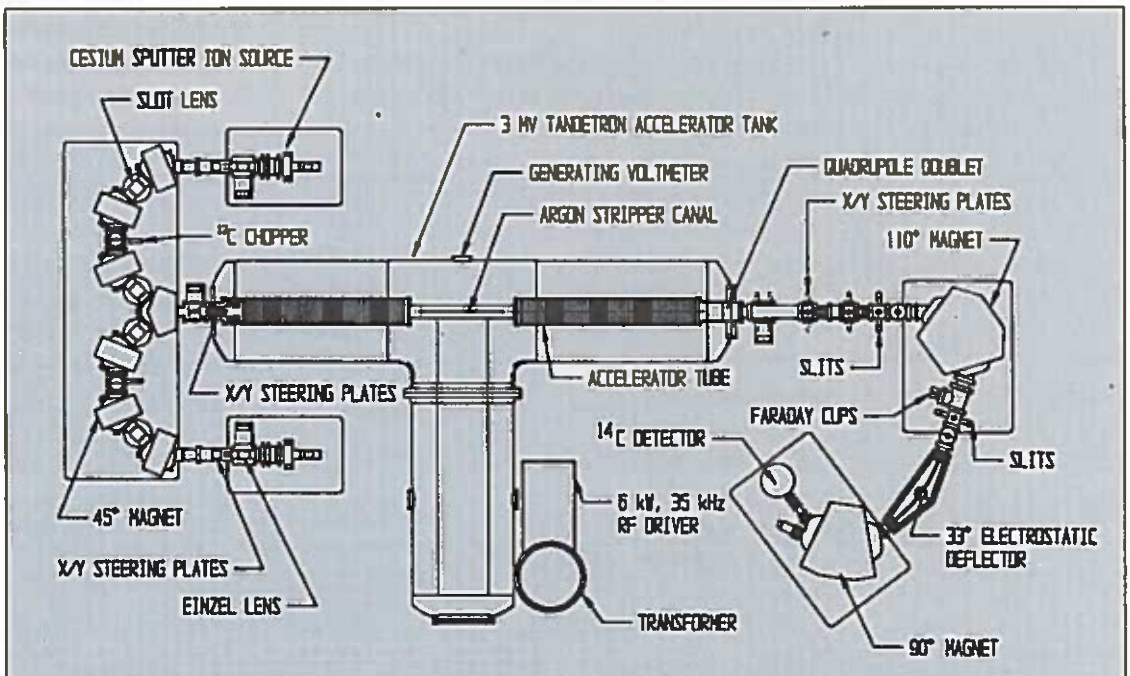


Figure 1 *– Schematic of the National Ocean Sciences Accelerator Mass Spectrometer System. Accelerator is approximately 10 meters long.*

Woods Hole NOSAMS Facility Proves Its Capabilities

(Continued from page 3)

specification of 0.5% precision for carbon 14/12 ratios after any fractionation corrections are determined from the $^{13}C/^{12}C$ ratios. To-date we have demonstrated a best performance of 0.4 % precision and the accelerator has been conditionally accepted less than 2 years after delivery to the NOSAMS facility. Machine and sample backgrounds are approximately 64,000 and 49,000 years BP respectively.

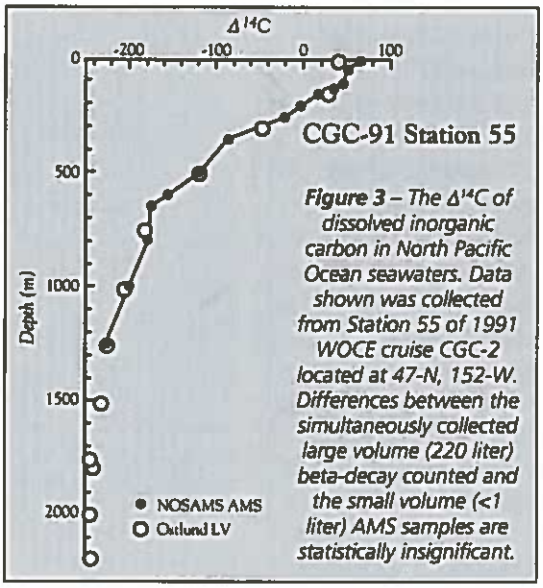


***Figure 3** – The Δ¹⁴C of dissolved inorganic carbon in North Pacific Ocean seawaters. Data shown was collected from Station 55 of 1991 WOCE cruise CGC-2 located at 47-N, 152-W. Differences between the simultaneously collected large volume (220 liter) beta-decay counted and the small volume (<1 liter) AMS samples are statistically insignificant.*

Selected Analysis

To demonstrate the NOSAMS facility's machine performance a direct intercomparison between simultaneously collected large volume and AMS seawater samples has recently been completed (Figure 3). These samples were collected in 1991 as part of World Ocean Circulation Experiment (WOCE) cruise CGC-2 in the North Pacific. The large volume samples were analyzed by Dr. H. Göte Östlund (University of Miami.) The agreement is quite good and demonstrates that the NOSAMS facility is ready to begin routine analyses for the WOCE program.

In addition, we show in figure 4 a series of samples encompassing radiocarbon activities from 150 % modern to background (0 %). These samples have either been analyzed at one other radiocarbon lab or are the consensus values obtained by international intercomparison studies. Our measured values agree, within the analytical precision of the measurements, with the expected values.

Conclusion

Funding for the NOSAMS facility began in January 1989. Since that time we have hired a staff of twelve, built a 9300 sq. ft. building to house the facility and had built and tested the next generation of accelerator mass spectrometer. By February 1992, we had begun analyzing samples and now routinely analyze samples of approximately 1 mg carbon with a precision of 0.7 %. Our throughput of 500 samples for 1992 is projected to expand to 4300/yr. by 1995. By all accounts the new design first proposed for the NOSAMS facility in 1988 has proven its merit and several facilities around the world are purchasing or discussing the purchase of accelerators of the "Woods Hole Type."

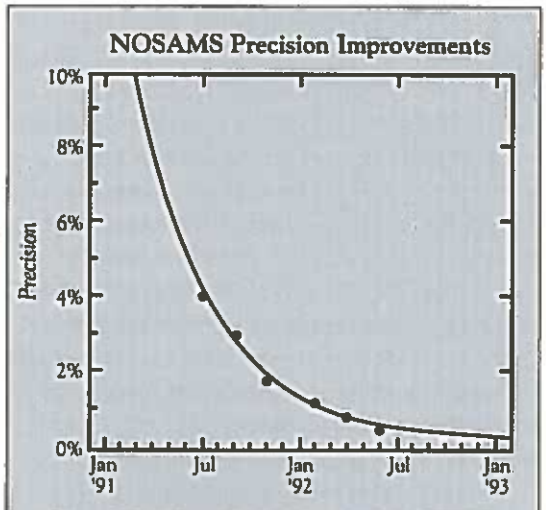


***Figure 2** – ¹⁴C was first detected at the NOSAMS facility in January 1991. The first test to evaluate precision was performed in July 1991 and since then, a similar test has been run every two months. The tests indicate a steady improvement in precision and involve the analysis of ten oxalic acid I/II standards analyzed for a minimum of 30 minutes each.*

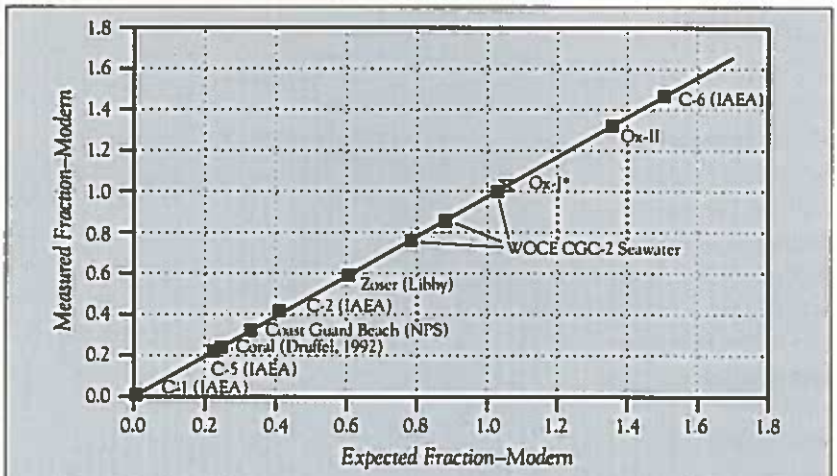


***Figure 4** – NOSAMS measurements vs. Accepted Values for Fraction-Modern. To illustrate the range of measurements we have made, the fraction-modern values for eleven different samples are shown. All values are normalized to 1.052 for Oxalic Acid I. Oxalic Acid II was calculated as an unknown. The sample from the tomb of Zoser was also Libby's first sample. The tree stump from Coast Guard Beach on Cape Cod was collected from a bog containing basal peats dated by the National Park Service.*

A Reexamination of the World's First ^{14}C Analysis

(Continued from page 1)

Libby won the Nobel Prize in 1960 for his work in developing the method of radiocarbon dating.

Dates in Debate

Egyptologists were surprised at the radiocarbon date of the Zoser wood. Based on astronomical events, hieroglyphics and other historical records, various Egyptologists have consistently dated the reign of King Zoser to about 2600 B.C. Libby dated the wood to 3980 +/-350 yBP or 2030 B.C. (Fig. 1).

Some Egyptologists began to wonder if the wood really did come from Zoser's tomb. Others did not trust radiocarbon dating.

Years later, when this dating technique was better understood and it was realized that corrections were needed to convert radiocarbon years to calendar years, Libby's initial results were recalculated. The tree-ring calibration age was placed between 3306 - 1451 B.C., with a 95 percent confidence (2σ). But the result was far too imprecise to be archeologically useful, and the discrepency remained unresolved until this past summer when that ancient, liver-shaped chunk of wood that almost became a paperweight found its way to the National Ocean Sciences-Accelerator Mass Spectrometer. The facility's director, Glenn Jones, wanted to date the wood with the WHOI AMS, the state-of-the-art in radiocarbon dating technology.

Accelerator mass spectrometry (AMS), first demonstrated in 1977, has been used as a scientific tool in many disciplines since the mid-1980s. The newest and most sophisticated AMS in the world is the facility at WHOI which operates the AMS largely for the national ocean sciences community.

AMS has great advantages over the traditional decay-counting method of radiocarbon dating.

The traditional technique is much too time consuming to be used on small samples, and the use of large samples makes it difficult or simply impossible to date many materials. For instance, a single measurement of seawater would require a 55-gallon drum of water. Dating a glacier would require transporting tons of ice. And even larger samples are required for very old material because as anything ages, it loses more and more carbon-14.

The sample size required for AMS is about 10,000 times smaller. AMS counts the atoms of carbon rather than the decay products. It needs only a scrap of cloth, a few ounces of seawater, a couple pounds of ice, a toothpick worth of the Zoser wood.

Jones is no pyramid buff. "I just thought it would be interesting from a historical perspective that the first sample to be run on the world's most sophisticated ^{14}C AMS should be the first sample that was ever radiocarbon dated," he said.

Jones wrote the Metropolitan Museum for permission to use a very little piece of the Zoser wood. "They weren't really wild about my idea," Jones says. So he visited the museum and spoke to the curators, again explaining that the amount the AMS needed was only a fraction of what Libby had used.

That argument worked for Jones. The New York City curators let him take a splinter of the Zoser wood back to Woods Hole.

As soon as WHOI's AMS was up and running in January 1992, it dated the wood as its first sample. Following various adjustments to the accelerator, the wood was dated again in July. The AMS radiocarbon age for the Zoser wood:

(Continued on page 6)

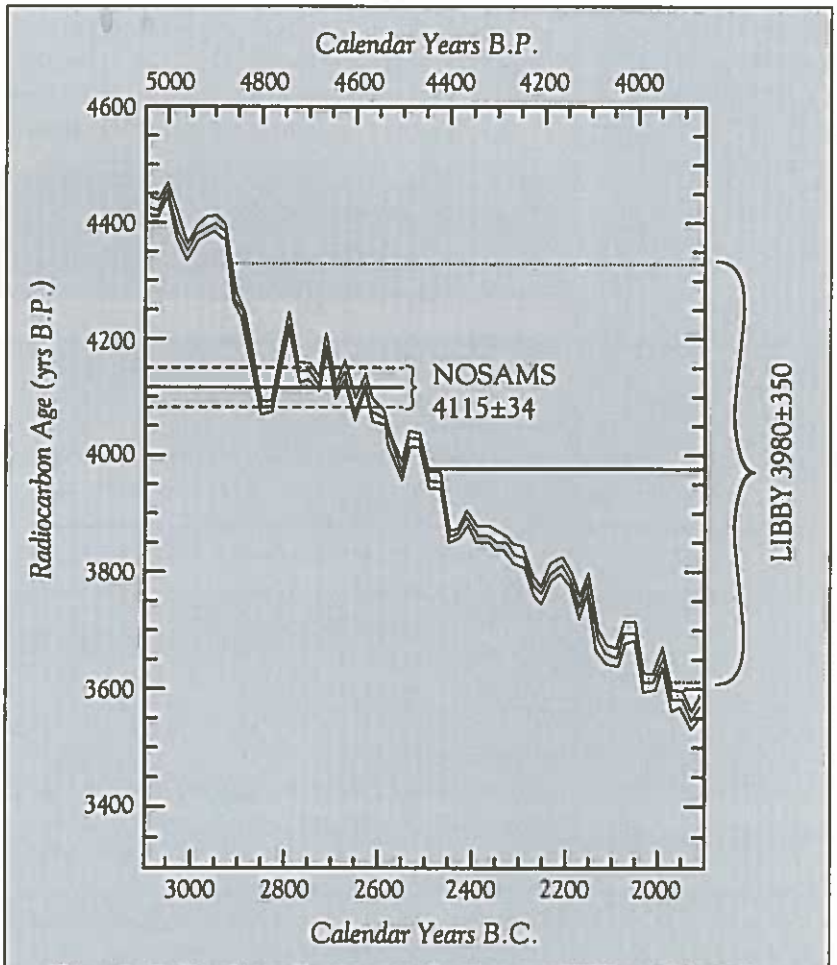


***Figure 1** – Radiocarbon calibration curve for the interval 3300 to 4600 yBP (from Pearson et al ,1986). The radiocarbon age and 1σ error for Libby's sample C-I from the tomb of Zoser is shown on right. The NOSAMS facility result for this same sample is shown on left. Note the step in the radiocarbon calibration curve for the interval encompassing the NOSAMS result for the reign of Zoser.*

To obtain a Sample Submittal Form:

Contact Glenn A. Jones (Director) or Diane Cook (Administrative Assistant) at the NOSAMS Facility:

Omnet:
OCEANWHAMS.C14

Telephone:
(508) 457-2000 X-2585

Mail:
NOSAMS Facility,
Woods Hole Oceanographic Institution,
Woods Hole, MA 02543

For assignment to time-sensitive queue, letters of justification must include:

I. Name of principal applicant, institutional affiliation or company name, title of proposed experiment or analysis, group or project name (if applicable), address, telephone number, fax number, OMNET or electronic mail address.

II. Statement of scientific merit of the proposed investigation: include benefits to ocean sciences and/or educational value.

III. Statement of estimated operational details: include special handling required, total number, and the size and type of sample.

IV. Send letters of submittal to: Dr. Glenn A. Jones, Director.

Queue Tips #1: Criteria for Sample Submittal

User demand for radiocarbon analyses already exceeds the capability of all AMS facilities worldwide. We have tried to establish an equitable plan to best meet the scientific community's needs. Prospective users of the facility are urged to contact either Glenn Jones, Director, or Diane Cook, Administrative Assistant, to receive an official Sample Submission Form.

Beginning in 1993, all samples submitted for analysis are assigned to one of three queues.

GLOBAL CHANGE QUEUE

During the active sample collection phase of the WOCE program (Projected 1990-1995) we anticipate that seawater samples will comprise up to 70% of the throughput at the NOSAMS facility. Due to the large number of samples collected and the low number of P.I.'s, the WOCE community has established an ad hoc review panel to prioritize their portion of the Global Change Queue. Without prioritization there would be a two to two and one half year backlog in reporting analysis results of seawater samples if a first-in-first-out system were employed for samples of this type.

INDIVIDUAL USER QUEUE

Non-Seawater Samples submitted for analysis will comprise up to 20 percent of the NOSAMS capacity. These samples will be placed into this queue upon receipt and run on a first-in-first-out basis. Based upon initial demand and inquires to the NOSAMS facility, as well as existing demand at the other AMS facilities, we anticipate an eventual six to nine month backlog from sample receipt to analysis.

TIME-SENSITIVE QUEUE

Ten percent of all analyses will be composed of those non-seawater samples deemed to have a higher priority and/or more immediacy for the scientific community. Samples are assigned to this queue through the submission of a one to two page letter of scientific justification to the NOSAMS facility. All letters are evaluated quarterly by a five-member National AMS Users Panel (NAUP). It is our goal that all samples approved by the NAUP will be analyzed within one to three months of submission.

Letters of scientific justification not selected by the NAUP will be used to reserve a slot in the Individual User Queue and the samples will have to be submitted to the NOSAMS facility in time to insure those reserved slots will be used for those samples.

Fees for 1992 & 1993 are set at $250 per sample for a standard seawater, carbonate hydrolysis or a total organic carbon analysis.

A Reexamination of the World's First ^{14}C Analysis

(Continued from page 5)

4115+/-34 yBP - within the 1σ error of Libby's first sample (Fig. 1). The tree ring calibrated age for the NOSAMS analysis results in two solutions with a 95% degree of confidence (2σ): 2877 to 2800 B.C. and 2780 to 2580 B.C. (Fig. 2). This result is consistent with the archeological estimates, but the marked step in the calibration curve during the time of Zoser's reign (Fig. 2) precludes a high precision calibrated age estimate being made from any high-precision radiocarbon measurement of Zoser material. Now if Willard Libby had only chosen the cedar wood beam from the tomb of Sneferu as his first sample....but that's another story.

For the history of radiocarbon dating we drew on Radiocarbon After Four Decades, *especially Chapter 1: "The Early Years With Libby At Chicago: A Retrospective," by James R. Arnold; Springer Verlag, 1992.*

–Story by Victoria Kaharl

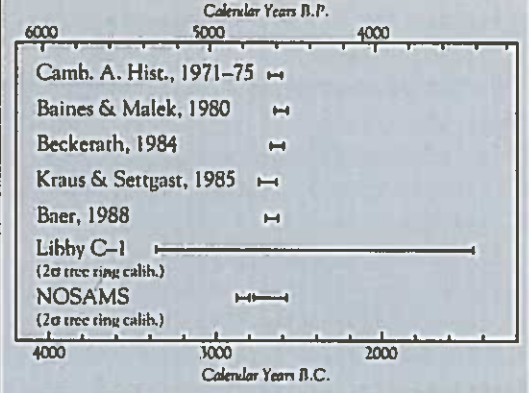
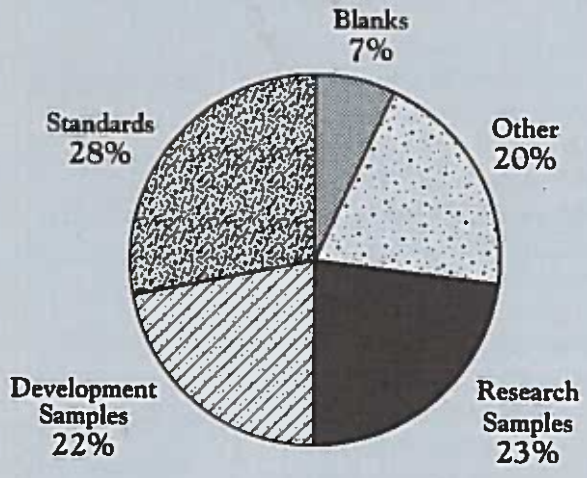


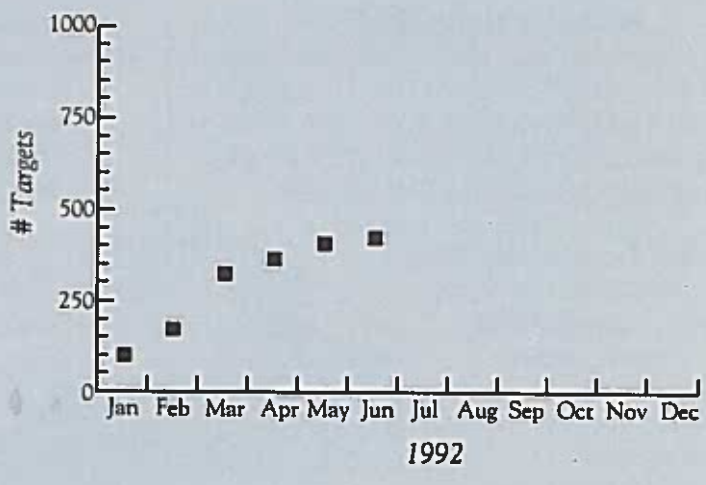
***Figure 2** – Estimates for the reign of Zoser from five different archeological studies and the 2σ (95% confidence interval) tree ring calibrated radiocarbon estimates from Libby's sample C-1 analysis and the NOSAMS facility reexamination of this same sample. The NOSAMS facility result is consistent with the archeological estimate. However, the calendar age estimate is less precise than the radiocarbon age estimate due to the step in the radiocarbon calibration curve for the interval encompassing the reign of Zoser (Fig. 1).*

Accelerator Usage by Sample Type

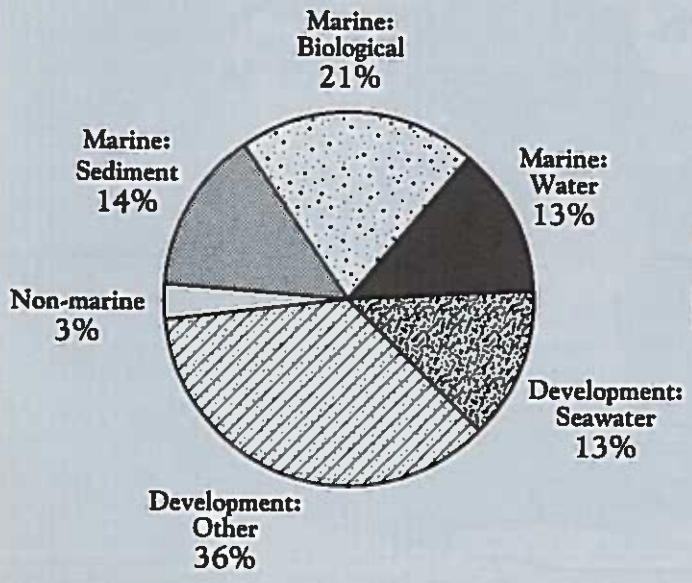
January 1 through June 30, 1992

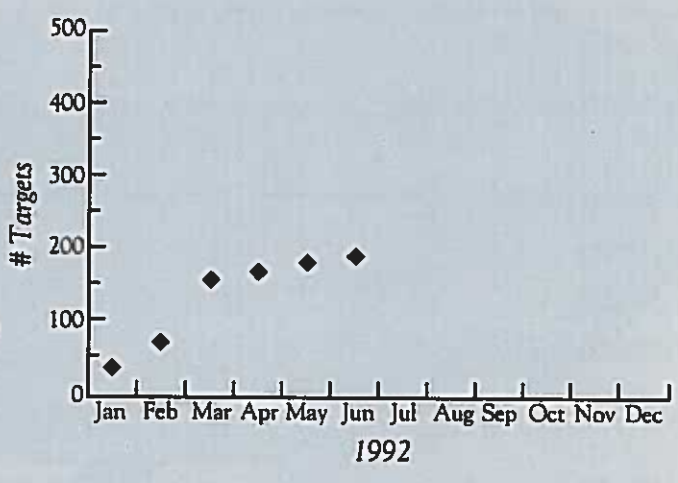
Total Targets – N=429





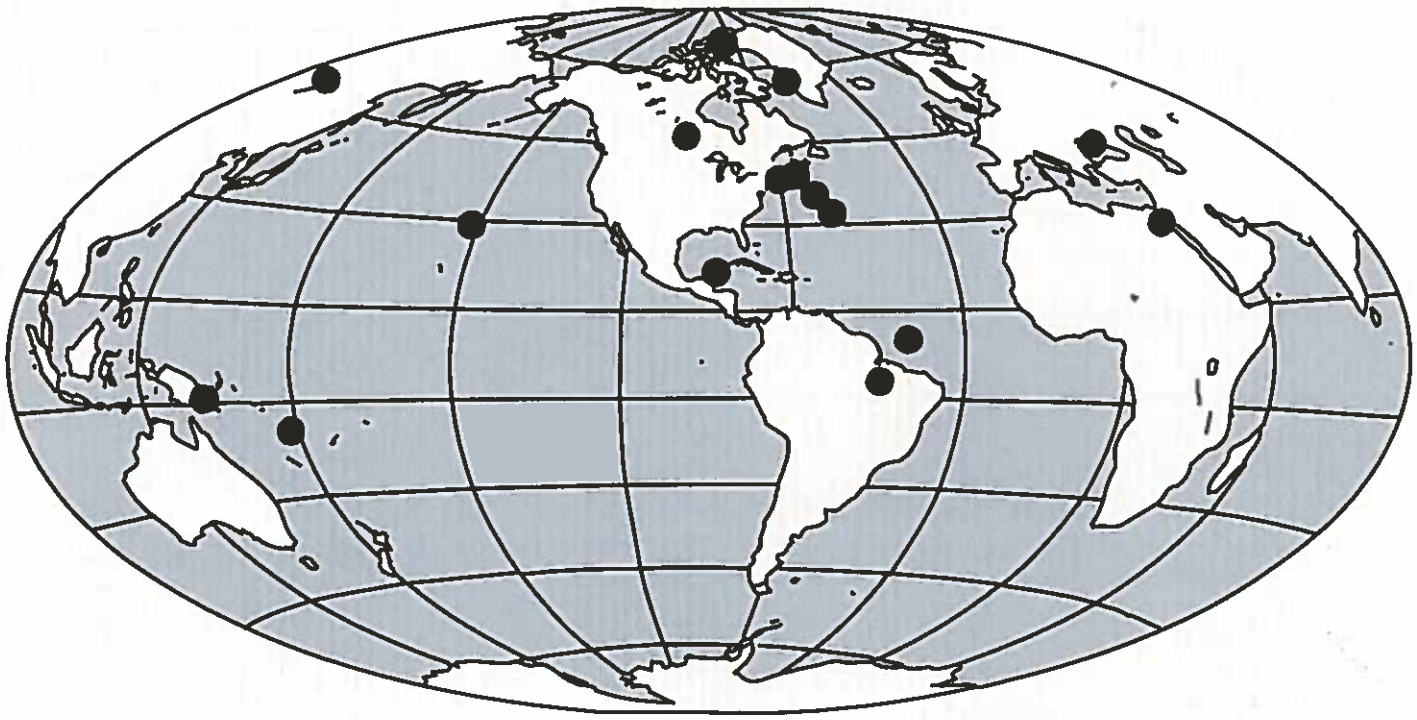
Research and Development Targets – N=196





AMS Pulse

National Ocean Sciences
Accelerator Mass Spectrometry Facility
Woods Hole Oceanographic Institution
Woods Hole, MA 02543



Site locations for samples analyzed at the National Ocean Sciences AMS facility during the period 1 January - 30 June, 1992.