Summer 1993

AMS Pulse

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The National Ocean Sciences Accelerator Mass Spectrometry Facility Newsletter

Tales of Black Sea Sedimentation, Exploration, and Colonization

"The ships of ancient Greece could be thought of as large floating bathtubs, taking on water in the Mediterranean and transporting it and its plankton into the Black Sea."

The Black Sea, the world's largest anoxic basin, is connected to the Mediterranean by the long (31km), narrow (0.7km width), and shallow (34m sill depth) Strait of Bosporus. From the last glacial, when sea level was approximately 130m lower, to approximately 9800 yBP, when sea level was approximately 34m lower than today, the Black Sea was isolated from the Mediterranean. During this time it was essentially the world's deepest fresh water lake. Once the reconnection with the Mediterranean resumed, dense saline water flowed into the basin steadily increasing the salinity to its present deep water value of 22ppt and 18ppt in the surface waters. The combination of prevailing Northeast winds and the salinity difference between the two seas leads to a steady strong surface current out of the Black Sea. Even today this flow can cause major problems for Black Sea-bound vessels. During the days of the ancient Greeks merchant ships could take as long as a month to make the Bosporus passage, and the Greek triremes several days.

Our knowledge of the timing of the Greek discovery and early settlement of the Black Sea is disconcertingly imprecise and uncertain. The earliest literary evidence of Greek knowledge of the Black Sea is perhaps the myth of Jason and the Argonaut's search for the Golden Fleece. This story had its roots, apparently in a number of preliterate poems and tales, and portions of the myth are handled by the 8th century B.C. epic poets Eumelus and Homer. The myth was first woven into one whole story by Appolonias Rhodius in the 3rd century B.C. He wrote the *Argonautica* so as ". . .to commemorate the heroes of old who sailed the good ship *Argo* up the Straits and into the Euxine (Black Sea) and between the Clashing Rocks in quest of the Golden Fleece."

Much better known however is that by the middle of the 7th century B.C. Greek colonies ringed the Black Sea (Figure 1), and were involved in extensive trade, with natural resources heading to "industrialized" Greece while finished products made their way back to the Black Sea colonies.

Our story now jumps twenty-seven centuries to the summer of 1988 when the National Science Foundation sponsored a major U.S.-Turkish expedition designed to remedy the deficiencies of previous Black Sea datasets. One of the foremost problems was the resolution of the late Quaternary Black Sea sediment chronology controversy. Determining the correct chronology has major implications for understanding: the initiation history of anoxia in the basin; the flux and preservation of organic matter in the basin; the interpretation of carbonaceous shale formation; and the role played by man in the development of this region's history.

In 1974 David Ross and Egan Degens of the Woods Hole Oceanographic Institution published the first radiocarbon dates of the lithostratigraphic boundaries found in the Black Sea (Figure 2). Their results suggested the first invasion of the coccolith *Emiliania huxleyii* from the Mediterranean Sea occurred between 3090 and 3450 yBP, and the timing of initiation of anoxia in the basin began at 7090 yBP. In 1980 Degens and colleagues counted the varves in these sediments

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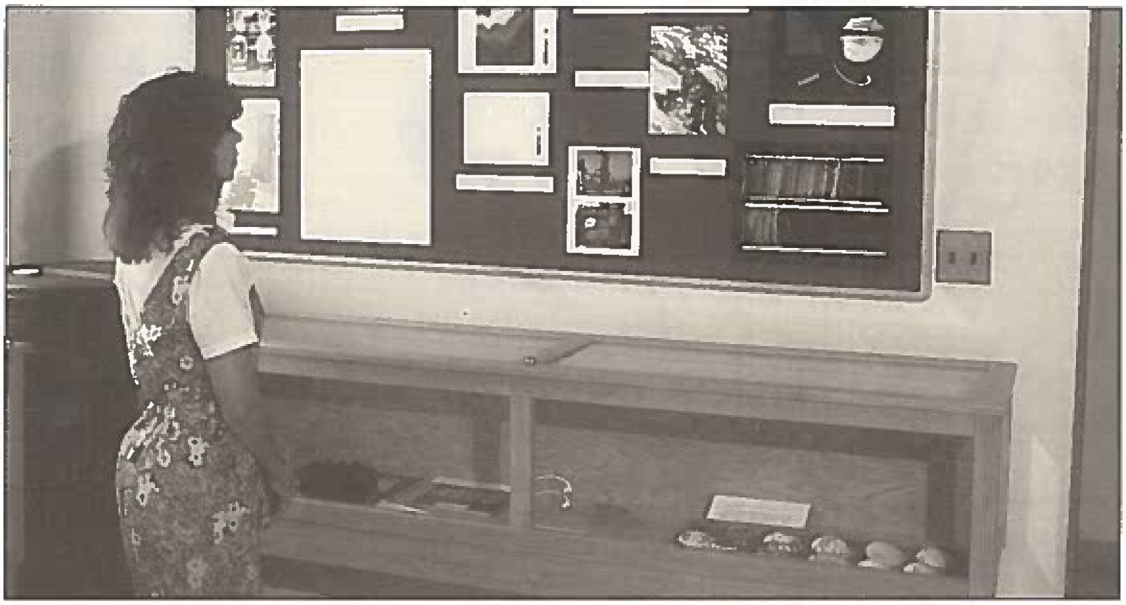

Diane Cook, (top photo) NOSAMS facility Administrative Assistant and Sheila Griffin, Research Associate with WHOI's former conventional radiocarbon lab, critique the NOSAMS facility's public display area.

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News From The Editor

The birth of the NSF-sponsored National Ocean Sciences AMS Facility came on January 1, 1989- the date upon which we could start to spend "officially" our NSF funds. On January 6, 1989 WHOI finished it's search for the successor to Dr. John Steele by naming Dr. Craig Dorman as Director of the Woods Hole Oceanographic Institution. Our first exposure to the ASW Admiral-turned-Director, and one of Craig's first major decisions, came at the end of what had been a long on-going series of sometimes heated discussions over just what should (would) be the extent of WHOI's commitment to creating a world-class AMS facility. After studying the different options and listening to all the arguments Craig pounded his fist on the table, looked around the room, and said "If we're going to do this thing, we're going to do it right!". For those of you who have had the opportunity to visit us, you know that the NOSAMS Facility was done right and stands as a proud testament to Craig's foresight in supporting state-of-the-art science and technology not just at WHOI but Internationally as well.

On May 18, 1993 Dr. Dorman announced that he would be stepping down as Director of the Woods Hole Oceanographic Institution. We would be remiss in not thanking Craig for his unfailing support of the NOSAMS facility over the past four and a half years, and we know that his contributions, enthusiasm and personal interest in the Institution as a whole will be sorely missed. We wish him the best in his future endeavors.

Best Regards,
Glenn A. Jones

DIOGENES:
The NOSAMS Facility Relational Database

The National Ocean Sciences Accelerator Mass Spectrometry Facility has recently completed the installation of DIOGENES, our relational database designed to accommodate our data storage and retrieval needs for the next decade. Along with the processing of some 4000 samples per year, in itself a phenomenal undertaking, the storage of vast quantities of information, precise sample tracking, and the timely processing of all this data creates unique problems in areas such as data entry and error checking. We minimize entry errors through the use of bar-code labels of sample identifying codes which aid in sample tracking. Validation checking at the database level identifies inconsistent values before they are stored. In addition, we have invested heavily in developing an interrelated software system for data collection, reduction and management. It is, in large part, this commitment to developing sophisticated data-handling systems that has permitted the NOSAMS facility to reach state-of-the-art status more rapidly than any prior AMS facility. In all, some 40,000 lines of computer code have been written to date.

Our early data handling efforts, involved a combination of paper records and loosely-linked, stand-alone spreadsheet and database packages such as Excel, Lotus 1-2-3, and/or Paradox. For example in the past, linking data supplied from the client to that generated in the NOSAMS Sample Preparation or Accelerator Labs involved extensive manual searching, cutting and pasting.

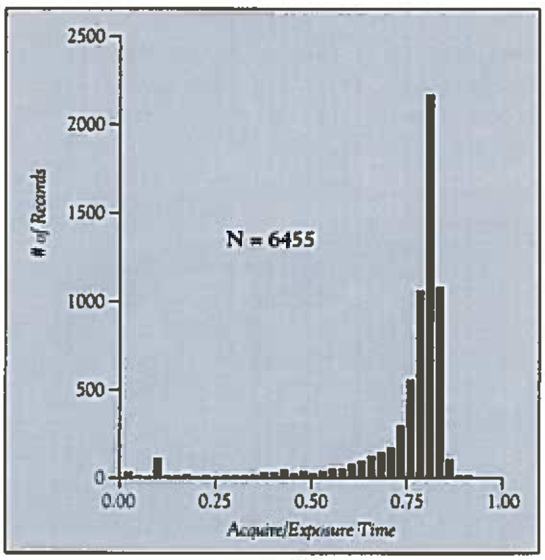

Figure 1: *Ratio of all Data acquisition and Target exposure times for the period April 1, 1992 to March 31, 1993. Median of dataset is 0.80 and the 5th percentile (2-sigma) is 0.41. For the purpose of this study all values <0.41 are identified as outliers.*

This type of system, though not ideal, is manageable for small numbers of samples and/or variables and is the norm at most labs of this type. As one moves to higher levels of throughput one solution is to minimize the amount of raw data that is stored. However, in order to fully understand and continuously improve all processes we have found a need to collect more than 200 parameters for each sample encompassing client supplied information (sample description, sample type, collection location, etc.); the continuous recording and storage of the temperature and pressure history for every sample graphitized; and the second-by-second recording of AMS stable carbon isotope current intensities and counts of ^{14}C atoms. All of this data, and a lot more, is stored digitally on an HP9000/755 workstation with companion 32 optical disk changer. This system can process information at speeds of 124 million instructions per second (MIPS) and can access up to 20 gigabytes ($2x10^{13}$ bytes) of on-line information. We estimate that all data generated in the first ten years of NOSAMS facility operation (1991-2000) will be on-line accessible. So far, the first two years worth of data occupies less than 6% of the system's hardware and software capabilities.

Relational Database vs. Spreadsheet

A database is simply a repository for large quantities of data. A spreadsheet is a single-user tool for analyzing data that has been retrieved from a database. A multi-user relational database management system (RDMS) stores complicated datasets in structures called tables. All tables are linked through hierarchical relationships where only one field in a table is directly related to a single field in only one other table. Although it is possible to do simple analysis of data directly in a database, and it is possible to save data into a spreadsheet, only a RDMS is powerful enough to accommodate all types of complicated querying.

To access this wealth of information we have developed a relational database system using Sybase SQL (Structured Query Language) Server combined with a 4th generation graphical front-end development system from PowerSoft. The twenty PCs in the NOSAMS facility are connected to the server through an HP STAR LAN network, which allows the server to send data directly to any specified PC after the SQL query has been processed.

To demonstrate the power of this system we give an example of the type of simple query session that can be used to identify and improve the quality of the data generated at the NOSAMS facility. We start by finding the Data Acquisition and Target Exposure times for every accelerator analysis during the period April 1,

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The NOSAMS Facility Relational Database

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1992 to March 31, 1993. The ratio of these two parameters is an indicator of target quality, where a perfect run will collect data for approximately 85% of the time that that target is exposed to the cesium ion beam. A target of poor quality will perform erratically and collect less usable data per run cycle than the high quality target. We find that there are 6455 records for this parameter in the database for this period (Figure 1). The median and 5th percentile (i.e. 2-sigma) values for this data are 0.80 and 0.41 respectively.

Since different sample types undergo different chemical procedures, we query the system to identify the percentages of each sample type exhibiting Acquire/Exposure times less than the 5th percentile value. Although the percentage of "bad" Acquire/Exposure times increases along with the degree of processing required to get from raw sample to graphite, the relationship is not very strong (Table 1). This result suggests that the different chemical procedures used are not preferentially contributing to the outlier Acquire/Exposure times. We now move to identify the temporal distribution of the outlier data. Figure 2 shows the percentage of outliers on each of the 24 wheels run during the one-year period beginning April 1, 1992. One wheel has a very high percentage of "bad" data, and further examination of the database reveals this was a rerun of an earlier wheel. Toward the end of this second run the cesium ion beam had sputtered away enough graphite to begin exposing the backing, with an attendant decrease in data quality.

	% Outliers	
Sample Material	Actual	Expected
Gas Samples	3.03	5.00±1.35
Oxalic Acid Standards	3.38	5.00±0.56
Hydrolysis Samples	5.30	5.00±1.15
Combustion Samples	5.02	5.00±1.09
Water Samples	5.50	5.00±0.58

***Table 1:** Five percent of the entire dataset is identified as outliers, and the insignificant differences in outlier percentages for each sample type suggests little-to-no contribution from a specific chemical procedure. Sample types are arranged from lowest (top) to highest (bottom) degree of processing required to make graphite.*

The remaining 23 wheels show a level generally near or less than the expected 5%. However, two intervals near July 1992 and Feb./Mar 1993 exhibit consistently low percentages of outlier data. During the development of the AMS system, a target cartridge and sample press were designed. As the AMS system developed, the target cartridges were slightly redesigned. These new cartridges, when used with the then already existing target press, resulted in a subtle decrease in overall target quality. Initial attempts to optimize target performance with the existing cartridge and press designs met with temporary success (see July data in Figure 2) but proved to be an impractical long-term solution. New cartridge and press designs were made and successfully implemented around February 1993 (see Figure 2).

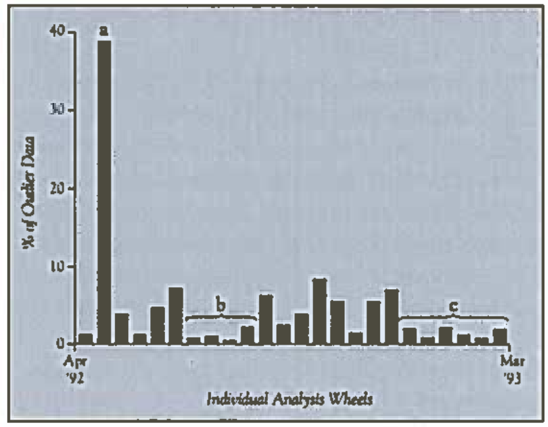

***Figure 2:** Temporal history of Acquire/Exposure time outlier data from April 1992 to March 1993 on a wheel by wheel basis. If there were no systematic temporal variability, approximately five percent of the data from each wheel would be identified as outliers. Note very high value for wheel run in early May (a) and low values for wheels run in July (b) and in Feb/Mar (c). See text for explanation.*

The above query was able to assemble an entire years' worth of data by collecting information from the accelerator and preparation labs as well as that supplied to us by the client. This entire "one-off" query took approximately 1 hr, including the writing of specific Power Builder code. Similar queries are routinely performed by the NOSAMS staff to evaluate those areas or procedures targeted for further improvement. With DIOGENES we can now pose a hypothesis, test it, and design solution procedures in only hours, rather than days or weeks without this system. It also permits us to easily monitor the long-term stability of a wide range of parameters. Such an ability has allowed us to recently improve our routine sample precision to better than 5 per mil for samples of near modern age and the implementation of these type of continuous improvements has no limits beyond that imposed by the $1/\sqrt{N}$ counting statistics barrier.

Contributed by Eric D. Kessel and Glenn A. Jones

Eric Kessel is the Information Systems Analyst for the NOSAMS Facility. His responsibilities include development and maintenance of the interactive database and providing user support and training. Eric graduated in 1992 with a B.S. in Computer Science from Rensselaer Polytechnic Institute in Troy, NY.

Tales of Black Sea Sedimentation & Exploration

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and estimated the first appearance of *E. huxleyii* at 1000 yBP and the initiation of anoxia at 5080 yBP. They speculated that the radiocarbon chronology was too old because of detrital carbon contamination. The radioisotope community has argued that the couplets or laminae were not true varves and sediment trap data supported the notion that a couplet would not necessarily form every year, thus making the "varve" chronology too young. A third hypothesis was presented by Jim Murray in 1991 when he argued that the difference between these two chronologies could be explained by invoking an anomalously large radiocarbon reservoir effect. Simple box modeling was used to argue that the radiocarbon age of the pre-bomb surface waters was more than 1430 years vs. an average age of 400 years for much of the world's oceans. Our participation in the 1988 expedition was to collect carefully preserved sediment records and water samples to help solve the chronology controversy.

Several conditions had never been met in previous studies: a measurement taken of the pre-bomb surface waters to determine directly the reservoir effect in the basin; recovery of the entire sediment record via box cores; no true surface sediments had been collected to calculate directly the detrital carbon contribution to the measured radiocarbon ages; and radiocarbon ages had not been converted to calendar ages to facilitate a direct comparison with the varve chronology. All of these conditions were met in our most recently completed AMS C-14 study. To measure the pre-bomb reservoir age of the surface waters, we obtained a shell from the Moscow State Museum that was collected "live" in 1931. The value was 460 years; close to the 400 year global average. Pre-bomb coretop sediment revealed the detrital age of the organic carbon and carbonate fractions to be 580 and 260 years respectively. The reservoir and detrital corrected radiocarbon ages were converted to calendar ages using the recently revised marine calibration dataset of Stuiver and Braziunas (1993). The results of this study are shown in Figure 2. The varve chronology is younger than the radiocarbon chronology by 20-30%. This value is consistent with a near decade long record of sediment trap data from the basin that suggests a visually identifiable varve would not have been formed in 20% of those years (Honjo, pers comm). This study suggests the controversy is largely solved.

Our study has serendipitously solved one other mystery along the way. What is the mechanism by which the coccolith *E. huxleyii* invades the Black Sea? For 25 years the explanation has been that *E. huxleyii*, which is abundant in the Mediterranean, was prevented from colonizing the Black Sea until the surface water salinity reached 11ppt (the lowest value in which this species has been found in the open ocean). However, recent modeling shows this salinity threshold would have been exceeded well before 5000 yBP. Yet the best estimate for the age of the first invasion is now 2720 +/ -160 yBP (Figure 1) which is equivalent to 930-610 B.C. So why was the invasion so much later? I would argue that the strong outward flowing current through the Strait of Bosporus prevents any passive passage of phytoplankton (that are restricted to living in the euphotic zone) across this oceanographic barrier and into the Black Sea. Rather, the transport vector is the extensive colonization of the Black Sea by the Greeks in the 7th century B.C. Figure 1 shows the major Greek colonies and the foundation dates of the more important of these. It can be seen that the dates of occupation for the major shipping ports coincide closely with the date marking the beginning of *E. huxleyii* in the Black Sea.

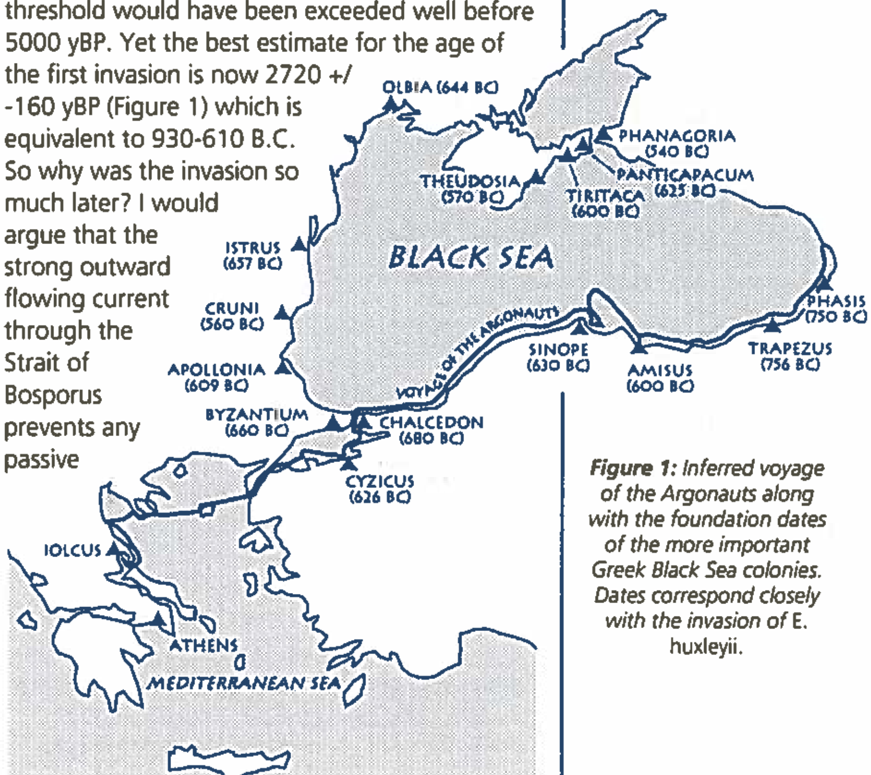

***Figure 1:** Inferred voyage of the Argonauts along with the foundation dates of the more important Greek Black Sea colonies. Dates correspond closely with the invasion of* E. huxleyii.

In the modern world the introduction of exotic species by ships ballast has reached critical proportions. The most deleterious introductions in recent years have been the zebra mussel into the Great Lakes, and toxic dinoflagellates into Australian waters. In the Black Sea recent documented introductions via this mechanism has been the jellyfish, *Mnemiopsis leida*, and the bivalve *Mya arenaria*. Although less common before the introduction of water ballast at the turn of the century, the Greek ships were low to the water, had open decks, no caulking was

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Queue Tips #4: The Client-NOSAMS Learning Curve

As Individual User Queue samples continue to arrive at a steady pace, we encounter an ever wider range of sample types, special handling requests, and unforeseen problems. Three of these will be highlighted in this issue: the information supplied to us via the Sample Submittal form, condition of the samples, and the way samples are sent.

First, the information supplied to us on the Submittal form must be as complete and accurate as possible. If an answer is not known do not try to guess without telling us it is a guess. A few months ago a number of organic carbon samples were lost when they exploded during the combustion procedure used to convert the organic carbon in a sample to CO_2. These explosions were due to very high CO_2 pressures being generated in the flame sealed combustion tubes. This dangerous situation resulted from a client assuming a much lower organic carbon content than was actually present. A later measure by us showed this estimate to be off by a factor of ten. The problem arises with total organic carbon percentages of bulk sediment, as these values can vary from less than 0.1% to more than 20%. With our latest version of the Sample Submittal form we are asking that the actual organic carbon percentages of bulk sediment samples be known before we start the combustion process. If the client so desires we can perform that analysis for an extra charge of $10 per sample.

Second, we have a rigorous QA/QC program to insure data quality. Several sample sets submitted to us recently have either been very dirty with up to 20% detrital contamination, or composed of mixed assemblages of biogenic material where the client has indicated they are mono-specific. We do not assign a receipt number for samples exhibiting these types of problems until the client has been contacted and a course of action decided upon. With the high throughput demands placed on the facility we can not act in the capacity of routinely preparing raw samples for analysis. In some cases the samples are returned to the client to be "cleaned up," and in others we will do the work for an extra charge. Depending on the amount of work involved that charge can average $10 to $30 per sample. If you want your samples into the queue as quickly as possible and/or as cheaply as possible please be sure that your samples are checked thoroughly before sending. A phone call to us while you are preparing your samples can go a long way in avoiding many of these easily corrected problems.

Third, care must be taken in the way samples are sent to the facility. Remember your samples are traveling via the U.S. Postal Service, UPS, or Federal Express. They are out of your hands and ours for 2 to 5 days. If you are sending microfossils DO NOT SEND them in the standard picking slide holders. We have had several shipments of samples where the wrong size glass or cardboard holder was used and portions of some samples were lost. Fortunately, no full sample has been lost due to shipping problems, but we've come close. For microfossils we recommend using 4 dram screw top vials that are securely shut, well labeled on both the vial and cap and the top taped to prevent opening during shipment.

To obtain a Sample Submittal Form:
Contact Glenn A. Jones (Director) or Diane Cook (Administrative Assistant) at the NOSAMS Facility:
Omnet: OCEAN\WHAMS.C14
Telephone: (508) 457-2000 X-2585
Mail: NOSAMS Facility, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

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used, and they frequently swamped in even light seas. Floor timbers had limber holes to allow the passage of bilge water, which was such a problem that generally the least able crew member was detailed to keep an eye on it (Athenaeus, 2nd centurey B.C.). These ships of ancient Greece could thus be thought of as large floating bathtubs, taking on water in the Mediterranean and transporting it and its plankton into the Black Sea. The introduction of *E. huxleyii* to the Black Sea may thus be the earliest documented anthropogenic introduction of an exotic species into an entire marine basin. Without the detailed AMS study of the Black Sea sediment chronology this relationship would have remained elusive.

Contributed by Glenn A. Jones

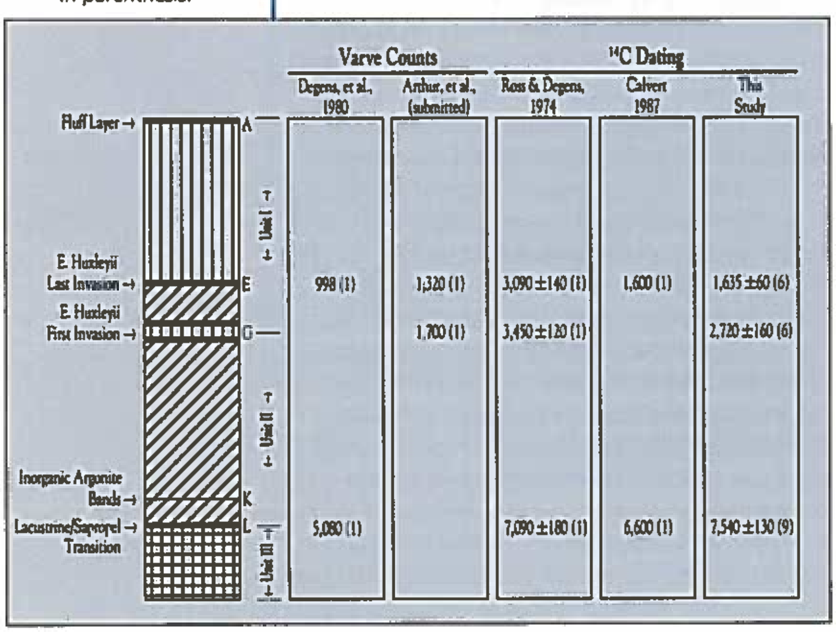
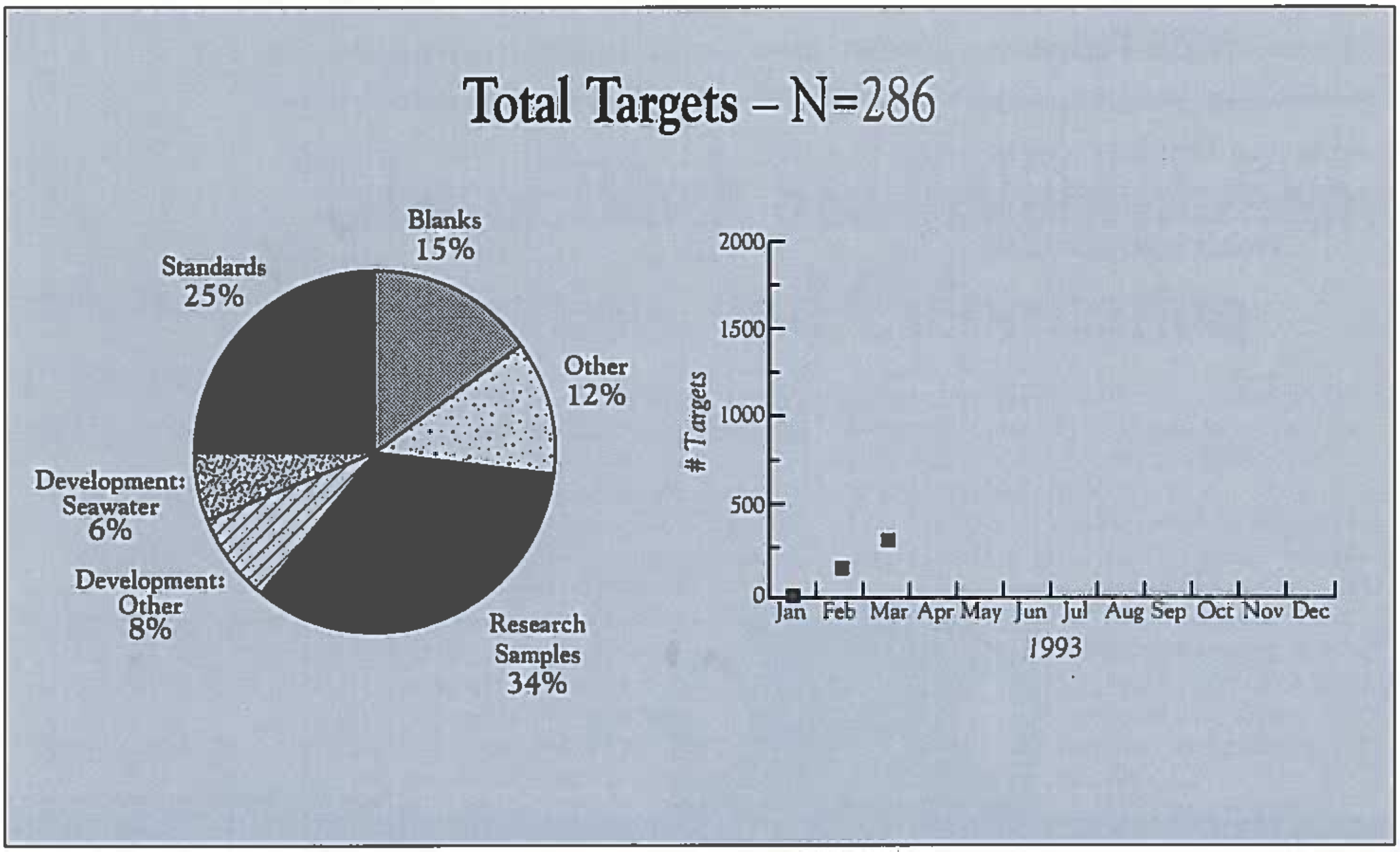
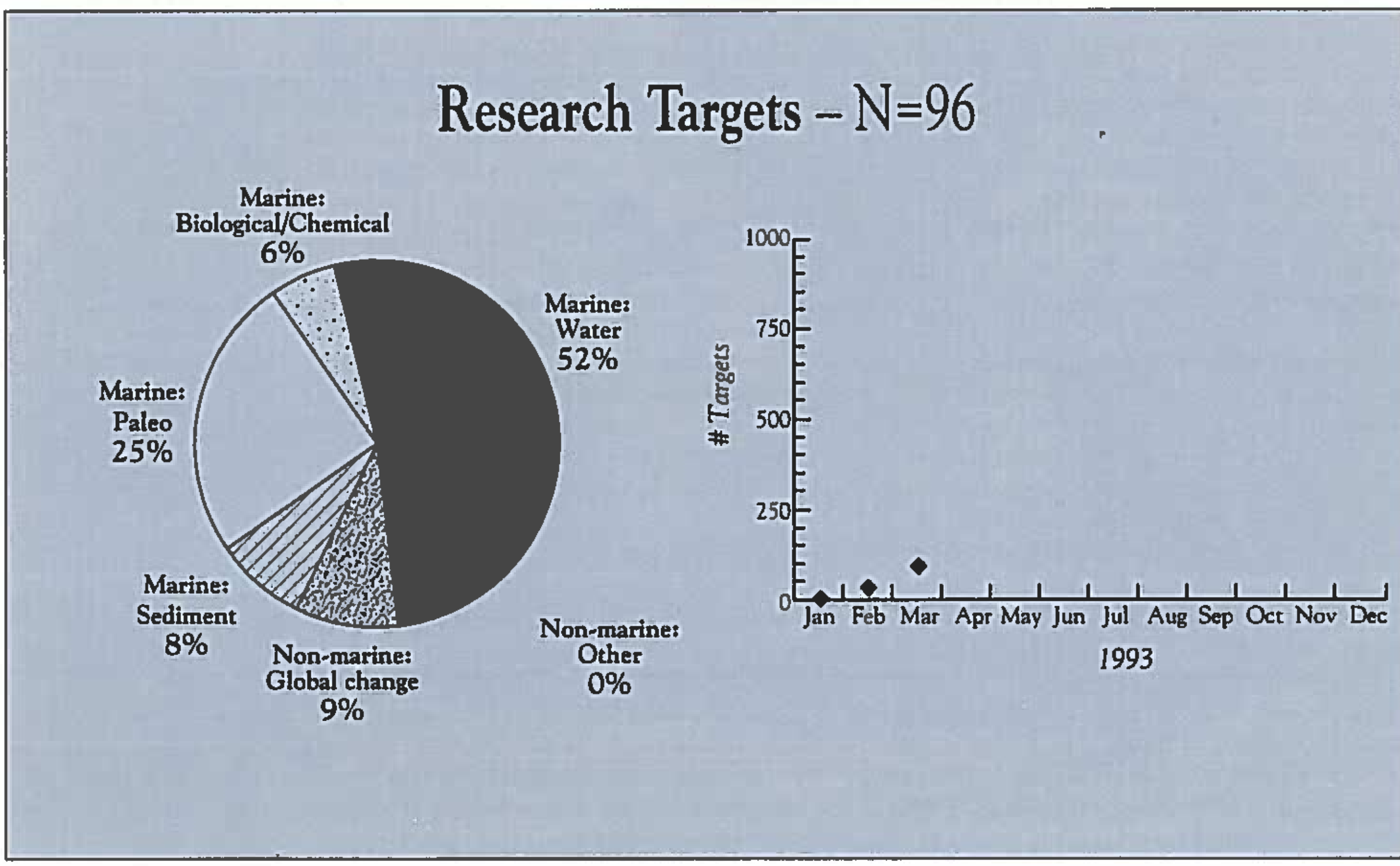


***Figure 2:** Comparison of different authors age estimates for various Black Sea sediment stratigraphic boundaries. Number of cores/measurements used to make age estimates are in parenthesis.*

Accelerator Usage by Sample Type

January 1 through March 31, 1993





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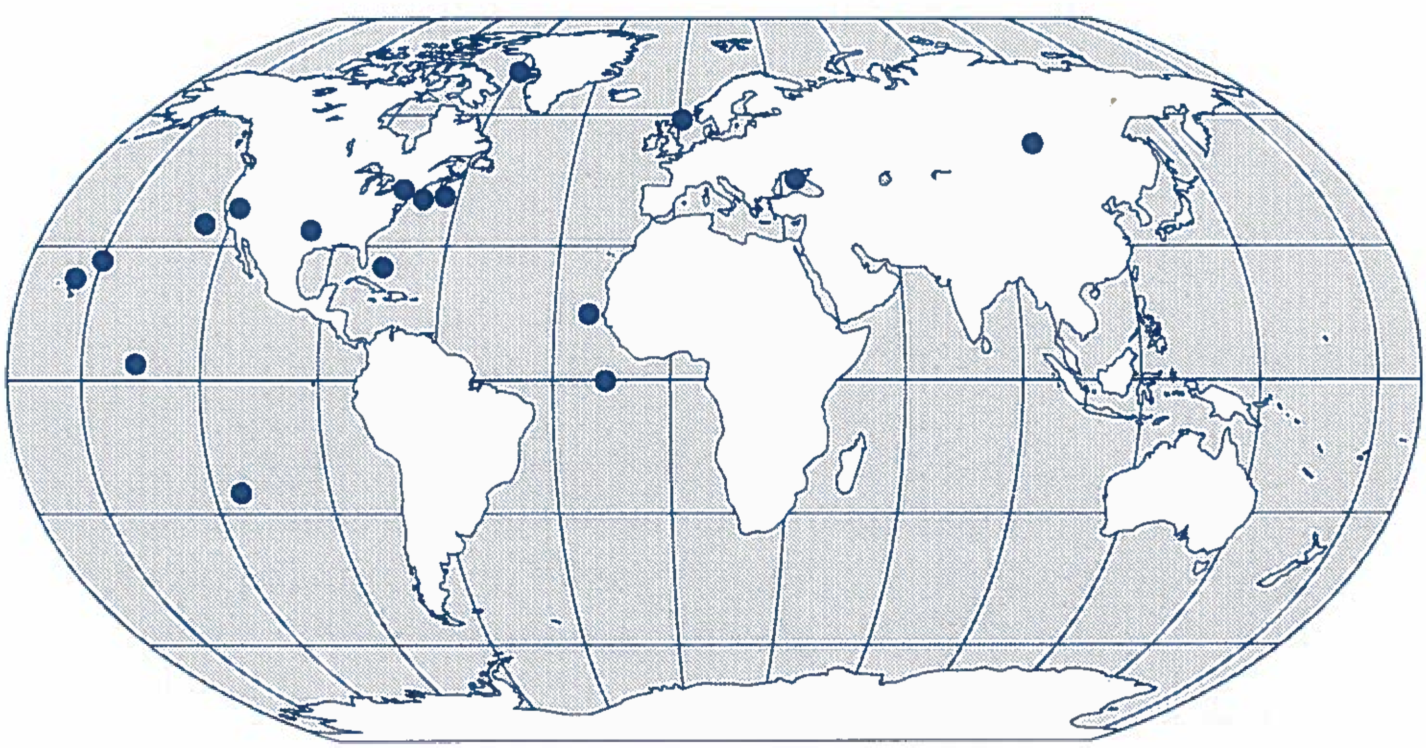

Site locations for samples analyzed at the National Ocean Sciences AMS facility during the period January 1 - March 31, 1993.