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Radiocarbon Dating of Wood Samples and Plutonium Sediment Disturbance Studies at the *Queen Anne's Revenge* Wreck Site

Christopher S. Martens

CB-3300, Department of Marine Sciences
University of North Carolina at Chapel Hill
Chapel Hill, NC 27599-3300
Email: cmartens@email.unc.edu

Ann P. McNichol

Department of Geology and Geophysics and National Ocean Sciences AMS Facility
Woods Hole Oceanographic Institution
Woods Hole, MA 02543-1539
Email: amcnichol@whoi.edu.

ABSTRACT

Radiocarbon dating of wooden and other organic artifacts from the putative *Queen Anne's Revenge* (*QAR*) wreck site (North Carolina Shipwreck 0003BUI) yields ages consistent with a ship construction date between 1690 and 1710 AD. Combined dates for twelve documented samples cluster between 1630-1670 AD using conventional radiocarbon ages calibrated by the OxCal program (Bronk, 1995; http://www.rlaha.ox.ac.uk/oxcal). The radiocarbon ages for two different anchor stocks found at the wreck site differ by 120 ± 85 radiocarbon years; however, OxCal calibrations based on changes in the abundance of natural radiocarbon in the atmosphere allow their calendar year ages to overlap in the mid 1600's.

Disturbances of the wreck site since the 1950's including potential exposure or exchange of sediments beneath presently buried hull components and ballast rocks with the surrounding sea floor environment were studied through measurements of bomb plutonium produced during the 1950's through early 1970's by atmospheric nuclear weapons testing. Sediments sampled from underneath the hull and ballast rocks contained from 9% to 41% of the plutonium activity measured in exposed surface sediments surrounding the wreck site. These low activities suggest little disturbance of the remaining intact hull and ballast rocks since the mid-1950's.

INTRODUCTION

A shipwreck (North Carolina Shipwreck 0003BUI) found near Beaufort Inlet, North Carolina, on November 21, 1996, may be the remains of the *Queen Anne's Revenge* (*QAR*), lost in the inlet in 1718 by pirate captain Edward Teach, better known as Blackbeard (Lawrence and Wilde-Ramsing, this issue). The shipwreck is the oldest documented in North Carolina waters, dating to the early 1700's. For convenience, we will refer to the site as the *QAR* wreck site throughout the paper. The primary objective of this paper is to estimate a construction age for the ship using radiocarbon dating of wooden and organic samples from the remaining hull structure and planking. All radiocarbon dates were obtained through a cooperative project with the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility located at the Woods Hole Oceanographic Institution.

In addition, measurements of the plutonium activity in sediments underlying the remaining hull fragments and ballast rocks as compared to that in surrounding exposed seafloor sediments are used to determine whether these artifacts have been disturbed since the mid-1950's. Radioactive isotopes produced artificially during nuclear weapons testing have proven extremely useful for tracing the movements, deposition,

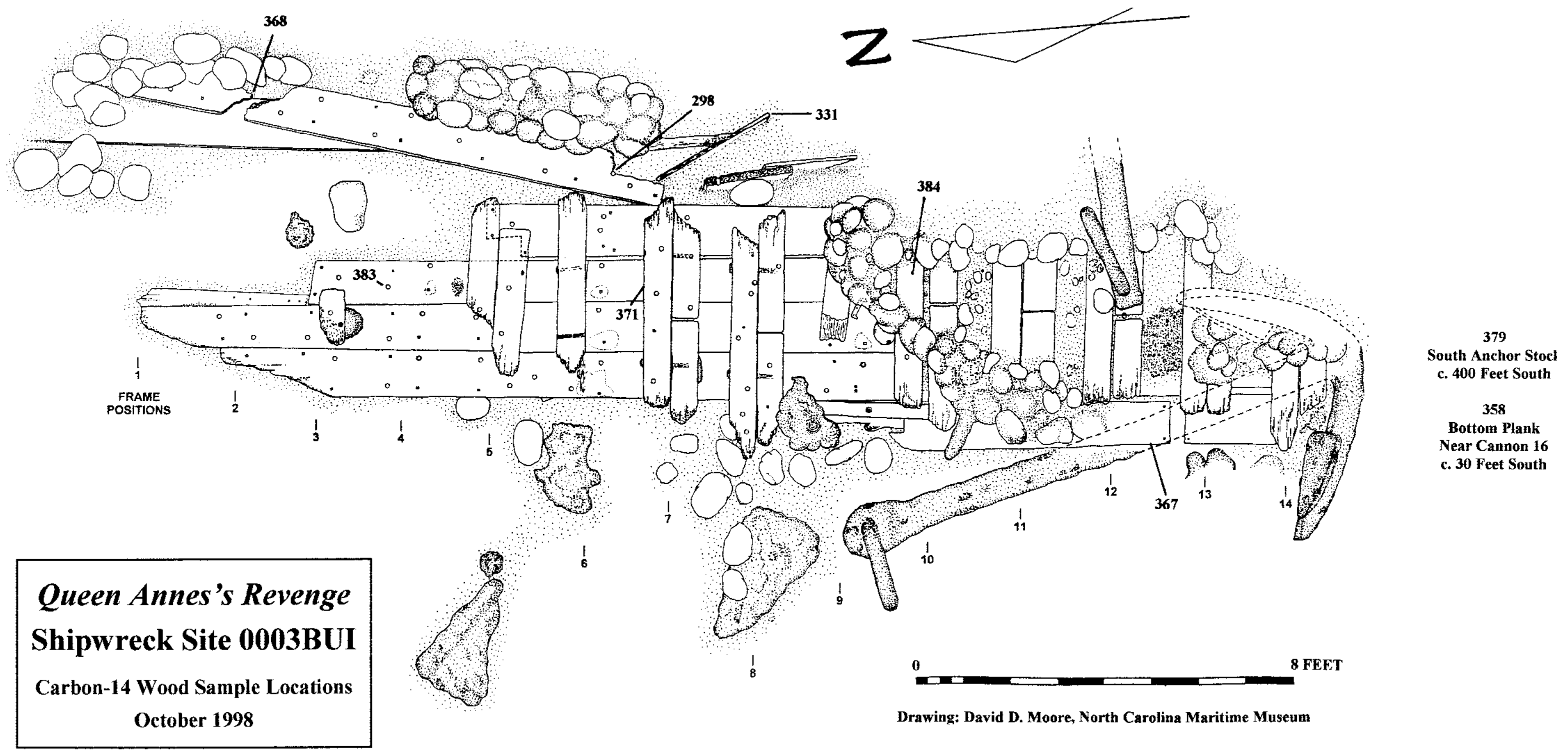


Figure 1. ***QAR*** **shipwreck site map showing remaining port side hull structure and locations of wood samples utilized for radiocarbon analyses. The south anchor (379 stock; 381 puddening) is located 128m SSW of the anchors in the main rubble pile. The north anchor (386 stock) is located 16m NNE of the rubble pile.**

Table 1. Summary of Preparation data for *Queen Anne's Revenge* samples. OS is NOSAMS run number, UAU# is the NC Underwater Archeology Unit sample number, Wt is the weight of the sample combusted in mg, Ct is the micromoles of CO_2 generated from the combustion, %OC-Ct is the percentage of C as organic matter by weight, #base is the number of base rinses required to remove all color from the sample, $\delta^{13}C$ is the value measured on the combusted sample, age is the Radiocarbon Age of the sample, fm is the fraction modern of the sample.

OS	UAU#, description	Wt	OC-Ct	%OC	#base	δ13C	age	error	fm	error
19822	331, No. 3 sacrificial plank	3.9	199.5	61.4	6	-25.48	350	60	0.9574	0.0038
19823	367, No. 7 sacrificial plank	4.7	221.0	56.4	6	-26.16	255	60	0.9687	0.0037
19920	368, No. 5 bottom plank	2.4	110.0	55.0	6	-26.95	275	70	0.9663	0.0044
19821	358, No. 1 south plank	3.8	132.4	41.8	6	-26.83	145	60	0.9820	0.0038
19824	371, frame No. 9	3.5	235.3	80.7	6	-26.59	290	60	0.9643	0.0036
19923	384, frame No. 8	1.6	66.4	49.8	6	-26.55	300	60	0.9635	0.0038
19825	298, treenail N90E92	3.5	159.0	54.5	8	-25.77	155	60	0.9809	0.0038
19820	383, treenail No. 5	3.9	168.5	51.8	6	-25.29	245	60	0.9703	0.0038
19922	386, north anchor stock	3.2	135.2	50.7	5	-23.59	210	60	0.9743	0.0037
19826	379, S. anchor stock E. tip	3.4	149.7	52.8	6	-25.50	330	70	0.9597	0.0041
19946	302, hair from lead strip	32.9	66.6	2.4	9	-25.55	385	40	0.9531	0.0040
20199	381, puddening from S. anchor	3.3	129.5	46.9	14	-28.71	60	90	0.9929	0.0057
19921	modern sand fence wood	5.0	200.6	48.1	3	-25.86			1.4196	0.0044

and accumulation rates of sediments, as well as some of the individual materials of which they are comprised. Of particular interest to our studies of the *QAR* wreck site is plutonium, which was first delivered to the environment as a result of atmospheric weapons testing beginning in the mid-1950's. The presence of plutonium activity in sediments under the hull and ballast rocks equaling that of surrounding exposed seafloor sediments would indicate complete sediment mixing and exposure of the artifacts during the past 50 years. A complete lack of weapons-produced plutonium underneath the wreck artifacts would prove that they have lain undisturbed since at least 1955.

SAMPLE COLLECTION AND DESCRIPTION

Radiocarbon Samples

Twelve samples for radiocarbon analysis were selected from documented components of the hull and anchors found at the wreck site and collected during October 1998 (Table 1). All wood samples were sectioned directly from these components using a clean metal saw. The wood samples from the wreck site included two pieces of oak plank, two pieces of sacrificial red pine plank, two pieces of oak frame, two sections of treenails used to join the planking, and single samples from the stocks of the south anchor and north anchor. In addition, a sample of what appeared to be modern wood derived from "sand fencing" used to control beach dune erosion was collected on the sediment surface at the wreck site. Two other non-wood samples were chosen for analysis. These samples consisted of preserved hair from a lead strip and puddening (cloth wrapping around anchor ring used to prevent anchor rope chaffing) scraped from the south anchor ring. Sub-samples were taken from plastic storage bags containing the original material. The *in situ* locations of each sample are illustrated in Figure 1.

Sediment Plutonium Samples

Sediment samples were collected for plutonium analysis at the wreck site on October 13, 1998 using SCUBA. Two coring methods were employed. Sediments under apparently undisturbed ballast rocks were sampled by prying up individual rocks and quickly inserting a 20 cm diameter PVC core pipe with a sharpened edge before disturbed sediment along the walls of the crater created could slump into it. In practice, it proved difficult to obtain sediments without addition of fine-grained sediment from the surrounding sea floor. After sealing the core top

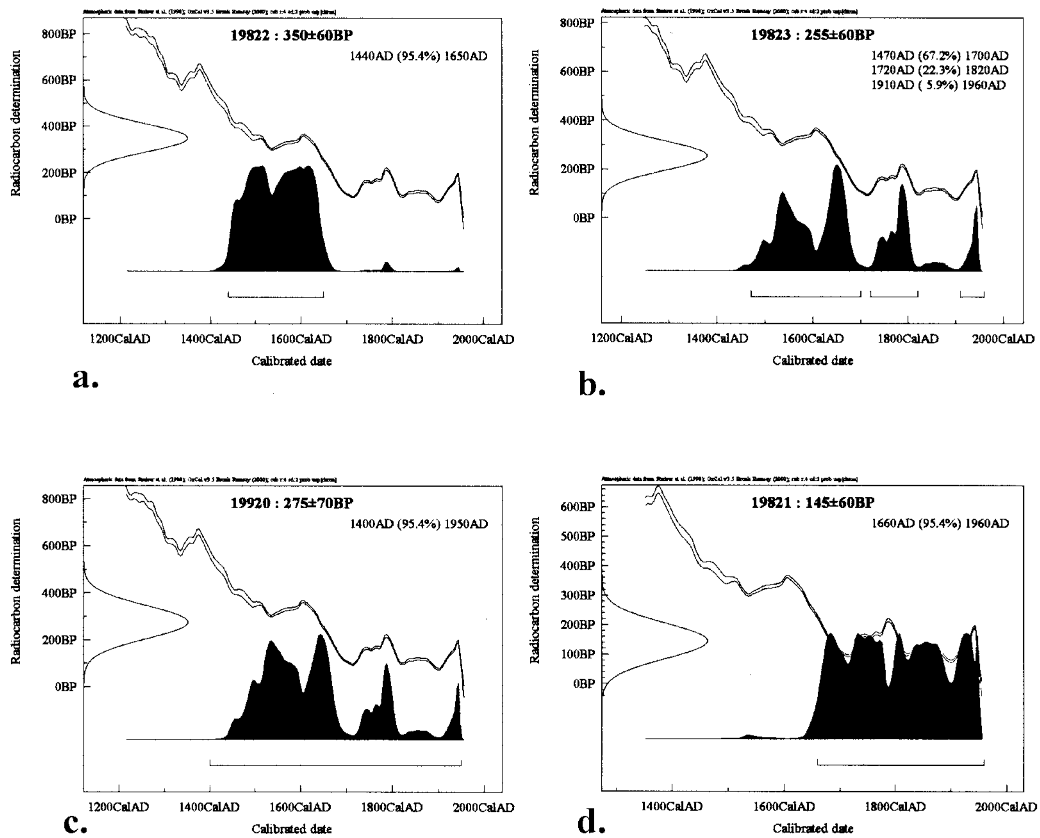


Figure 2. Radiocarbon and calculated calendar age range probability from the plank samples described in Table 1: a) sacrificial pine plank 331, b) sacrificial pine plank 367, c) oak bottom plank 368, d) oak bottom plank 358. In Figures 2-4, the RA, the relevant portion of the calibration curve, and the probability of a sample with the reported RA and error having a particular calendar age range are shown for each sample. The line along the vertical left axis displays the RA and its error. The irregular pair of lines display the relevant portion of the radiocarbon calibration curve. It can be seen that the reported RA will intersect with the calibration curve at many spots thus giving rise to a number of potential calendar age ranges. The black shaded regions show the probability the sample will have a particular calendar age range.

with a fitted plastic top to keep out sediment raised into suspension or filling in from the sides, the core was vigorously rotated and pushed down for up to a minute in order to drive it as far into the sandy sediment as possible. A bottom plate then was fitted under the corer after digging out around it. All three samples reported here were collected near the east test trench whose location is illustrated on the cover of this issue. Sediment samples were collected under the wooden planks of the remaining hull structure between frame samples 383 and 373 (see Figure 1). Sections of 10 cm OD core liner were shoved repeatedly back and forth under the planks by hand in order to obtain sufficient sample size. The liners were sealed at each end with rubber stoppers. No attempt was made to avoid homogenization of the sample inside the liner. Some contamination of these samples with surrounding seafloor material is likely to have occurred as material caved into space created during the initial insertion and repeated back and forth movements of the core liner.

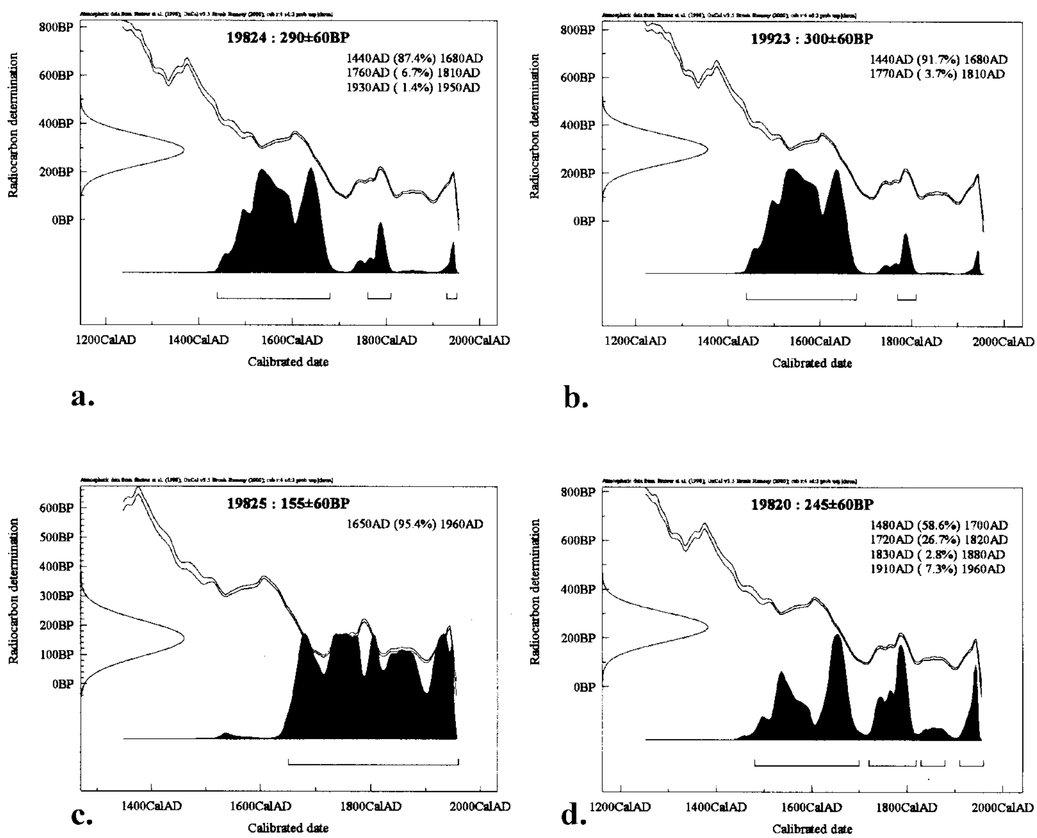


Figure 3. Radiocarbon and calculated calendar age range probabilities from the frame and treenail samples described in Table 1: a) oak frame 371, b) oak frame 384, c) treenail 298, d) treenail 383.

LABORATORY METHODS

Radiocarbon Sample Preparation Procedures at NOSAMS

All of the *QAR* samples (Table 1) underwent normal pre-treatment procedures for the NOSAMS Sample Preparation Laboratory. Samples that arrived as large pieces were divided with a razor blade. The razor blades were washed with Sparkleen detergent, rinsed with distilled water, rinsed with a 10% solution of hydrochloric acid (HCl), then rinsed a final time with organic free distilled water (MilliQ H_2O). When slicing off a piece of wood, we tried to obtain material from the inner, unexposed part of the sample. A number of smaller slices were obtained and processed for each sample.

Each sample was put into a clean, baked-out glass centrifuge tube. Approximately 8-10 ml of organic-free 10% HCl solution (enough to cover the sample) were added to the tube, which was then capped and placed in a 60°C water bath for 3 hours. Next, the acid was decanted from the tube using a baked-out disposable glass pipette, and the sample was rinsed using MilliQ H_2O. After rinsing the sample to neutral pH, the first base rinse was performed. Approximately 20 ml of 2% sodium hydroxide (NaOH) solution was added to the centrifuge tube, which then was capped, and placed in the water bath for one hour. After that time, the color of the solution was observed. If any brown discoloration was seen, the base was decanted and then another 20 ml of "fresh" base was added. The tube was then put into the water bath for another hour. This step was repeated until the solution appeared clear (free of any humic and/or

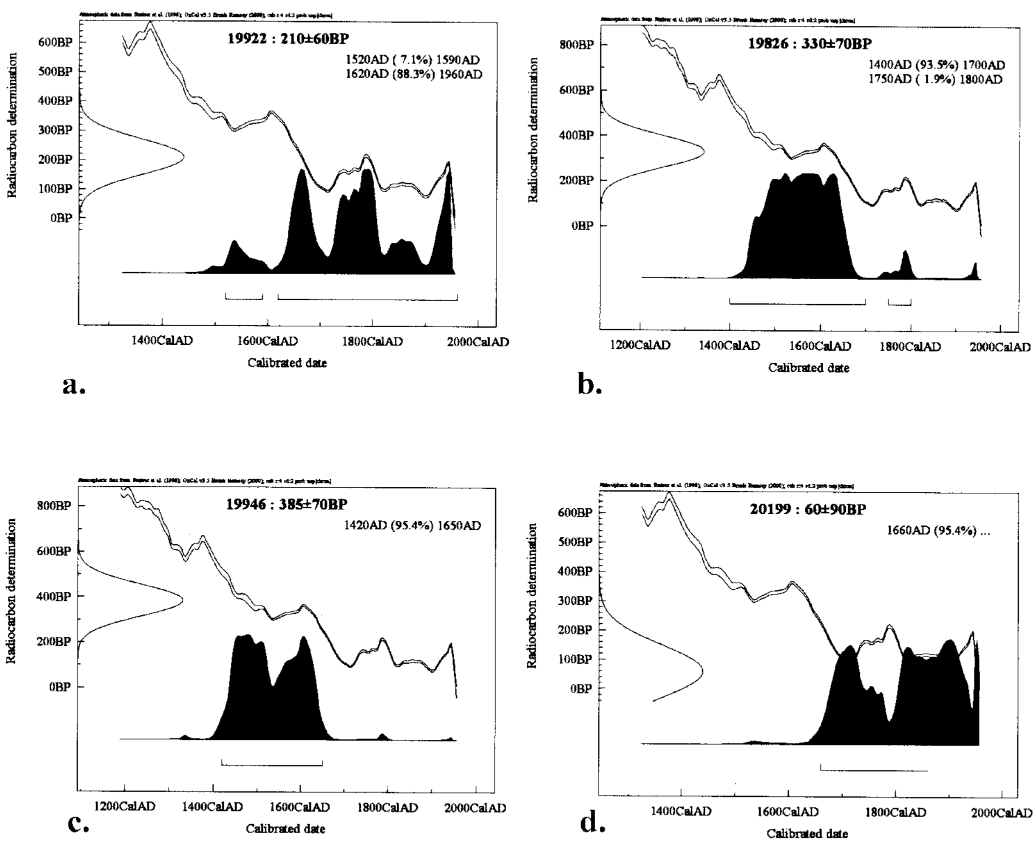


Figure 4. Radiocarbon and calculated calendar age range probabiliies from the remaining *QAR* samples described in Table 1: a) North anchor stock 386, b) south anchor stock 379, c) caulking hair 302, d) puddening from south anchor ring 381.

fulvic substances). Table 1 indicates the number of base steps required for each of these samples.

Once the solution was clear, it was decanted from the centrifuge tube, and the sample was rinsed well using MilliQ H_2O. After rinsing the sample to neutral pH, a final acid step was performed. About 5-10 mL of 10% organic free HCl were added to the tube, which was again capped and placed in the 60°C water bath for one hour.

After the final acid step, the sample was rinsed to neutral and then filtered using a vacuum-pump filtration unit. The sample was dried at 60°C in a glass petri dish. After drying, the sample was placed in a dessicator box until further processing.

All of the samples except OS 19923 were combusted using a closed-tube technique. A portion of the processed sample was transferred to a Vycor tube containing CuO and Ag. The tube was evacuated, flame-sealed and baked in a muffle furnace at 850°C for 5 hours. OS 19923 was combusted with a CN analyzer combustion/CO_2 trapping system. A small amount of sample was weighed into a tin cup, which was subsequently loaded into the sample carousel to await combustion within the CN analyzer. Following combustion, samples were converted to graphite and run on the NOSAMS accelerator using standard techniques (McNichol and others, 1995; Schneider and others, 1994; 1995).

Plutonium Analysis

Methods utilized to analyze the plutonium samples are described in detail by Benninger (1998). Whole wet sediment core samples were

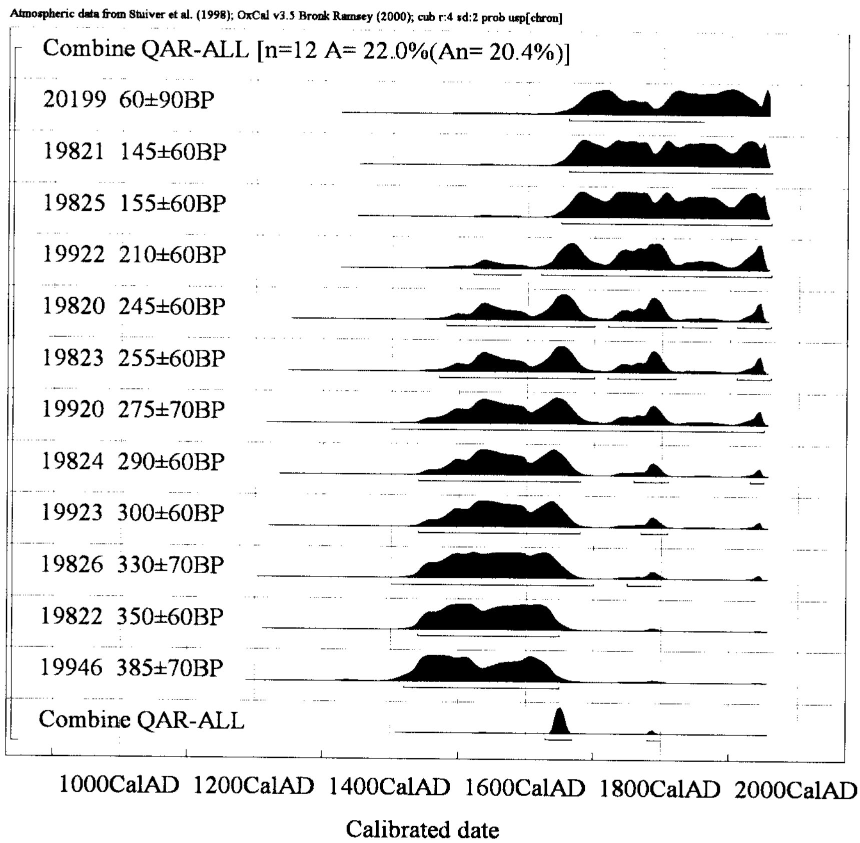


Figure 5. Summary of the calculated calendar age range probabilities for all the *QAR* samples.

oven-dried and extracted for 5-6 hours with hot, ~12M HCl. Following evaporative concentration of the filtrate and addition of ^{242}Pu as a yield tracer, the nuclides were scavenged by precipitating hydroxides and counted using alpha spectrometry.

RESULTS AND DISCUSSION

Radiocarbon Results

In Table 1, we report the radiocarbon concentration as fraction modern and as Radiocarbon Age (discussed below). The errors reported in the table are twice the reported accelerator error. We feel this represents the true sample to date error more accurately. The sand fence sample placed in the *QAR* sample group as a "ringer" gave the expected 1.42 fraction modern (fm) result indicating bomb carbon enrichment and will not be discussed further.

Conversion of Radiocarbon Ages to Calendar Ages

The amount of radiocarbon in a sample does not convert directly to a calendar or chronological age and is reported as a Radiocarbon Age (RA). Radioactive "clocks" will record the correct "time" **if** they all start with the same amount of radioactive material when they are set. The radiocarbon clock is set as living organisms grow and acquire ^{14}C naturally either photosynthetically through the atmosphere or through the carbon they eat. The amount of ^{14}C in the atmosphere has varied significantly over time and therefore requires calibration of the radiocarbon clock. Researchers have calibrated the clock using the radiocarbon stored in tree rings from long-lived, known-age trees (see

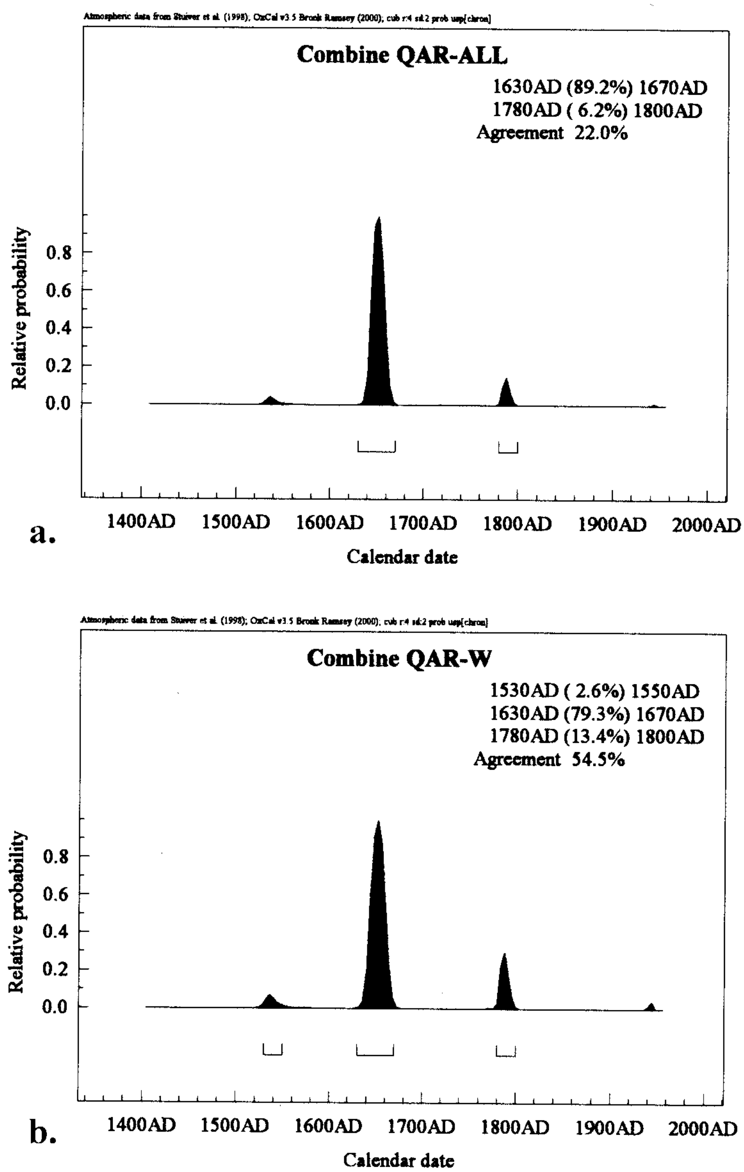
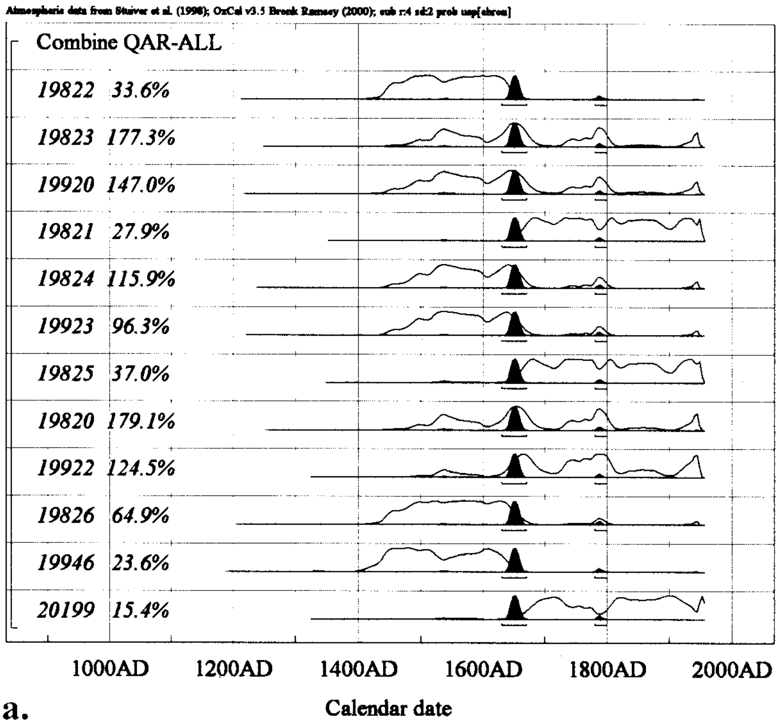
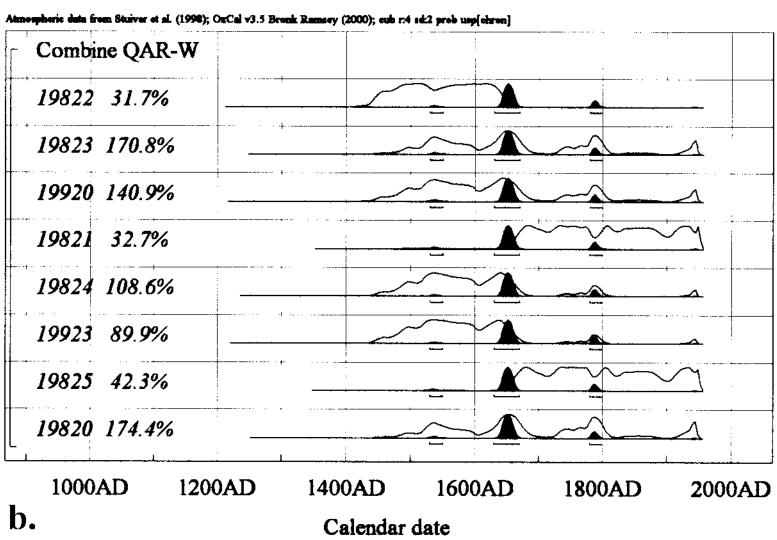


Figure 6. a) The most probable age ranges for the combined *QAR* total sample suite (*QAR*-ALL) shown as the black peaks. b) The most probable age ranges for the eight *QAR* hull wood sample suite (*QAR*-W) are shown as the black peaks. The total sample suite (*QAR*-ALL) and hull wood (*QAR*-W) sample suite and yield 89.2% and 79.3% calculated probabilities, respectively, for the age range 1630 to 1670 AD.

Calibration Issues of the journal Radiocarbon). Unfortunately for this project, the past 350-400 year period is a particularly difficult one for determining calendar ages. So much natural variation has occurred that each RA corresponds to more than one discrete calendar age. For example, we report a RA of 290 ± 60 yr BP for Sample OS 19824 (Table 1, UAU#371, frame No. 9). This age and error were entered into the OxCal calibration program (Bronk, 1995; OxCal web site is http://www.rlaha.ox.ac.uk/oxcal) to calculate the possible calendar ages and the



a.



b.

Figure 7. a) The most probable age range for the total *QAR* sample suite (*QAR*-ALL) shown as the black peaks superimposed on the individual sample age probabilities. On the left-hand side of the figure the OS number is shown along with a percentage that is related to how well the individual age agrees with the combined age as described in the OxCal manual (http://www.rlaha.ox.ac.uk/oxcal). The value may rise above 100% and the greatest confidence is found in samples showing an agreement greater than 60%; this is equivalent to a 5% confidence level for a chi squared test. b) the most probable age range for the combined *QAR* plank, frame and treenail samples (*QAR*-W). It is indistinguishable from that of the total combined samples.

Table 2. Summary of plutonium data from the Queen Anne's Revenge wreck site. The raised ballast stones were all along the east transect line. The sediments collected under planking all came from under the remaining hull structure between radiocarbon samples 383 and 371 (Figure 1).

Sample No.	Description	$^{239,240}Pu$ mBq/kg	Error 1 SD
H 376	Sediment under ballast stone	1.61	0.52
H 377	Sediment under ballast stone	3.25	0.69
H 378	Sediment under ballast stone	2.94	0.86
LC 2	Sediment under planking	5.87	1.29
LC 6	Sediment under planking	6.42	0.92
SC 25	Background sediment	15.9	1.6
SC 75	Background sediment	18.3	2.3

probability for each (Figure 3a) using the relevant portion of the calibration curve. The line along the left vertical axis displays the RA and its error. The pair of irregular lines descending across the figure illustrate the relevant portion of the calibration curve. It can be seen that the reported RA will intersect with the calibration curve at many spots thus giving rise to a number of potential calendar ages. The black shaded regions show the probability that the sample will have a particular calendar age range.

Calculated Radiocarbon Ages

Potential calendar year age ranges have been calculated for each of the samples; the results are shown in Figures 2-4. Comparison of the potential calendar age distributions for all 12 samples (Figure 5) indicates an overlap of the probability distributions in the region between 1600 and 1700 AD. The program OxCal allows combination of the probability distributions of a suite of samples to calculate the most probable age calendar age of the suite, assuming all these samples had a similar origin. The combined results for the eight hull wood samples (*QAR*-W: planks, frames and treenails) and the entire twelve samples (*QAR*-ALL) from the *QAR* site are shown in Figures 6a and b respectively. The *QAR*-W suite and *QAR*-ALL suite yield 79.3% and 89.2% calculated probabilities, respectively, for the age range 1630 to 1670 AD (Figure 6). Not surprisingly, other information from the site independently rules out the1780-1800 age range which has a lower probability according to our radiocarbon results (see Wilde-Ramsing and others, this issue). The most probable age distributions for the two different sample suites (*QAR*-W and *QAR*-ALL) are plotted with the data for each individual sample in Figures 7a and b. The suite probable ages are shown as the black peaks superimposed on the individual sample age probabilities. On the left-hand side of the figure the OS number is shown along with a percentage that is related to how well the individual age agrees with the combined age as described in the OxCal manual (http://www.rlaha.ox.ac.uk/oxcal).

The radiocarbon ages (Figure 4a and b) for the two different wooden anchor stocks found at the wreck site differ by 120 ± 85 radiocarbon years (Table 1). However, OxCal calibrations based on changes in the abundance of natural radiocarbon in the atmosphere allow their calendar year ages to overlap in the mid 1600's (Figures 4 through 7).

The combined radiocarbon results are consistent with an age range from1630 to 1670 for the randomly collected samples from planks, frames, treenails and anchor stocks. Tree ring counts (Michael Baillie, personal communication, 20 July, 2000) of several large oak samples from the ship yield a maximum number of growth rings of 62 (plus 1 incomplete). None of the timbers seems to be older than about 70 years at most. Thus, the potential ages of the wood sampled should span a period of approximately 70 years when missing sapwood is included. No younger sapwood was present at the site, suggesting that the wood used to construct the ship should have been growing at least 10 and possibly 20 years later. A correction for this lack of sapwood suggests that the 1670 age, the younger end of the 1630 to 1670 range, should be extended to approximately 1680 or 1690. In addition, uncertainties in individual sample ages combined with the limited number of randomly selected wood samples analyzed suggest that the overall age range likely covers the early 1700's, at least as recent as 1710.

Plutonium Activities

The plutonium activities measured in all sediment samples are summarized in Table 2. The activity of ^{239,240}Pu in two samples from shelf sediments surrounding the wreck site ranged from 15.8 to 18.3 mBq/kg, a range expected for shallow inner shelf sandy environments from previous surveys of North Carolina sediment activity distributions (Benninger, 1998). Plutonium activities in sands cored from underneath three ballast stones ranged from 1.6 to 3.3 mBq/kg. The ballast stones and sediment underlying them should contain zero plutonium activity if they had remained in place since before the mid-1950's. However, the low activities found may be a result of sampling difficulties. During diver removal of each ballast stone, a small amount of sediment from the adjacent seafloor surface cascaded into the newly created crater-shaped cavities. Thus, some contamination of the sediment underlying each stone by plutonium-enriched surrounding sediment would be expected. The low plutonium values found under ballast stones in comparison with those for the surrounding seafloor probably represent a mixture of the two sources. Similarly, plutonium activities in two sediment samples collected under the shipwreck's remaining planking were relatively low, ranging from 5.9 to 6.4 mBq/kg. These activity values probably reflect a mixture of low plutonium material from under the wooden structure mixed with sediment from the surrounding seafloor.

Sediments collected under the remaining hull structure and ballast stones contain plutonium activities ranging from 9% to 41% of that found in exposed surface sediments surrounding the wreck site. The source of at least some of the plutonium under the shipwreck artifacts is exposed surface sediment that was mixed in during sampling. In spite of this contamination problem, the results suggest little disturbance of the remaining intact hull and ballast rocks since the mid-1950's.

CONCLUSIONS

Radiocarbon ages for the randomly collected samples from planks, frames, treenails, anchor stocks and other organic materials found at the putative *QAR* wreck site are consistent with a calendar year age range from1630 to 1670 AD. The combined data yields ages consistent with a ship construction date between 1690 and 1710 AD.

Sediments sampled from underneath the remaining hull structure and ballast rocks of the *QAR* contained from 9 to 41% of the plutonium activity measured in surrounding exposed surface sediments. These results suggest that little disturbance of the remaining intact hull and ballast rocks have occurred since the mid-1950's.

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laboratory of L.K. Benninger at UNC-CH.

REFERENCES

Benninger, L.K., 1998, Carbon cycling on the continental margin: Evidence from sediment ^{14}C and nutrient elements. Final report, Grant DE FG 92ER61413, Office of Energy Research, U.S. Department of Energy.

Bronk, Ramsey C., 1995, Radiocarbon calibration and analysis of stratigraphy: The OxCal program. Radiocarbon 37, p.425-430.

Bronk, Ramsey C., 1998, Probability and dating. Radiocarbon 40, p. 461-474.

http://www.rlaha.ox.ac.uk/oxcal

Lawrence, R.W. and Wilde-Ramsing, M., 2001, In search of Blackbeard: Historical and archaeological research at Shipwreck Site 0003BUI. Southeastern Geology, this issue.

McNichol, A.P., Gagnon, A.R., Osborne, E.A., Hutton, D.L., von Reden, K.F., and Schneider, R.J., 1995, Improvements in procedural blanks at NOSAMS: Reflections of improvements in sample preparation and accelerator operation. Radiocarbon, 37:683-691.

Schneider, R.J., Jones, G.A., McNichol, A.P., von Reden, K.F., Elder, K.A., Huang, K., and Kessel, E.D., 1994, Methods for data screening, flagging, and error analysis at the National Ocean Sciences AMS Facility: Nuclear Instruments and Methods in Physics Research, B92:172-175

Schneider, R.J., McNichol, A.P., Nadeau, M.J., and von Reden, K.F., 1995, Measurements of the Ox-II/Ox-I ratio as a quality control parameter at NOSAMS. Radiocarbon, 37:693-696.