

## AMS-GRAPHITE TARGET PRODUCTION METHODS AT THE WOODS HOLE OCEANOGRAPHIC INSTITUTION DURING 1986–1991<sup>1</sup>

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**ABSTRACT.** In July 1986, an AMS radiocarbon target preparation laboratory was established at the Woods Hole Oceanographic Institution to produce graphite to be analyzed at the NSF-Accelerator Facility for Radioisotope Analysis at the University of Arizona (Tucson). By June 1991, 923 graphite targets had been prepared and 847 analyzed. Our lab procedures during this time included the careful documentation of weights of all starting samples, catalysts and final graphite yields, as well as the volume of CO<sub>2</sub> gas evolved during CaCO<sub>3</sub> hydrolysis or closed-tube organic carbon combustions. From these data, we evaluate the methods used in general and in our lab.

### INTRODUCTION

We present here the sample preparation and graphitization procedures used at the Woods Hole Oceanographic Institution (WHOI) AMS-Graphite Target Preparation Laboratory from July 1986 through June 1991. The methods are based on those developed by Jull *et al.* (1986) and Slota *et al.* (1987) and modified slightly by Jones *et al.* (1989). We describe additional refinements or changes to these methods. All graphite produced during this period was analyzed at the NSF-Accelerator Facility for Radioisotope Analysis at the University of Arizona (Linick *et al.* 1986). L. Toolin from the Arizona TAMS facility assisted with the initial design and setup of the glass vacuum lines for this lab. The initial line was designed to produce and quantify CO<sub>2</sub> generated from either CaCO<sub>3</sub> hydrolysis or closed-tube organic carbon combustion reactions and reduce the CO<sub>2</sub> gas to graphite in two reactor ports (Fig. 1). By June 1988, we had expanded our capabilities to include extraction of dissolved inorganic carbon (DIC) from seawater and increased the number of graphite reactor ports to six. A typical work day consisted of graphitizing five carbonate or organic carbon samples and either an NBS oxalic acid I (OX I) or oxalic acid II (OX II) gas standard. We generated vacuum line blanks (<sup>14</sup>C-“dead” carbonate) at the beginning, middle and end of each graphite target preparation batch run of *ca.* 100–120 targets.

Of the 923 targets produced from July 1986 to June 1991, 847 were AMS-dated at the Arizona facility. All targets produced after June 1991 were analyzed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility (Jones *et al.* 1990) located at the Woods Hole Oceanographic Institution. In July 1991, the lab was moved and integrated with the newly completed NOSAMS graphite preparation lab. We present summary results on 528 CaCO<sub>3</sub> hydrolysis reactions (497 AMS-dated), 144 closed-tube organic carbon combustion reactions (129 AMS-dated), and 38 DIC extractions from seawater (32 AMS-dated). We also present summary results for 170 NBS OX I and OX II standards (156 AMS-dated), 36 CaCO<sub>3</sub> hydrolysis blanks (27 AMS-dated) and 7 closed-tube organic carbon combustion blanks (6 AMS-dated).

Laboratory procedures during this time consisted of documenting and recording into a database the starting sample and catalyst weights, reactor port utilized, CO<sub>2</sub> reaction pressures, final graphite yields and the volume of CO<sub>2</sub> gas evolved by CaCO<sub>3</sub> hydrolysis or closed-tube organic carbon combustion of the samples. Also included in the database are fields such as the date the sample

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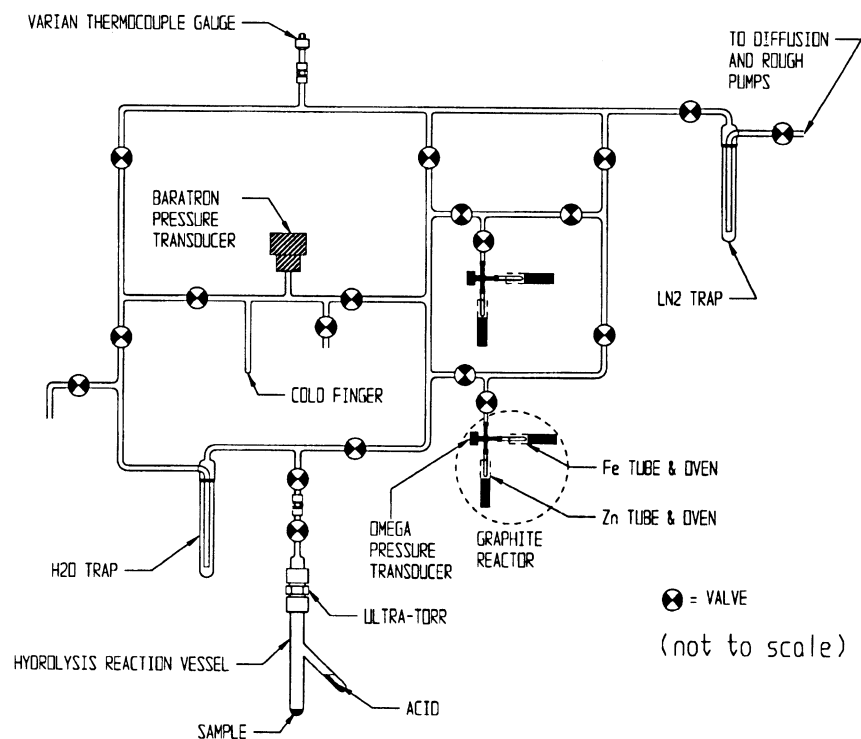


Fig. 1. Schematic of the initial WHOI graphite preparation vacuum line. Shown is the typical  $\text{CO}_2$  transfer setup for a  $\text{CaCO}_3$  hydrolysis reaction prior to acidification of the sample.

was AMS-analyzed, the  $^{14}\text{C}$  age and precision, fraction modern and precision and the corresponding Arizona AMS target accession numbers. Using this database, we can sort and calculate a wide range of parameters that allow us to evaluate the methods used in general and in our lab.

## METHODS

### NBS Oxalic Acid Standards

We made NBS oxalic acid standards using the wet digestion methods presented in Valastro, Land and Varela (1979). Our standards were made at the WHOI Radiocarbon Laboratory using the techniques outlined in Griffin and Druffel (1985). We synthesized 5 liters each of clean  $\text{CO}_2$  gas from NBS OX I and OX II. We used an approximate 3.05 cc aliquot of  $\text{CO}_2$  gas, resulting in a 1.5 mg graphite target, for each oxalic acid graphite target produced. We used the same 5-liter bulbs of OX I and OX II  $\text{CO}_2$  standards during the entire period, 1986–1991.

### $\text{CaCO}_3$ Hydrolysis

The primary carbonate sample types processed were open-ocean microfossil species of foraminifera (both benthonic and planktonic), miscellaneous macrofossil bivalve shell species and total carbonate from ocean sediments. These samples were weighed (8–15 mg  $\text{CaCO}_3$ ) and transferred to a glass reaction vessel (Fig. 1). We added 4 ml of 85% phosphoric acid to the side arm of the reaction vessel, and connected a glass-plug vacuum valve to the vessel *via* a Cajon Ultra-Torr union. We connected the vessel to the vacuum line and applied a dewar containing a dry ice/isopropanol slush

trap to the acid arm to contain water residing in the acid. The valve was opened slowly until vacuum was achieved, as indicated on a Varian 801 thermocouple gauge. The valve was closed, the vessel removed from the vacuum line and the acid warmed to ambient temperature. The vessel was tilted manually to allow the acid to flow from the side arm until it made contact with the carbonate. We added the acid slowly to prevent the sample from “splashing up” into the upper part of the reaction vessel. We then heated the acid/sample mixture to near boiling with a Bunsen burner every 30 min until we observed no reaction. Reaction time was usually *ca.* 2 h.

Once the reaction was completed, the vessel was re-attached to the vacuum line, a dry ice/isopropanol slush trap was attached to the lower finger of the reaction vessel, a second dry ice/isopropanol slush trap was attached to the vacuum line, the reaction vessel was opened and the gas was transferred cryogenically for 3–4 min to a region of known volume. The CO<sub>2</sub> was expanded in the known-volume region, warmed to ambient temperature, measured with an MKS Baratron 222BA pressure transducer and transferred directly to the graphite reactor (Fig. 1).

All carbonate blanks were made from a Pennsylvanian limestone obtained from the Arizona lab. From September 1986 to June 1989, CaCO<sub>3</sub> blanks were made without pretreatment (acid etching) of the sample. A 40–50 mg sample was crushed, *ca.* 10–15 mg were acidified and the evolved CO<sub>2</sub> was graphitized. The remaining 30–40 mg of crushed carbonate were saved for the two remaining blanks associated with each batch run of 100 target preparations. This approach resulted in each successive blank giving increasingly higher backgrounds due to adsorption of atmospheric CO<sub>2</sub> onto the carbonate. After May 1989, we implemented the following procedure for each blank produced. About 15–20 mg limestone were placed in a precleaned beaker and acidified for 1–3 min with 10% organic-free HCl (Froelich 1990). The limestone was rinsed thoroughly with double-distilled water (DDH<sub>2</sub>O) (Froelich 1990) to remove the acid and placed in a 50°C oven until dry. A precleaned (10% HCl, DDH<sub>2</sub>O rinse) agate mortar and pestle were used to crush the sample to a fine powder. The powder was weighed (10–15 mg), transferred to a reaction vessel and hydrolyzed according to the procedures outlined above. Any remaining CaCO<sub>3</sub> powder was discarded.

### Closed-Tube Organic Carbon Combustion

The primary organic carbon sample types were derived from total organic carbon and miscellaneous organic fragments in ocean sediments, wood fragments, insect parts and egg cases, and particulate organic matter from deep-ocean sediment traps. CO<sub>2</sub> was generated from each sample using the methods outlined in LeFeuvre and Jones (1988), with slight adjustments by the authors. This combustion method was chosen from review of studies conducted by Leventhal (1976). These modifications follow closely the study performed by Swerhone *et al.* (1991), which showed this method to be scientifically viable, economical and simple to perform. All materials used for these analyses (*i.e.*, beakers, syringes, tweezers and aluminum foil) were precleaned with 10% HCl and baked at 550°C in a muffle furnace for 2 h.

All sediments for <sup>14</sup>C organic carbon analysis were weighed and placed in a precleaned Pyrex beaker, acidified with 10% organic-free HCl, filtered onto a prebaked (600°C) quartz fiber filter (5 × 5 mm) and rinsed with DDH<sub>2</sub>O. The filter was wrapped lightly in precleaned aluminum foil and dried in a 50°C oven. Sample combustion tubes (9 mm o.d. × 200-mm-long Pyrex glass) were soaked overnight in Chromerge, rinsed with distilled water, then dried and baked at 550°C for 2 h in a muffle furnace. Two grams CuO (prebaked at 850°C) and a silver foil strip (4.0 × 5.0 mm, cleaned in 10% HCl, rinsed with methanol and baked at 550°C) were added to the tube. The dried, filtered sample was rolled tightly using clean stainless-steel tweezers, and fitted into the combustion tube. The tube was re-attached to the vacuum line and flame-sealed *in vacuo*. Samples were

combusted at 550°C for 5 h in a muffle furnace. After cooling slowly, the tubes were cracked under vacuum, evolved water vapor was trapped with a dry ice/isopropanol slush trap, the CO<sub>2</sub> was cryogenically transferred to a region of known volume, and the frozen sample was opened to vacuum for 10–30 s to remove incondensibles. The CO<sub>2</sub> was then measured manometrically with an MKS Baratron 222BA pressure transducer and transferred to a graphite reactor. Experiments performed on plant material by Swerhone *et al.* (1991) showed no significant fractionation in δ<sup>13</sup>C values utilizing this method.

All other material selected for organic carbon analysis was placed in a clean Pyrex beaker, acidified with 10% organic-free HCl and rinsed with DDH<sub>2</sub>O. A 2% NaOH solution was added, and the beaker placed in a 60°C constant-temperature water bath for 1 h. To remove all humic acids, the NaOH step was repeated (discarding the supernatant, usually 2–4 times, but occasionally left overnight) until the solution remained clear. The sample was rinsed with DDH<sub>2</sub>O, re-acidified with 10% organic-free HCl, and rinsed again with DDH<sub>2</sub>O during filtering (as previously described). CO<sub>2</sub> was generated by closed-tube combustion as outlined above.

To test the background of the closed-tube organic carbon combustion procedure, we generated ~1.5 cc of CO<sub>2</sub> from the Pennsylvanian limestone in the same manner as outlined for carbonate blanks in the CaCO<sub>3</sub> hydrolysis section. The CO<sub>2</sub> evolved was transferred cryogenically to a Pyrex glass combustion tube containing the following precleaned ingredients; 2 g CuO, a strip of silver foil and a quartz fiber filter that had been rinsed with DDH<sub>2</sub>O and dried. The tube with CO<sub>2</sub> was flame-sealed *in vacuo* and combusted according to the procedures outlined above.

### DIC from Seawater

We adapted methods described in Bard *et al.* (1987) to strip CO<sub>2</sub> from seawater. Each sample for DIC <sup>14</sup>C analysis was drawn from a Niskin bottle, stored in a precleaned 1-liter glass bottle and poisoned with a saturated HgCl<sub>2</sub> solution. We transferred 0.5 liter of the 1-liter sample to a stripping vessel. Ultra-pure helium was used as the carrier gas. We added 4 ml of 85% phosphoric acid to the water, and the sample was bubbled in a helium atmosphere for 1 h at a flow rate of 0.10 cfh. The vacuum-line trapping sequence consisted of 1 dry-ice/isopropanol slush trap followed by 3 liquid nitrogen traps. After 1 h, the helium was pumped away, and the LN<sub>2</sub> traps were replaced by 3 dry-ice/isopropanol slush traps (to dry the CO<sub>2</sub> thoroughly). The CO<sub>2</sub> was transferred cryogenically to a region of known volume and measured manometrically with an MKS Baratron 222BA pressure transducer. Splits for <sup>13</sup>C analysis and an archive were saved in flame-sealed glass tubes. The <sup>14</sup>C split was transferred directly to a graphite reactor. Tests performed on samples of known ΣCO<sub>2</sub> concentrations, measured coulometrically, showed that our technique recovers >99.0% of the ΣCO<sub>2</sub>.

### Graphite Target Preparation

The methods used follow closely those detailed in Slota *et al.* (1987). Glass tubing used in the reaction was precleaned with the following procedure: Vycor (quartz) and Pyrex tubing (6 mm o.d. × 130 mm) were soaked overnight in a Chromerge solution, and then baked for 3 h at 850°C for Vycor, and 550°C for Pyrex, in a muffle furnace. The Vycor tube was preweighed, 1–2 mg of 200 mesh Fe powder added, and the tube reweighed. About 50–80 mg of 300 mesh Zn powder was added to the Pyrex tube. The tubes were connected to the reactor *via* a 6.5 mm Cajon Ultra-Torr tee fitting with an attached Omega PX176 pressure transducer (Fig. 1). The reactor ovens were placed on the tubes and the catalyst and reagent roasted *in vacuo* for 20 min. Reactor-oven temperatures were 650°C for Fe and 435°C for Zn (controlled by variable transformers). We

removed the ovens, isolated the reactor from the vacuum pump and monitored the reactor pressure for 1–2 h to guarantee no leaks to atmosphere. A known amount of CO<sub>2</sub> gas was transferred cryogenically to the reactor, brought to ambient room temperature and the pressure recorded. The 435°C oven was placed over the Pyrex tube containing the Zn, so that the tip of the tube was located at the “hot spot” ( $\pm 5^\circ\text{C}$ ) of the oven. We monitored the pressure until stable (*ca.* 30 min). Residual gas analysis (RGA) performed on several reactions showed that most CO<sub>2</sub> had dissociated to CO by this time (McNichol *et al.* 1992). The 650°C oven was then placed over the Vycor tube containing the Fe, so that the tip of the tube was within the “hot spot” ( $\pm 5^\circ\text{C}$ ). The reaction proceeded overnight, and was complete (typically, 7–10 h) when the pressure in the reactor returned to zero (Fig. 2), indicating a manometrically determined 100% yield. The ovens were removed from the tubes, and the reactor cooled to room temperature. Vacuum was broken slowly at the Zn tube Ultra-Torr connector, and the Zn tube discarded. The Fe tube (with graphite) was removed immediately and weighed. A graphite yield was determined gravimetrically. The tube containing graphite was then labeled, capped with parafilm and stored in a desiccator.

## RESULTS

Having stored all of the graphite reaction values in a database file, we were able to determine a range of relations. As a check on the CO<sub>2</sub>-to-graphite reaction, several graphitizations were manometrically monitored overnight with the Omega PX176 pressure transducer connected to a HP9000 UNIX workstation *via* an HP3852 data acquisition control unit. A final pressure of zero would indicate a 100% yield. The reaction time for three different initial CO<sub>2</sub> pressures of OX II

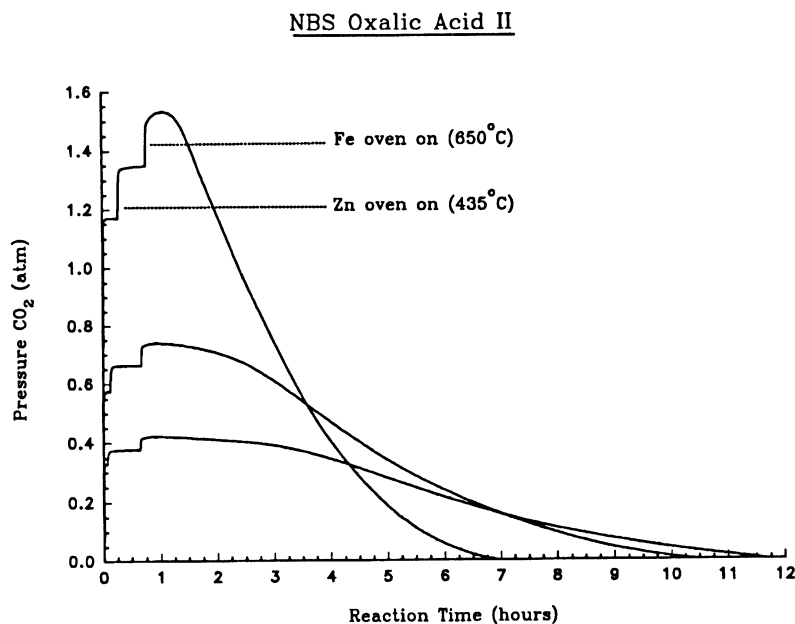


Fig. 2. Reaction times for catalytic reduction of CO<sub>2</sub> to graphite using Fe-Zn. With a starting CO<sub>2</sub> pressure of 1.1 atm (6.5 cc), the reaction was complete in 7.0 h. The reaction time increased to 10.5 h by halving the CO<sub>2</sub> pressure (0.58 atm = 3.25 cc). Reducing the CO<sub>2</sub> to 0.25 (0.33 atm = 1.8 cc) further increases the reaction time to 11.6 h. A manometrically determined 100% graphite yield was obtained from all three reactions.

## Woods Hole Graphites 045–969

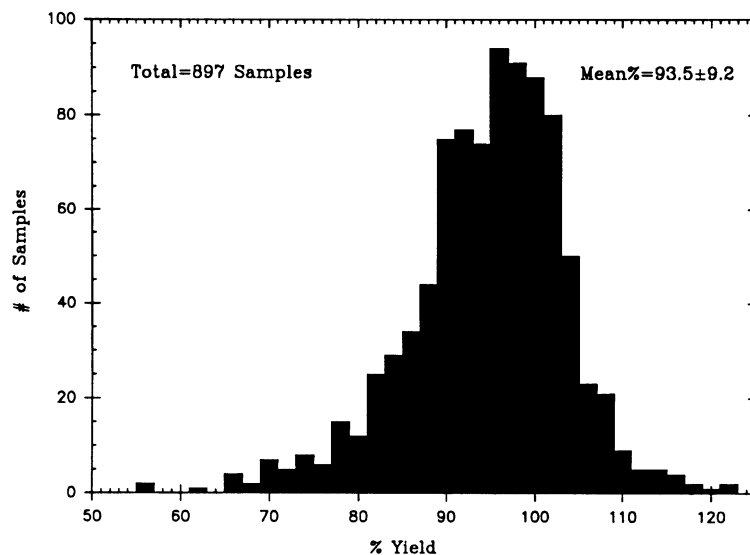


Fig. 3. Histogram of all Woods Hole graphite yields of samples produced between 1987 and 1991. Manometric measurements of the initial and final pressures for all samples indicate that all  $\text{CO}_2$  is converted to graphite; however, gravimetric measurements of the graphite suggest an average yield of 93.5%. We believe the slightly lower yields calculated gravimetrically are due to pre-roasting and vacuum pumping on the iron catalyst and tube, which occurs after the iron has been weighed into the tube. Much of the scatter in the data is due to the precision limitations of the gravimetric measurements. Mean weight of graphites produced was  $1.3 \pm 0.45$  mg where the precision of the analytical balance used was  $\pm 0.05$  mg or 4% of the mean. Percent yields are calculated as actual weighed graphite divided by the theoretically calculated graphite as determined manometrically.

increased from *ca.* 7 h for initial pressures of  $\sim 1.2$  atm (STP) to *ca.* 12 h for initial pressures of  $\sim 0.4$  atm (STP) (Fig. 2). The average  $\text{CO}_2$  pressure of samples analyzed at this lab from 1987–1991 was 0.6 atm (STP). Monitoring the reaction with  $\text{CO}_2$  evolved from closed-tube organic carbon combustion yielded a reaction time of 8–10 h for a nominal pressure of 0.8 atm (STP).

A comparison of the gravimetrically measured graphite vs. that calculated manometrically from the  $\text{CO}_2$  pressure gave a mean yield of  $93.5 \pm 9.2\%$  (Fig. 3). Monitoring the initial and final gas pressure within the reactors *via* the pressure transducer indicated a 100% conversion of  $\text{CO}_2$  to graphite. Samples were weighed immediately after vacuum was broken at the reactor to reduce moisture absorption from the atmosphere. Much of the scatter ( $\pm 9.2\%$ ) can probably be attributed to weighing the increase of 1–2 mg (graphite yield) in a tube that initially weighed 4–5 g (typical weight of tube + Fe) on an analytical balance that has an internal reproducibility of  $\pm 0.05$  mg. The difference between the mean manometric (100%) and mean gravimetric (93.5%) yields may be, in part, a result of pre-roasting and pumping on the iron catalyst after initial weighing.

On each target wheel run at the Arizona facility, there were 10 positions consisting of 8 samples, an OX I (position 1), and an OX II (position 6) standard. An OX II/OX I ratio was calculated for each wheel, and the mean value obtained from 75 pairs of OX II/OX I graphite targets produced in our lab between 1987 and 1991 was  $1.292 \pm 0.012$  (Fig. 4). The OX II/OX I value used by the Arizona facility was 1.2909 (Donahue, Linick & Jull 1990). Our standard method of interaction



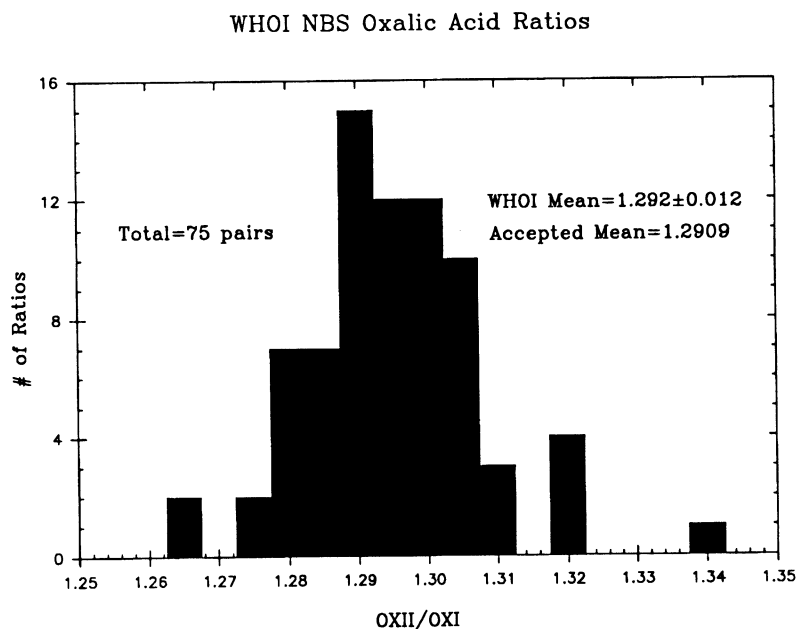


Fig. 4. Results of all Woods Hole NBS oxalic acid standard ratios obtained from 1987–1991. On each wheel of 10 WHOI targets analyzed at the Arizona TAMS facility, there is 1 OX I and 1 OX II standard. The WHOI OX II value is divided by the value of OXI (= 1.046 fraction modern), yielding a mean of  $1.292 \pm 0.012$ . The OX II/OX I ratio used by the Arizona facility was 1.2909 (Donahue, Linick & Jull 1990). The differences in the ratios determined by the two labs are statistically insignificant.

with the Arizona facility was to produce 100 targets (10 wheels = 1 WHOI batch run) consisting of 75–76 unknown samples, 10 OX I standards, 10 OX II standards, 3  $\text{CaCO}_3$  hydrolysis blanks, and 1–2 closed-tube organic carbon combustion blanks.

Figures 5A and 5B show the precision vs. the  $^{14}\text{C}$  age (in ka BP) for all Woods Hole graphite targets run at Arizona. Over 80% of the graphite targets analyzed were younger than 15 ka BP (Fig. 5B). The precision obtained for all Woods Hole graphite samples of near modern age, based largely on counting statistics and random laboratory error, is 0.6–0.7%.

Figures 6A and 6B show histograms of uncorrected percent modern carbon (pMC) values for carbonate blanks analyzed before June 1989 and from June 1989 to June 1991, respectively. Before we began pretreating (acid-etching) our carbonate blank material in June 1989, as described in the methods section, our mean blank value was  $0.556 \pm 0.37$  pMC, with higher values obtained for increased time between the crushing of the blank material and graphitization (Fig. 6A). This increase probably results from adsorption of atmospheric  $\text{CO}_2$  on the crushed  $\text{CaCO}_3$  powder (*i.e.*, large surface-to-volume ratio). After May 1989, the pre-etching of the carbonate blank material with 10% organic-free HCl for 1–3 min before crushing decreased our  $\text{CaCO}_3$  blank value to  $0.256 \pm 0.12$  pMC (Fig. 6B). The results suggest that atmospheric  $\text{CO}_2$  can contribute to contamination of old  $\text{CaCO}_3$  samples, which, in turn, can result in erroneous  $^{14}\text{C}$  values. Several tests of pre-etching vs. no treatment on foraminifera recovered from marine sediments show that pre-etching results in 2–3 ka older ages for samples near 30 ka BP (2.4 pMC). Our standard procedure is to pre-etch, with 10% organic-free HCl, all  $\text{CaCO}_3$  samples estimated to be >25 ka BP (<4.4 pMC). Our closed-tube organic carbon combustion blanks show an uncorrected value of  $0.762 \pm 0.12$

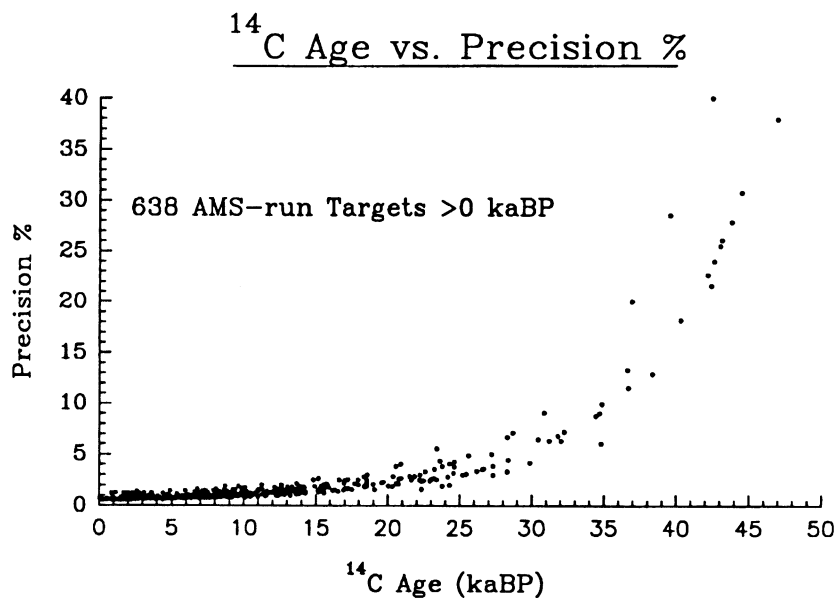


Fig. 5A.  $^{14}\text{C}$  age vs. precision % for all targets produced at WHOI and run at the Arizona TAMS facility with ages >0 ka BP (excluding blanks). Precision % is calculated by dividing the value of fraction modern error by the actual fraction modern multiplied by 100.

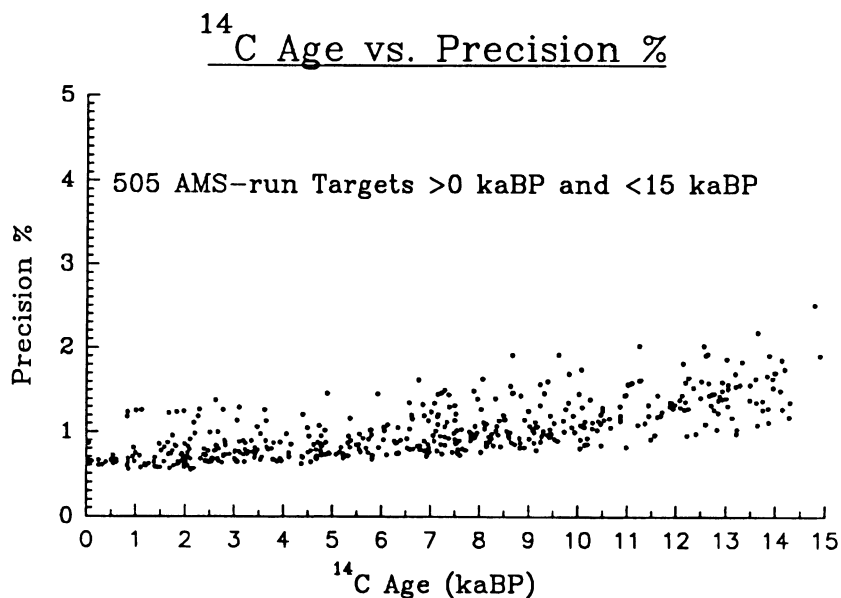


Fig. 5B.  $^{14}\text{C}$  age (<15 ka BP) vs. precision % showing only those samples in Figure 5A that are younger than 15 ka BP. Note that sample precision approaches  $\pm 0.6$ – $0.7\%$ .



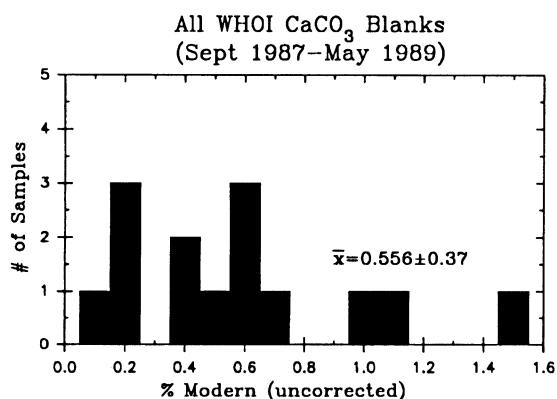


Fig. 6A. Uncorrected  $^{14}\text{C}/^{12}\text{C}$  values for 14 WHOI CaCO<sub>3</sub> blanks run before June 1989. Samples were not subjected to the pretreatment procedures outlined in the CaCO<sub>3</sub> hydrolysis methods section. Our mean pMC during the period was  $0.556 \pm 0.37$ .

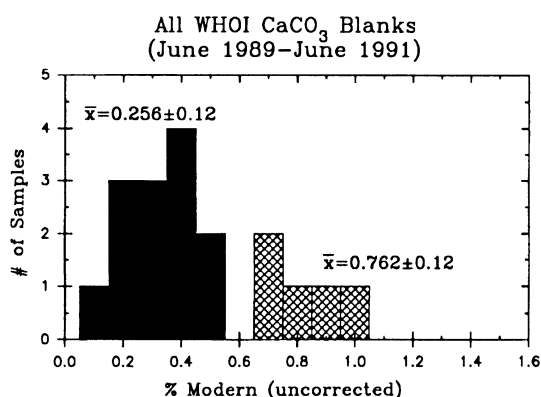


Fig. 6B. Uncorrected  $^{14}\text{C}/^{12}\text{C}$  values for 13 WHOI CaCO<sub>3</sub> blanks and 5 organic carbon blanks (hatched). All blanks made after May 1989 were subjected to the pretreatment procedures outlined in the CaCO<sub>3</sub> hydrolysis methods section. Our mean pMC during the period was  $0.256 \pm 0.12$  for CaCO<sub>3</sub> and  $0.762 \pm 0.12$  for organic carbon blanks.

pMC. Our laboratory CaCO<sub>3</sub> hydrolysis and closed-tube organic carbon combustion blank values are indistinguishable from similar results obtained in Arizona (Jull, personal communication).

## CONCLUSIONS

Between July 1986 and June 1991, we produced 923 graphite targets at the Woods Hole Oceanographic AMS Graphite Preparation Lab using the methods of Slota *et al.* (1987). Our results are consistent with those obtained at the NSF-Arizona Accelerator Facility for Radioisotope Analysis, using the same methodology. We have also shown that the graphite yields obtained with these methods have a mean yield of *ca.* 94%, with a reaction time of 7.0–12.0 h. Analysis of 75 pairs of OX I and OX II standards reveal an OX II/OX I ratio of  $1.292 \pm 0.012$ , which is in agreement with the value used by Arizona (Donahue, Linick & Jull 1990). Our background correction is 0.25 pMC (48 ka BP) for CaCO<sub>3</sub> hydrolysis samples and 0.76 pMC (39 ka BP) for closed-tube organic carbon combustion samples.

Samples estimated to be older than 25 ka BP should be pre-etched in dilute acid to remove the surface layer of CaCO<sub>3</sub>. Although this pre-etching should be performed on all samples, the very small samples often available for AMS dating preclude this as a routine procedure, and, in fact, result in an insignificant improvement in accuracy for samples younger than 25 ka BP at the levels

of precision obtained routinely. Limestone used for carbonate blanks should be pre-etched in dilute acid and converted to CO<sub>2</sub> on the same day to reduce the effect of atmospheric CO<sub>2</sub> contamination.

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