

**WOODS HOLE OCEANOGRAPHIC INSTITUTION  
RADIOCARBON LABORATORY: SAMPLE TREATMENT AND  
GAS PREPARATION**

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INTRODUCTION

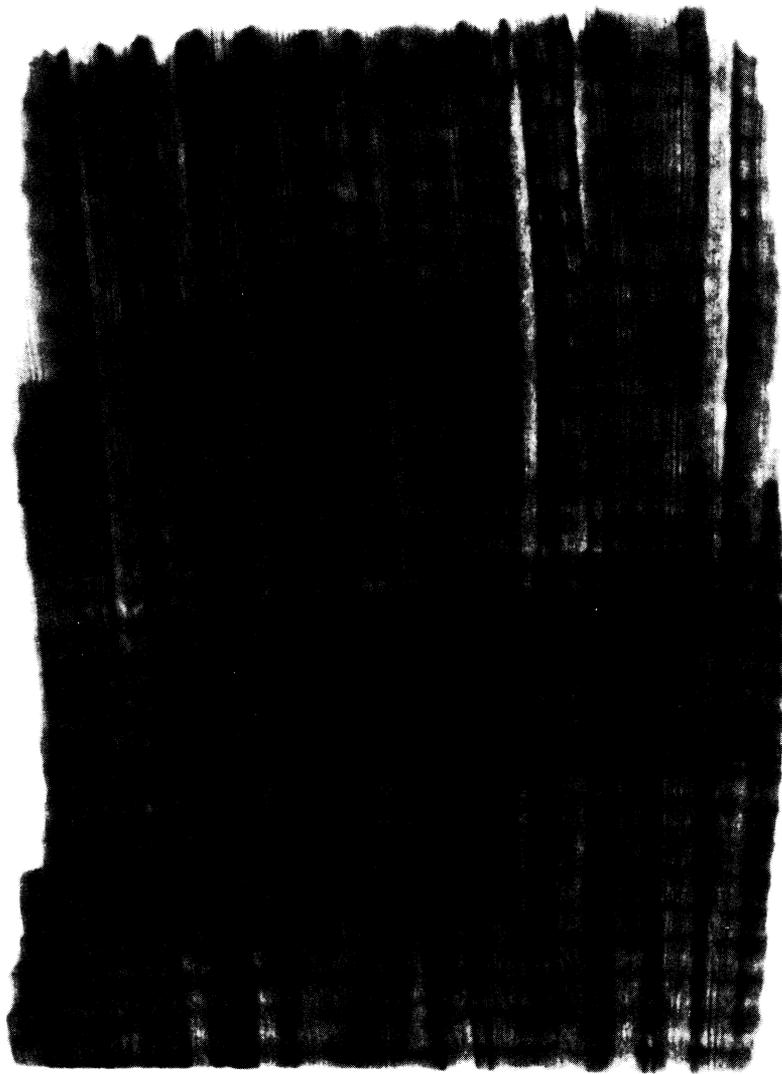
The purpose of this paper is to present the methodology used for sample preparation at the Woods Hole Oceanographic Institution Radiocarbon Laboratory. The WHOI lab is dedicated to oceanographic research supported by the National Science Foundation (OCE81-11954). We began operation in March 1982. The methods used for the production of samples are based on those developed previously (Barker, 1953; Suess, 1954; Noakes, Kim, & Stipp, 1969; Linick, 1975). Subsequent changes and refinements to these methods are described. This paper will present detailed descriptions of how various samples are collected and sectioned, then converted to  $\text{CO}_2$  and to  $\text{C}_2\text{H}_2$ , the primary counting gas for most of our samples.

Use of acetylene as a counting gas for radiocarbon detection was initiated by Suess (1954). He precipitated  $\text{SrCO}_3$  in a strong ammonia solution and then produced  $\text{SrC}_2$  by reduction with Mg. Subsequent hydrolysis of  $\text{SrC}_2$  produced  $\text{C}_2\text{H}_2$  gas. Methods were also developed during the early 1950's, that used direct absorption of  $\text{CO}_2$  into molten Li and subsequent hydrolysis of the  $\text{Li}_2\text{C}_2$  (Barker, 1953; Noakes, Kim, & Stipp, 1969; Linick, 1975). The preparation of acetylene from coralline aragonite, the primary oceanographic substrate used in our research, is described here.

Acetylene gas is used for two major reasons. First, our past experience at the La Jolla Radiocarbon Laboratory in collaboration with Hans E Suess was with acetylene detection systems (Suess, 1954). Second, higher levels of impurities are tolerated when counting acetylene than with  $\text{CO}_2$  counting, with no significant alteration of counter pulse height or energy. Thus, it is feasible to use one-channel detection systems for monitoring radiocarbon pulses from acetylene gas. Carbon dioxide gas is counted for samples smaller than 900mg carbon.

Research topics of major interest to us are those involving the cycling of carbon between atmosphere and ocean, as well as determination of past ocean circulation. We are particularly concerned with those mixing processes in the upper few hundred meters of the water column. Skeletons of corals are excellent monitors of various physical and chemical processes in the oceans. Hermatypic, or reef-building, corals accrete calcium carbonate using mainly the dissolved inorganic carbon (DIC) extracted directly from the surrounding sea water. They accrete density layers, which are detectable using X-rays. Plate 1 shows an X-radiograph of a slab of *Diploria strigosa* (8mm thick) cut along the vertical axis of growth from a massive (hemispherical) head (1.3m diameter) collected from the south shore of Bermuda (33°N, 63°W). Each alternating light and dark density band constitutes one

## PLATE 1



X-ray positive of a slab of coralline aragonite, 9mm thick, cut along the axis of growth of *Diploria* from North Rock in Bermuda.

year's growth, the dark band having been accreted during the warm months (30°C) of July–September.

Recorded within known-aged coral bands are time histories of: 1) sea surface temperature and salinity from  $^{18}\text{O}/^{16}\text{O}$  ratios (Weber & Woodhead, 1972; Fairbanks & Dodge, 1979); 2) input of anthropogenic Pb from Pb/Ca ratios (Shen & Boyle, 1983); 3) fossil fuel  $\text{CO}_2$  and bomb-produced  $^{14}\text{C}$  from  $^{14}\text{C}/^{12}\text{C}$  ratios (Druffel & Linick, 1978; Druffel & Suess, 1983); 4) bomb-produced fallout products, such as  $^{90}\text{Sr}$  (Toggweiler, 1983) and  $^{239,240}\text{Pu}$  (Purdy, Livingston, & Druffel, unpub data). For the results of our research, the reader is referred to other publications (Druffel, 1980, 1981, 1982).

It is our purpose here to describe in detail the technical aspects of our methods for sample collection, sectioning, and gas preparation. Attention to detail and inclusion of “tricks of the trade” are important to the scientist who intends to set up his/her own lab. Intercalibration of the counting systems with other labs will appear in a later publication.

## METHODS

### *Sample Description and Preparation*

Coral for  $^{14}\text{C}$  analysis is collected using a hydraulic drill fitted with a diamond bit and a core barrel 3 to 4 inches in diameter. This arrangement is driven by a small hydraulic pump which is operated from aboard ship (Hudson *et al.*, 1976). Using extensions, cores up to 14 feet long have been obtained. The cores are cleaned by placing them under running water for approximately four hours to remove most of the polyps and residual sea salts. The cores are dried and sliced along the vertical growth axes using a diamond rock saw. Slabs, 4 to 10mm thick, are ultrasonically cleaned to remove dust imbedded in the skeleton. The dried coral slabs are X-rayed at the Falmouth Hospital x-ray facility. Yearly growth bands appear as alternating high and low density bands (pl 1). A map is made from the X-ray by tracing the high density bands onto an acetate sheet, which is then transferred onto the coral slab. It is below this line that the coral is cut into one-year growth bands using a band saw. Bands cut in this manner from *Diploria* collected off Bermuda represent a September-to-August time interval. These bands are then ground into coarse fragments using a porcelain mortar and pestle. If seasonal growth bands are desired, then the one-year growth bands are sectioned into four equidistant parts. These small bands are sanded off using a Dremel tool. Sanding minimizes the amount of sample lost due to the thickness of the saw blade.

Other types of samples are also prepared at the WHOI lab. Cellulose from tree rings, hydrothermal vent samples (shells and tissue), seawater marine biomass and ocean sediments are pre-prepared in accordance with standard techniques described previously.

### *Preparation of Counting Gas*

The WHOI lab uses acetylene as the counting gas for most  $^{14}\text{C}$  analyses. Initially, each sample is converted to carbon dioxide using either the

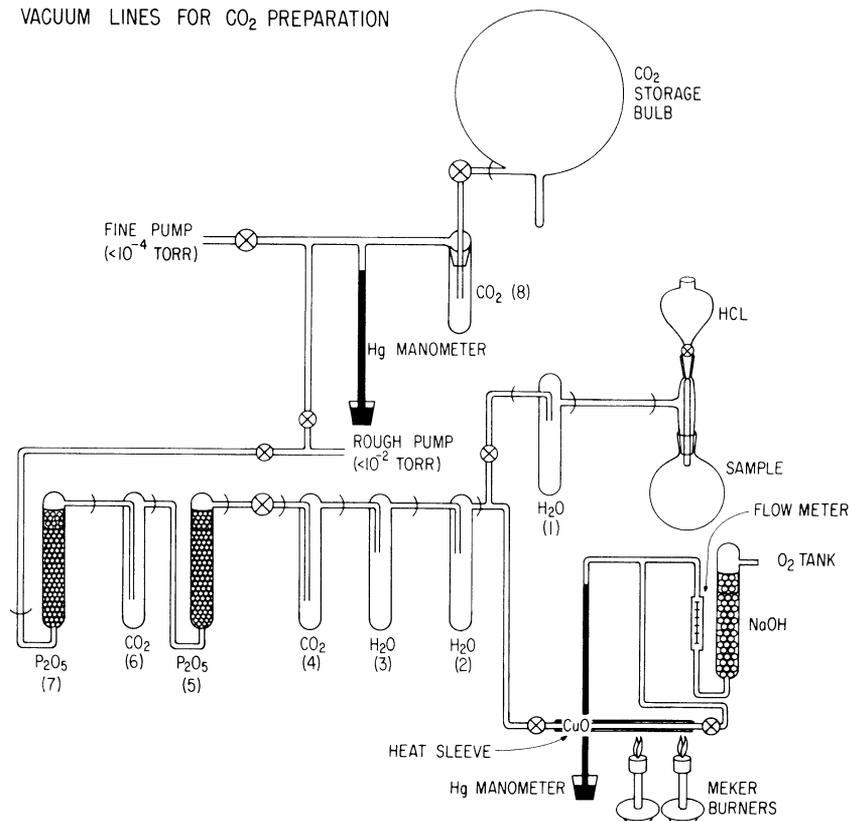
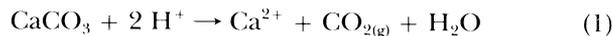
VACUUM LINES FOR CO<sub>2</sub> PREPARATION

Fig 1. Schematic of vacuum system used for CO<sub>2</sub> preparation. Carbon dioxide is produced initially either by acidification with HCl or by heat in a stream of oxygen gas. Subsequent elimination of water is achieved in traps 1, 2, 3, 5, and 7 (see text for detail).

acidification or burning methods (fig 1) and then reduced to acetylene gas via lithium carbide (fig 2). The vacuum lines are constructed of borosilicate glass (Pyrex). The stopcocks are glass barrel o-ring construction; o-ring ball joints are also used to reduce the risk of contamination from stopcock grease.

*Acidification.* Ca 22g of coralline aragonite is acidified in order to generate enough gas (2.35L acetylene) for the 1.5L quartz counter. The sample is placed in a 3L round-bottom flask, and air is evacuated to a pressure of  $10^{-3}$  torr using mercury diffusion and two-stage mechanical pumps (fig 1). Small aliquots of 4N HCl are then added to the sample over a 30-minute period. The amount of time it takes to complete the reaction is dependent on the weight, grain size, and percent organic carbon content of the sample. Carbon dioxide evolves according to this reaction:



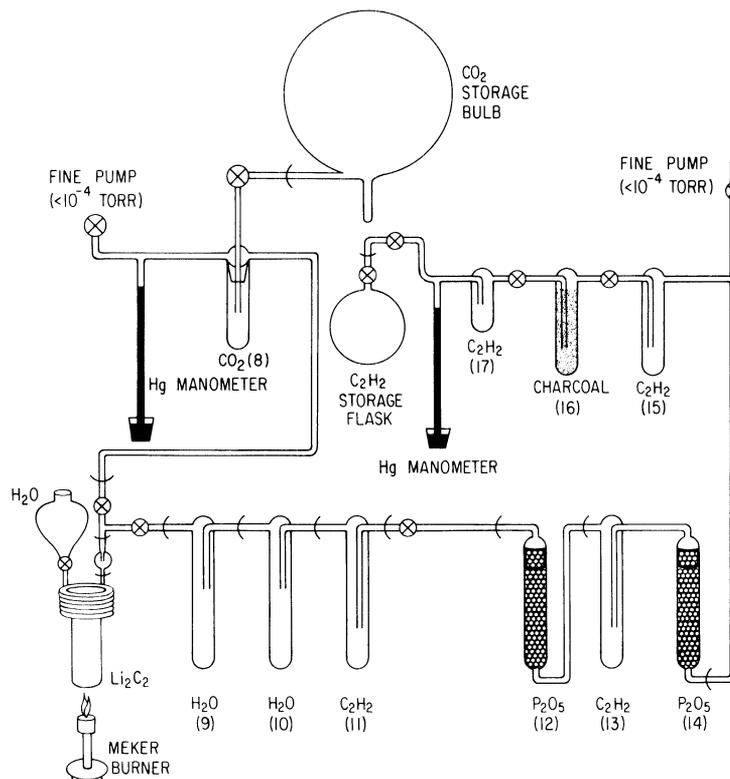
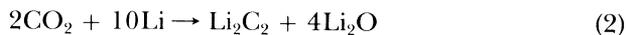
VACUUM LINES FOR  $C_2H_2$  PREPARATION

Fig 2. Schematic of vacuum system used for  $C_2H_2$  preparation. Carbon dioxide is absorbed into molten lithium, cooled, and hydrolyzed with well water. Water is eliminated by traps 9, 10, 12, and 14 and the resultant  $C_2H_2$  is purified in trap 16. The triple point of each sample is measured to insure 99.9% acetylene content (see text for detail).

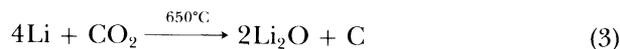
The gas passes through a series of traps. Traps 1, 2, and 3, surrounded by dewars filled with isopropanol/dry ice slushes ( $-77^\circ\text{C}$ ), collect water that distills over from the reaction vessel. Carbon dioxide is frozen into trap 4, which is surrounded by liquid nitrogen ( $-192^\circ\text{C}$ ). When the reaction is finished, as evidenced by the cessation of small bubbles, the liquid nitrogen is removed from trap 4. A stirring bar is then activated in the flask for a minimum of 15 minutes to rid the solution of traces of  $\text{CO}_2$ . Meanwhile, the  $\text{CO}_2$  is expanded through phosphorous pentoxide covered glass beads (trap 5) and frozen into trap 6. Trap 6 is then isolated and pumped to a pressure of  $10^{-4}$  torr. The  $\text{CO}_2$  is then dried by an additional  $\text{P}_2\text{O}_5$  trap (7), and expanded into a 12L holding flask and the pressure recorded.

*Reduction of carbon dioxide to acetylene.* The carbon dioxide is reduced to acetylene gas via lithium carbide (fig 2). Carbon-free lithium is purchased

from Lithium Corporation of America in rod-form, dry packed in argon gas. The lithium is stored under vacuum and away from direct light in a greaseless o-ring desiccator. We found that these refinements reduced the buildup of white lithium oxide on the surface of the rods, thus increasing the shelf-life of the lithium. A 10% stoichiometric excess of lithium is used for each conversion (Linick, 1975):

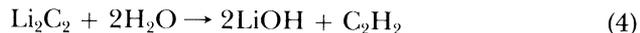


The lithium is placed in the bottom of a cylindrical pot. The pot is constructed of 316 stainless steel with an OD of 33cm and 36cm high. The pot is then pumped to a pressure of  $<10^{-2}$  torr. A Meker burner fueled by propane gas is used to heat the lithium to 600°C. An Omega K-199 temperature probe placed 2mm above the inside bottom of the pot is used to monitor the temperature of the lithium. The CO<sub>2</sub> gas is ready to be absorbed into the molten lithium when the lithium has a mirror-like finish, visible through dual windows on top of the pot, and the pot is fully degassed ( $<10^{-2}$  torr). The flame under the pot is then reduced slightly so that a 600–650°C temperature is maintained during the absorption, as this reaction is highly exothermic. If the CO<sub>2</sub> is added too quickly, the lithium becomes too hot and another reaction is favored (Linick, 1975):



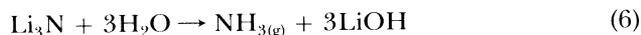
After the absorption reaction is complete, the pot is maintained at a temperature of 625–650°C while the pot is vacuum pumped for a period of 90–120 minutes. The purpose of this after-burning is to remove any residual gases, including radon (<sup>222</sup>Rn) which decays with a half-life of 3.8 days. The afterburning also allows any elemental carbon that may have formed (equation 3) to be converted to lithium carbide. The lithium mixture is then allowed to cool overnight.

The lithium carbide is hydrolyzed by the addition of well water to the pot:



The well water is collected at a free-flowing aquifer at Chekika State Recreation Area, Florida. It has been tested by H G Östlund, RSMAS, University of Miami, and is found to contain negligible amounts of tritium ( $\leq 0.2$  TU). We have observed that too low a volume of well water used for hydrolysis reduces the yield of acetylene from Li<sub>2</sub>C<sub>2</sub>. We suspect this is a function of the solubility of Li salts in aqueous solution. An average yield of 98% is standard when using 1200ml of well water for Li<sub>2</sub>C<sub>2</sub> equivalent of 10–12L of CO<sub>2</sub>. The well water is added slowly to the carbide, as the production of acetylene from lithium carbide is violently exothermic. A pressure of 60cm Hg is maintained in the system; most of this pressure is due to hydrogen from the hydrolysis of excess lithium metal. The evolved acetylene is then dried by two slush traps (9 and 10) and frozen (trap 11). Termination of the hydrolysis is indicated when hydrogen production drops markedly and the temperature of the hydrolysis solution is ca 27°C. Pres-

sure in the vacuum system is slowly reduced to  $10^{-2}$  torr. The acetylene (trap 11) is dried over  $P_2O_5$  (trap 12), frozen (trap 13) and pumped to  $10^{-3}$  torr. The acetylene is then dried a second time (trap 14) and frozen (trap 15). The sample is then distilled through activated charcoal (trap 16) which has been cooled to  $0^\circ\text{C}$ . This step removes residual gaseous impurities in the sample. After each use, the charcoal trap is vacuum pumped overnight at  $500^\circ\text{C}$ . The distilled acetylene is frozen into trap 17. The triple point of the gas is checked to test for impurities. The triple point of pure acetylene occurs at  $-80.8^\circ\text{C}$  and 96cm Hg. Ammonia ( $\text{NH}_3$ ) may be present if the pot leaked during any part of its heating:

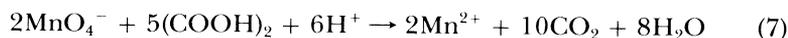


A few parts per thousand of ammonia will not affect the manner in which the sample counts, but it will dilute the gas and lower the apparent  $^{14}\text{C}$  activity. If the triple point of a sample is depressed by more than 1cm, the concentration of  $\text{NH}_3$  most likely exceeds 0.1% in the sample. In this event, the sample is distilled through syrupy phosphoric acid (85%) and then through  $P_2O_5$  and charcoal traps. When water is present in the sample, visible detection is apparent by a flaky white crust that is present before and during the triple point. Samples are distilled through an isopropanol-dry ice slush trap to remove water. In contrast to acetylene, carbon dioxide as the counting gas is affected by oxygen and to a lesser extent by nitrogen in amounts of a few parts per million (Brenninkmeijer & Mook, 1979). The sample is stored in a pyrex flask for at least three weeks to allow for the decay of any  $^{222}\text{Rn}$  that might still be present.

*Oxidation by burning.* Samples containing organically-bound carbon, (such as wood, animal biomass, ocean sediments, etc) are placed in porcelain boats and then into a large Vycor tube (31mm OD, 24mm ID) (fig 1). Medical grade oxygen, which is free of petroleum products, is passed through a trap filled with sodium hydroxide pellets in order to remove any  $\text{CO}_2$ . Initial heating of certain samples (*ie*, cholesterol, wood, etc) is performed slowly in order to avoid distillation of volatile organics. Each sample is burned for a period of 1 to 4 hours with an oxygen flowrate of 5–10ml/min, using two Meker burners. The combustion products are passed over wire-form  $\text{CuO}$  ( $600^\circ\text{C}$ ) in order to oxidize  $\text{CO}$  and other carbonaceous distillates to  $\text{CO}_2$ . Water is eliminated by using a dry-ice slush (trap 2). The carbon dioxide is then passed through a trap containing chromic acid (trap 3). Subsequently, the samples are treated in the same manner as described above for acidified samples (figs 1, 2).

*NBS oxalic acid standard.* The acetylene prepared from an NBS oxalic acid standard (#SRM 4990-B) is used to monitor the sensitivity of all the  $^{14}\text{C}$  counters. We use the wet digestion method for preparation of carbon dioxide from oxalic acid (Valastro, Laud & Varela, 1979). The oxalic acid is oxidized by potassium permanganate in an acidic aqueous media to produce

CO<sub>2</sub>:



The reaction vessel is left open to the vacuum line while being stirred for a minimum of 30 minutes after completion. This allows for the decomposition of all oxalate compounds and eliminates significant isotopic fractionation of the collected CO<sub>2</sub>. The evolving CO<sub>2</sub> gas is treated and collected in the same manner as that described above for coral samples (fig 1) and then converted to acetylene gas (fig 2).

*Preparation of background samples.* A carbonaceous compound that contains essentially no <sup>14</sup>C is used to measure the background activity of each proportional counter. Limestone is converted to calcium carbide by Union Carbide, Inc. The calcium carbide is then converted to acetylene in the laboratory:



Chekika well water is used to hydrolyze the CaC<sub>2</sub> in a 3L round-bottom flask. The evolved acetylene is dried by three slush traps and two P<sub>2</sub>O<sub>5</sub> traps. Other gaseous contaminants are removed by passing the acetylene over activated charcoal cooled to 0°C. The acetylene is then aged for at least six weeks, to allow for the decay of <sup>222</sup>Rn, which is present in significant quantities immediately after preparation.

#### *Cleaning Procedures*

All the pyrex traps used for acidifying, burning, and reduction are cleaned after each sample. They are rinsed with 6N HCl, tap water, distilled water, and finally with reagent-grade acetone and dried at room temperature. The porcelain boats and vycor tubes used during the burning of samples are cleaned occasionally by soaking them in a dilute solution of HF.

After hydrolysis of each sample, the stainless steel pot is cleaned with 6N HCl and rinsed with tap water, distilled water, and finally with reagent-grade acetone. No additional steps are taken to remove a layer of stainless steel from the pot, as we have determined that no significant memory from previous samples is retained within the walls of the pot, in contradiction to the findings of Radnell and Muller (1980).

#### CONCLUSIONS

Our methods for collection, mapping, and cutting of hermatypic corals are described in detail. Preparation of acetylene from aragonitic coral bands is essentially the same as that described by Linick (1975) for sea water carbonate. We have made refinements to this method, which include: 1) a minimum amount of well water is required to obtain maximum yield during hydrolysis; 2) close monitoring of Li temperature is important for complete conversion to Li<sub>2</sub>C<sub>2</sub>; 3) careful storage of lithium, under low light conditions in a vessel free from all carbon-based stopcock grease (o-ring type) reduces dramatically the degradation of lithium metal. It is necessary to stress that checking the triple point of the acetylene (George Bien, pers

commun; Linick, 1975) is an important step in determining the purity of the resultant sample gas.

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