

## THE RAPID PREPARATION OF SEAWATER $\Sigma\text{CO}_2$ FOR RADIOCARBON ANALYSIS AT THE NATIONAL OCEAN SCIENCES AMS FACILITY

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**ABSTRACT.** We have established a laboratory for extracting  $\Sigma\text{CO}_2$  from seawater samples for AMS analysis of the radio-carbon content. The seawater samples are collected at sea, poisoned and stored until analysis in the laboratory. Each sample is acidified; the inorganic carbon is stripped out as  $\text{CO}_2$  with an inert carrier gas and then converted to graphite. We present results for Buzzards Bay surface  $\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3$  standards that demonstrate we strip >98% of inorganic carbon from seawater. Stable isotope analyses are performed to better than 0.2‰, and the reproducibility of  $^{14}\text{C}$  measurements on Buzzards Bay seawater is better than 13‰. Finally, we compare data from samples collected in 1991 to those collected in the 1970s and to large volume samples.

### INTRODUCTION

Early studies demonstrating the viability of using accelerator mass spectrometry (AMS) to measure  $^{14}\text{C}$  in seawater inorganic carbon (Bard *et al.* 1988; Kromer *et al.* 1987; Ostlund *et al.* 1987a; Schlosser *et al.* 1987) led to the inclusion of an AMS  $^{14}\text{C}$  sampling program in the World Ocean Circulation Experiment (WOCE). One component of the WOCE Hydrographic Program (WHP), the collection of thousands of seawater samples for AMS  $^{14}\text{C}$  analysis, was a driving force for the establishment of the National Ocean Sciences AMS (NOSAMS) facility at the Woods Hole Oceanographic Institution (WHOI). The WOCE program requires a precision of 5–10‰ for the AMS analysis of  $\Delta^{14}\text{C}$  (Joyce, Corry and Stalcup 1991) in surface seawater samples and a precision of 3–4‰ for deepwater samples, *i.e.*, samples below *ca.* 1000 m.

Östlund *et al.* (1987a), Bard *et al.* (1987) and Kromer *et al.* (1987) made the first AMS measurements of seawater. In general, the methods used to strip  $\text{CO}_2$  from an acidified seawater sample were either bubbling with a carrier gas (Bard *et al.* 1987; Ostlund *et al.* 1987a) or extraction with a vacuum source (Dörr and Münnich 1980). Bard *et al.* (1987) reported results with a standard deviation of 11‰, Kromer *et al.* (1987) reported a standard error of 5‰ and Ostlund *et al.* (1987a) reported a precision of 5–10‰.

Our laboratory was set up for the rapid preparation of inorganic carbon in seawater for analysis by AMS. In this paper, we describe in detail our method for extracting  $\text{CO}_2$  from seawater, and we demonstrate our ability to accurately and reproducibly prepare seawater samples for AMS. We also present results from the analysis of local surface seawater and two WOCE  $^{14}\text{C}$  AMS depth profiles.

### METHODS

Seawater for all WOCE analyses is collected in pre-weighed 500-ml borosilicate glass bottles with high-quality ground-glass stoppers and poisoned according to a published protocol (McNichol and

Jones 1991). Dissolved inorganic carbon ( $\Sigma\text{CO}_2$ ) is extracted as  $\text{CO}_2$  gas from the samples on the vacuum line shown in Figure 1; the vacuum system consists of a molecular drag pump in tandem with a diaphragm pump. The samples are stripped in the bottles in which they are collected. Up to five samples can be attached to the line at one time. Samples to be analyzed are weighed and transferred to a glove bag where stripping probes are attached in an  $\text{N}_2$  atmosphere (insert, Fig. 1). The bottles are then attached to Region I of the vacuum line, and the line is evacuated up to the valves on the stripping probe (Valves V1 and V2). Each sample is acidified by adding 4 ml of 85%  $\text{H}_3\text{PO}_4$  by injection through a rubber septum. When the line has been evacuated, high-purity  $\text{N}_2$  gas (99.99%) is added to Regions I, II and III to a pressure of *ca.* 0.8 atm. A cold bath at  $-80^\circ\text{C}$  is placed on the trap in Region II and liquid nitrogen baths ( $-190^\circ\text{C}$ ) are placed on the loop traps in Region III. When the cold traps are in place and all the valves in the circulation loop are open, a recirculating pump (Parker Hannifan Metal Bellows MB-10) is turned on, forcing the carrier gas through the fritted end of the probe and producing a stream of fine bubbles throughout the seawater. Gaseous  $\text{CO}_2$  partitions into the  $\text{N}_2$  bubbles and is swept into the cold traps where it is frozen down. After 10 min, the pump is shut off, the  $\text{N}_2$  carrier gas is slowly pumped away, the liquid nitrogen baths on the loop traps are replaced with  $-80^\circ\text{C}$  cold baths and the  $\text{CO}_2$  is collected in a calibrated volume (Region IV). The gas pressure is recorded and used to calculate the concentration of  $\text{CO}_2$  ( $\Sigma\text{CO}_2$ ) in each sample; the gas sample is then transferred to a storage manifold (Region V). Typical yields for seawater samples are *ca.* 1 mmol of  $\text{CO}_2$ . While the sample is being quantified, the vacuum line is prepared for the next sample. The average analysis time is *ca.* 45 min.

After ten samples have been stripped, the storage manifolds are removed from the water line and attached to the graphite transfer line (Fig. 2) where the gas is split into aliquots for graphite target

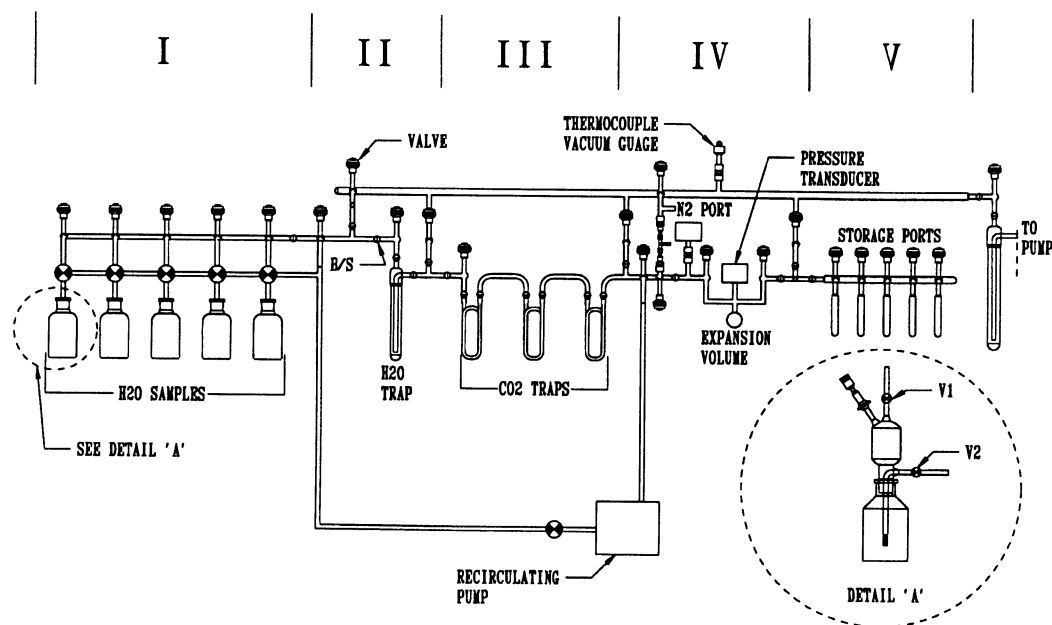


Fig. 1. Water stripping line and stripping probe (insert). Ball and socket O-ring joints (B/S) were added to facilitate dismantling and cleaning. The use of a glass system reduces the number of parts that must be replaced due to corrosion from salt water vapor. The stripping probe is designed to fit directly on bottles with a standard taper high-quality ground-glass joint. Valves V1 and V2 are integral parts of the stripping probe and are not part of the stripping line.

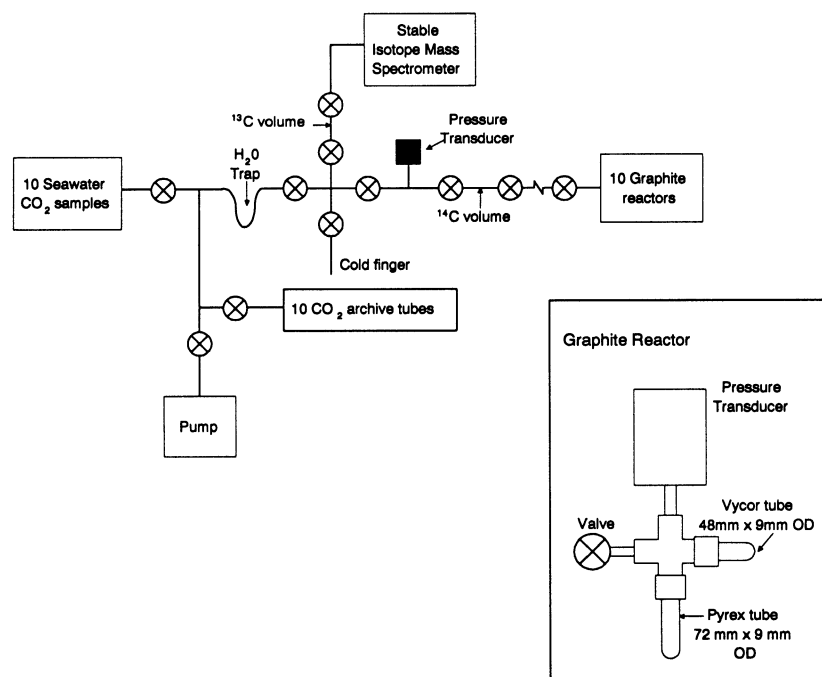


Fig. 2. Schematic diagram of graphite transfer line for seawater samples. A blowup of the reactor is shown in the insert. Sample manifolds are attached, and each sample is sequentially transferred to the cold finger. From the cold finger, splits of each sample are transferred to an isotope ratio mass spectrometer, to an archive tube and to a graphite reactor.

preparation (20%), stable isotope ratio analysis (10%) and archiving (70%). The graphite target preparation method used at NOSAMS has been described elsewhere (McNichol *et al.* 1992). Briefly,  $\text{CO}_2$  is transferred to a reactor, where it is catalytically reduced to carbon filaments at high temperature ( $625^\circ\text{C}$ ) using  $\text{H}_2$  gas as the reducing agent and Fe as the reduced metal catalyst; the reaction takes *ca.* 4 h. During 1992 and the first half of 1993, stable isotope analyses were performed on three different mass spectrometers—a VG Micromass 602E in the laboratory of Lloyd Keigwin (WHOI), a VG Prism in the Earth and Planetary Sciences Department at Harvard University and a VG Prism at our facility. Since June 1993, most stable isotope analyses for seawater samples are performed in the NOSAMS sample preparation lab on an in-line VG Optima mass spectrometer.

We use two types of samples as standards— $\text{Na}_2\text{CO}_3$  solutions and local surface seawater. We prepare our  $\text{Na}_2\text{CO}_3$  standards in batches of 9–12 samples;  $\text{Na}_2\text{CO}_3$  is dried overnight in a  $250^\circ\text{C}$  oven; *ca.* 424 mg are weighed accurately ( $\pm 0.01$  mg) and quickly transferred to a 2-liter volumetric flask. Exposure to air is minimized because  $\text{Na}_2\text{CO}_3$  absorbs water from air and forms a basic solution that absorbs  $\text{CO}_2$  from the surrounding air. This is more likely to have an effect on the isotopic measurements than on the concentration measurements. Distilled water is degassed by bubbling with  $\text{N}_2$  for at least 1 h, added to the volumetric flask and the solution is transferred to 500-ml sample bottles in an  $\text{N}_2$ -filled glove bag. We have found that degassing reduces the inorganic carbon concentration of distilled  $\text{H}_2\text{O}$  by *ca.* 85% to a level where it contributes only 0.3% of the carbon in our standards. Local surface seawater (0–1 m depth) from Buzzards Bay, Massachusetts is collected in 20-liter carboys and transported to the sample preparation laboratory, where it is transferred to 500-ml sample flasks, poisoned with 100  $\mu\text{l}$  saturated  $\text{HgCl}_2$  solution, capped and stored until processing. After

preparation, both the  $\text{Na}_2\text{CO}_3$  and Buzzards Bay seawater standards are handled in exactly in the same manner as the samples. Our standard procedure is to measure 1  $\text{Na}_2\text{CO}_3$  and 1 Buzzards Bay seawater standard after each suite of 16 WOCE samples.

## RESULTS

From January 1992 to July 1993, we stripped over 850 samples and standards. Figure 3 shows concentration and stable isotope results for the  $\text{Na}_2\text{CO}_3$  and Buzzards Bay samples. The  $\text{Na}_2\text{CO}_3$  graph comprises data from many different batches and the Buzzards Bay graph displays results from four sample collections. To determine our analysis precision, we averaged the results from each data set shown in Figure 3, and rejected any point that deviated from the average by  $>3$  standard deviations. Using the selected data, we calculate that for the  $\text{Na}_2\text{CO}_3$  standards, we extracted  $100.9 \pm 2.2\%$  of the inorganic carbon added to the standards and measured an average  $\delta^{13}\text{C}$  of  $-1.46 \pm 0.18\text{‰}$  (Table 1). To study the Buzzards Bay data, we separated the samples into batches to remove seasonal and interannual variability. From the two batches for which we have enough data (2/92 and 8/92), we measured the concentration to at least  $\pm 0.04 \text{ mmol kg}^{-1}$  and  $\delta^{13}\text{C}$  to better than  $\pm 0.15\text{‰}$  (Table 1). The precision observed in the August 1992 samples is greatly improved from that observed in the February 1992 samples. We believe this is due to the steady improvement of our procedures.

TABLE 1. Concentration and isotope data for Buzzards Bay and  $\text{Na}_2\text{CO}_3$  standards. Results presented in this table use the data remaining after applying the rejection criteria discussed in the text. Values in parentheses represent  $1 \sigma$  error; the range is reported when there are only two analyses. Percent yield is the quantity [(mmol  $\text{kg}^{-1}$  measured)/(mmol  $\text{kg}^{-1}$  prepared)]  $\times 100$ .

Sample	$\Sigma\text{CO}_2$ (mmol $\text{kg}^{-1}$ )	n	$\delta^{13}\text{C}$ (‰)	n	$\Delta^{14}\text{C}$ ‰	n
<i>Buzzards Bay</i>						
2/91	1.953 (0.044)	3	1.125 (0.211)	2	61.5	1
2/92	1.981 (0.034)	36	1.183 (0.146)	31	65.4 (12.8)	13
8/92	1.898 (0.040)	16	1.244 (0.062)	14	69.4 (12.1)	4
6/93	1.782 (0.159)	3	1.318 (0.030)	3		
<i><math>\text{Na}_2\text{CO}_3</math></i>						
	%Yield	n	$\delta^{13}\text{C}$	n		
	100.91 (2.20)	61	-1.457 (0.180)	52		

Some of the Buzzards Bay samples were used in a sample storage experiment; bottles collected in February 1991 were stripped and analyzed over a 500-day period (Fig. 4). Within the error of the analyses, it is not possible to distinguish the sample analyzed almost 1.5 yr after the date of collection from those analyzed immediately after collection.

We have analyzed Buzzards Bay samples collected in February 1991, February 1992 and August 1992 for  $\Delta^{14}\text{C}$  (Table 1, Fig. 4). Samples collected in February 1992 were analyzed 13 times using AMS between March 1992 and March 1993. For this period, we calculate a weighted average  $\Delta^{14}\text{C}$  of  $65.4\text{‰}$  with a standard deviation of  $12.8\text{‰}$ . Reported  $\Delta^{14}\text{C}$  values have been corrected for  $^{13}\text{C}$  fractionation and adjusted to 1950 according to Stuiver and Polach (1977). At present, we observe no significant seasonal or annual differences. Although this particular set of samples does not reflect it, in recent months, our method has produced results demonstrating a precision of  $\pm 3\text{‰}$  for individual AMS analyses (Jones *et al.* 1994).

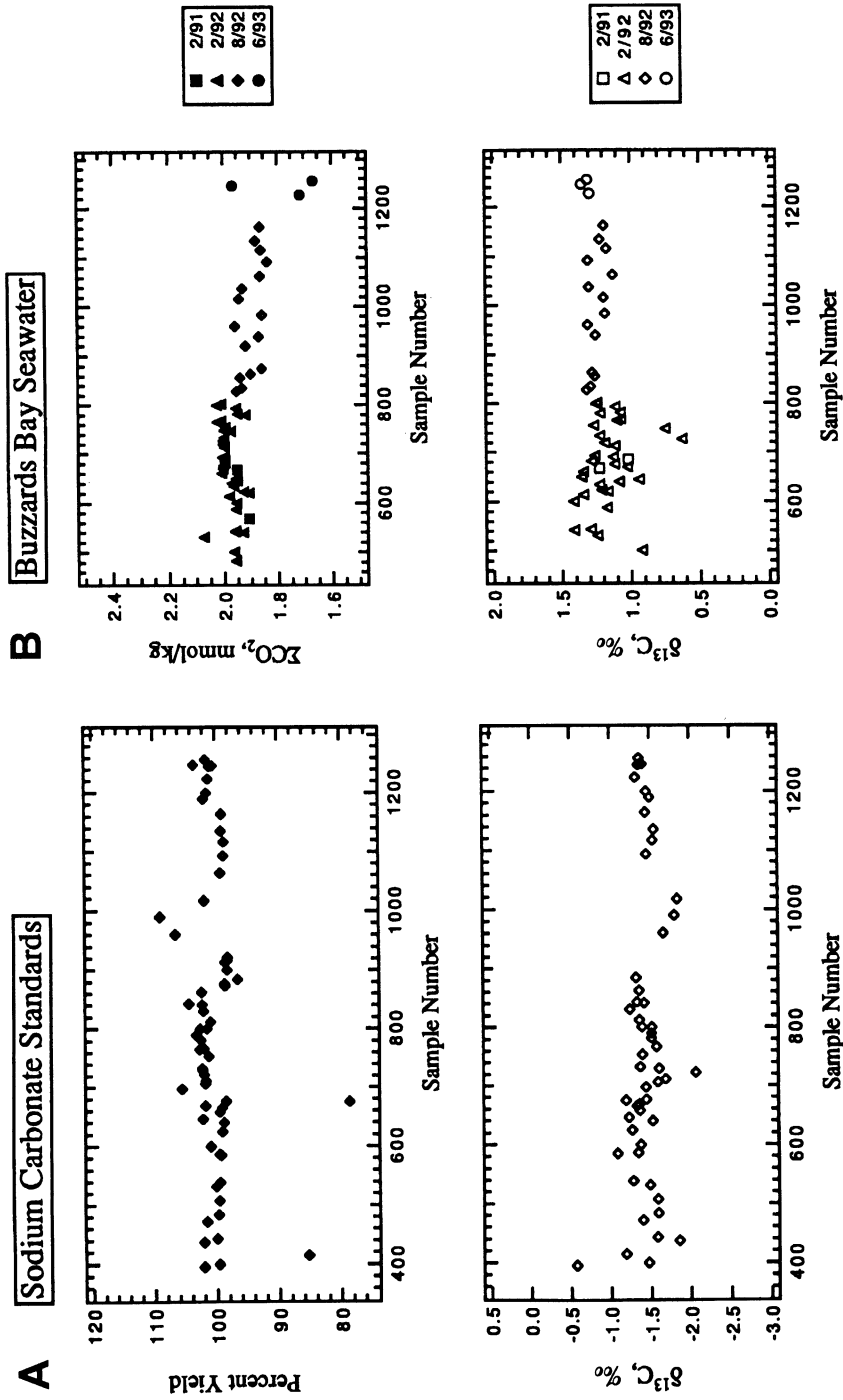


Fig. 3. Concentration and stable isotope results from (A)  $\text{Na}_2\text{CO}_3$  and (B) Buzzards Bay standards. Sample number refers to the order in which the standards were stripped; all were stripped between January 1, 1992 and June 31, 1993. The dates in the key (B) refer to the month and year in which the batch of seawater was collected.

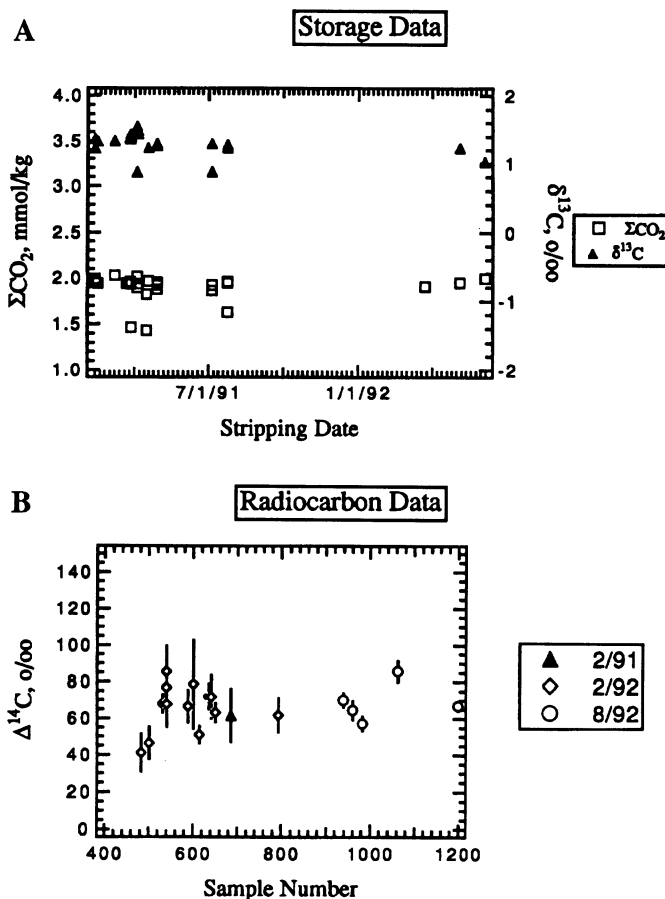


Fig. 4. (A) Storage and (B) radiocarbon data from Buzzards Bay seawater. Error bars shown in (B) represent the one-sigma error from the AMS analysis.

We have analyzed > 800 WOCE seawater samples and present  $^{14}\text{C}$  data from two stations. The samples were collected during Cruise CGC-91 along WOCE line P16N. We present data from Stations 12 (35°N, 152°W) and 48 (42°N, 152°W) (site locations are shown in Fig. 5). In Figure 6, the WOCE data are compared to those from nearby GEOSECS stations and from samples measured using the  $\beta$ -decay counting technique. The WOCE samples were collected in March 1991, stripped and converted to graphite between January 1992 and July 1992, and analyzed on the AMS between September 1992 and December 1992.

## DISCUSSION

To produce useful data for the WHP, we must provide results with an overall precision of  $\pm 5$ –10‰ in surface seawater and  $\pm 3$ –4‰ in deepwaters. These requirements are driven by the magnitude of the  $^{14}\text{C}$  gradients observed in the different layers of the ocean. We have demonstrated through the analysis of standards that we can reproducibly and accurately strip  $\text{CO}_2$  from seawater for stable and  $^{14}\text{C}$  isotopic analysis. To achieve a precision of  $\pm 3$ ‰ in our  $^{14}\text{C}$  measurements, we must know the  $\delta^{13}\text{C}$  of the sample to better than 1‰, so that the stable isotope fractionation correction does not

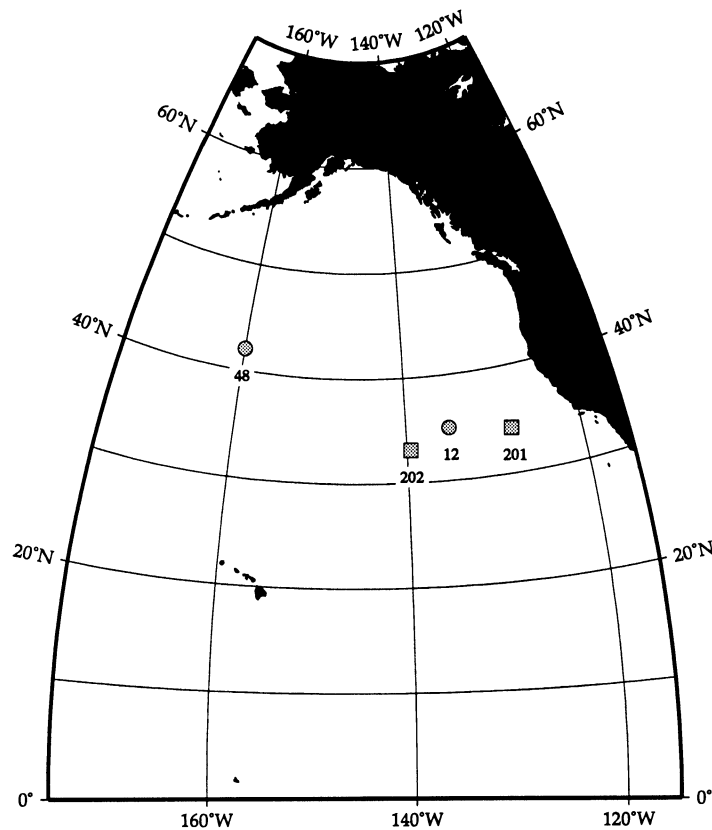


Fig. 5. Sample collection sites in North Pacific Ocean. Stations 12 and 48 were occupied in 1991 as part of the WHP, and Stations 201 and 202 were occupied in 1973 as part of the GEOSECS Program.

introduce a significant error to our final number. We have shown that we know the  $\delta^{13}\text{C}$  of the  $\text{CO}_2$  gas stripped from seawater to much better than this ( $\pm 0.06\text{--}0.18\text{‰}$ ), and we make the assumption that reducing  $\text{CO}_2$  to graphite does not greatly increase this error. Fractionation that is constant for all samples and standards will not compromise the overall precision as long as the standard deviation is  $< 1\text{‰}$ . We reported previously that our graphitization process introduced a stable isotopic fractionation of  $ca. 1.2 \pm 0.3\text{‰}$  that was constant for a wide range of  $\delta^{13}\text{C}$  values (McNichol *et al.* 1992). More recent results show that, because of improvements in our techniques, no fractionation is introduced during the graphitization process (Osborne *et al.* 1994).

We measure the inorganic carbon concentration as an internal laboratory quality check. Our average measured concentration for Buzzards Bay seawater in February 1991 ( $1.95 \pm 0.04 \text{ mmol kg}^{-1}$ ) agrees with the measurement on three samples from the same batch using a coulometric method (Goyet and Hacker 1992) as an independent measure ( $1.938 \pm 0.008 \text{ mmol kg}^{-1}$ ). We do not attempt to make a precise measurement of this parameter, and we report an error of  $\pm 2\%$ . One potential source of error in our concentration measurement is the lack of precise temperature control during our manometric measurements. For example, if the temperature of the glass expansion volume is just  $3^\circ\text{C}$  hotter or colder than the air surrounding the thermometer we use to read the ambient tem-

perature, we will introduce an error of ~1%. Other potential sources of error we have identified are listed in Table 2. Most of these sources affect only the concentration measurement and not the isotopic ratios.

TABLE 2. Potential Sources of Error in Seawater Measurements

Error	Parameter affected
Exclusion of weight of stopcock grease in “empty” bottle weight	$\Sigma\text{CO}_2$
Chipping of glass bottles during sampling/processing	$\Sigma\text{CO}_2$
Small temperature fluctuation during manometric measurements	$\Sigma\text{CO}_2$
Multiple gas transfers	$\delta^{13}\text{C}, \Delta^{14}\text{C}$

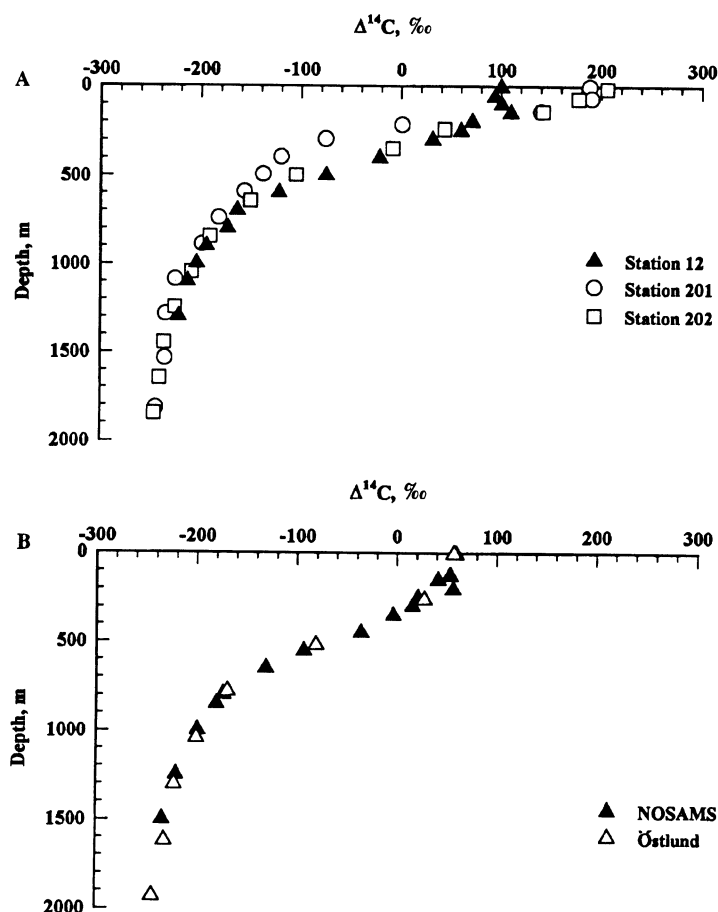


Fig. 6. A. NOSAMS data from Stations 12 (▲) collected in 1991, GEOSCECS data from Stations 201 (○) and Station 202 (□) collected in 1973 (Östlund *et al.* 1987); B. comparison of NOSAMS small volume AMS results (▲) with RSMAS Tritium Laboratory large volume counting results (△) (Östlund 1992) from Station 48 collected in 1991.



The results of the storage experiment indicate that samples can be stored for prolonged periods without jeopardizing their integrity. This is important for the analysis of WOCE samples, because investigators in the WOCE program are collecting seawater samples at a much faster rate than they can be analyzed, and samples remain in their collection boxes for prolonged periods. Although we strip the samples as quickly as possible, often well before they are analyzed on the AMS, some samples can be stored for as long as 2–2.5 yr before analysis. Therefore, it was essential for us to demonstrate that samples can be stored for long periods of time without undergoing significant changes in concentration and/or isotopic composition.

The comparison of our data to those collected from similar locations during the GEOSECS program in 1973 (Östlund *et al.* 1987b) and to those collected in large-volume Gerard barrels provides further confirmation of the validity of our results (Fig. 6). At Station 12 (Fig. 6A), we observe that, below 1000 m within the error of the measurements, our analyses agree with the GEOSECS data, but that above this depth, the results differ. In the surface waters, results from the water samples between 0- and 200-m depth reflect the decrease in atmospheric  $^{14}\text{C}$  concentration from 1973 to 1991 and, between 200 and 800 m, the results reflect the penetration of the “bomb signal” deeper into the water column. Below 1000 m, we do not expect the seawater  $\Delta^{14}\text{C}$  to have changed significantly over the 20-yr period. At Station 48 (Fig. 6B), our data are compared to those reported by Östlund (1992) from 250-liter samples. We observe excellent agreement; the average reported error for the large-volume samples is  $\pm 2\%$  and, for the AMS samples,  $\pm 3\text{--}7\%$ . This comparison shows that results from the two methods are indistinguishable and that AMS will provide a viable substitute for large-volume oceanographic sampling.

## CONCLUSION

We have successfully established a laboratory capable of rapidly analyzing large numbers of seawater samples for AMS  $^{14}\text{C}$  analysis. We have analyzed > 800 seawater samples since 1992 with a precision and accuracy that meet the demands of the WHP, and anticipate analyzing at least 2000 samples per year in the future. With the anticipated completion of our laboratory automation this year, increased throughput will not present a problem, and we should easily meet the demands of the U.S. WOCE  $^{14}\text{C}$  program over the next five years.

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