PREPARATION OF INORGANIC AND ORGANIC CARBON FOR ^{14}C ANALYSIS FROM A SINGLE MARINE SAMPLE

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ABSTRACT. We have developed a technique using a single apparatus to recover the inorganic and organic carbon from a small (few milligrams) aliquot of dried marine material for radiocarbon analysis. The main advantages of using a single apparatus are: 1) less sample is required, 2) decreased handling reduces contamination, and 3) less time and materials are used. Blank values of ~5 μg and 19–44 μg are obtained for the inorganic and organic carbon extractions, respectively. $\Delta^{14}C$ results from sinking particulate organic and inorganic carbon are presented for samples collected in deep-sea sediment traps deployed for 10–30 day periods at 650 and 100 m above bottom (mab) in the northeast Pacific Ocean.

INTRODUCTION

Sampling Site

Our area of study was a single site (Station "M", 34°50′N, 123°00′W, 4100 m depth) located 220 km west of Point Conception, California, in the northeast Pacific Ocean. Samples used in this study were collected from deep sediment traps moored at station "M". Traps were deployed on June 24, 1992 (Pulse 12 cruise) and February 23, 1993 (Pulse 16 cruise). These cruises were part of larger programs that studied the cycling of carbon in the water column (Druffel *et al.* 1996) and the coupling between near-bottom pelagic particulate organic carbon (POC) fluxes and benthic processes (Smith, Kaufmann and Baldwin 1994).

METHODS

Sediment traps were used to collect sinking POC and sinking particulate inorganic carbon (PIC) at 650 and 100 mab. The traps were Teflon®-coated fiberglass cones (120 cm long, 57 cm diameter) with a mouth opening of 0.25 m^2 (Bruland *et al.* 1981). Collections were for 10–30 days at each depth, and mercuric chloride was used in all trap deployments as a poison of biological activity. Sinking POC was concentrated by gentle vacuum filtration. *Ca.* 0.7 L trap liquid was filtered through an acidified, combusted (550°C) all-glass filter holder onto a precombusted, 45 mm diameter, 0.8 μm pore diameter (550°C), quartz fiber filter (Whatman type QM-A). A GAST Laboratory Oilless Piston Vacuum Pump and Compressor was used to eliminate contamination of the sample with pump oil. There are usually two filters obtained per trap cup, but depending on the amount of POC, up to six filters have been collected. The filters containing the sinking POC and PIC were placed in acidified, combusted (550°C) glass jars and promptly frozen to –20°C.

In the lab, the filters were removed from the freezer and allowed to thaw. One filter was weighed in a clean beaker and a portion of the wet sample was removed with a cleaned spatula. Aliquots of the samples were then dried to a constant weight at 50°C.

The dried sample was put into a cleaned glass vial and crushed using a glass rod. A small (10–20 μg) aliquot was subsampled and measured for CHN content on a Carlo Erba 200. The percent organic carbon (OC) and percent inorganic carbon (IC) values were salt-corrected by subtracting the amount of salts that remained in the sample based on a salinity of seawater of 34.6%. Based on the total percent OC, an amount of sample that would generate 3 mL of CO_2 at STP (*ca.* 1.5 mg OC) from the POC fraction was weighed on acidified, combusted aluminum foil.

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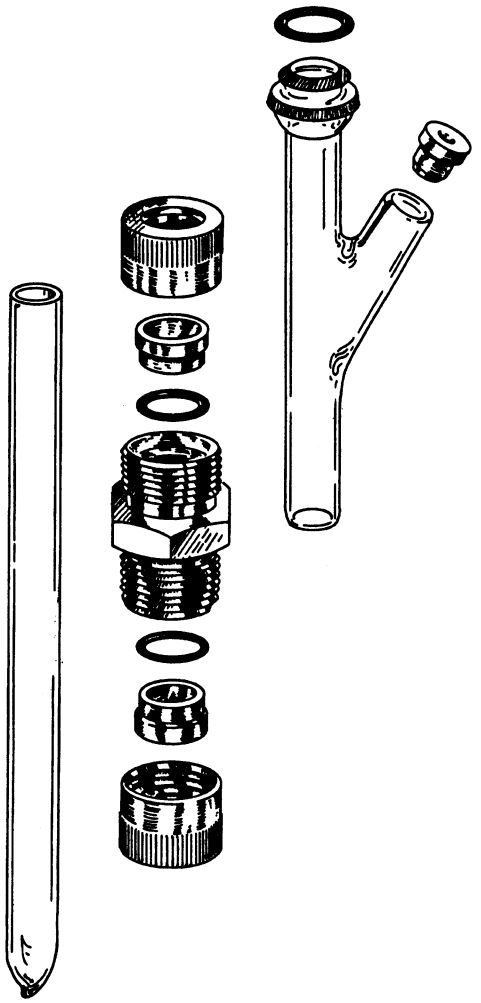

Fig. 1. Drawing of apparatus used to acidify and combust the sinking POC and PIC samples used in this study

The sample was transferred into an acidified, combusted 12.5 mm OD quartz combustion tube (150 mm long) with a fire-polished rim (Fig. 1). Attached to the combustion tube *via* a stainless steel ½-inch Ultra Torr Union joint is a 12.5 mm OD Pyrex piece of tubing (105 mm long) with a 18/9 O-ring ball joint on one end and a fire-polished opening at the other. A side arm is attached (12.5 mm OD tubing and 40 mm long at its base, at 35°) *ca.* 35 mm up from the fire-polished edge. Into this side arm fits a Vacutainer serum tube stopper. Since the Ultra Torrs, stoppers and syringe cannot be cleaned using our traditional methods (which include combustion in a muffle furnace for 1 hr at 550°C), they are cleaned of inorganic and organic carbon by scrubbing with hot soapy water then rinsing with hot tap water, methanol, and tap water. The equipment is then soaked in a 10% solution of HCl. After the acid soak, all parts are rinsed very well with deionized water, the metal parts are dried in a 50°C oven and the plastic and rubber parts are allowed to dry, loosely covered on cleaned aluminum foil in a chemical fume hood overnight.

The combustion tubes containing the samples and the side-armed tubes were joined together with the Ultra Torr fittings and attached to a manifold with ten 18/9 glass socket joints and pumped to

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high vacuum. Each individual sample reaction apparatus was then closed off to the pump and allowed to sit for *ca.* 5 min to test that all seals were leak tight. After each apparatus was determined to be leakproof, 2 mL of 3% H_3PO_4 was injected through the rubber septum using a Hamilton Gastight Syringe with a Hamilton point style 5 needle with a side hole, which minimizes septum coring. The samples were then left on the vacuum line to acidify overnight. A vortex mixer was used to vibrate the base of each sample tube after 30 min of acidification and again at *ca.* 30 min before the end of the acidification.

The CO_2 evolved from the sinking PIC fraction was transferred from the apparatus by opening a stopcock leading to a 50 mL finger flask cooled with liquid N_2 for 2 min. All non-condensable gases were pumped off of the frozen sample, the pump turned off and then a dry ice/isopropanol slush was placed onto the finger flask to retain the large amount of water in the frozen mixture. After *ca.* 30 min the CO_2 was again transferred to another finger flask with liquid N_2. The sample was dried again with a dry ice/isopropanol slush before volumetric measurement of the CO_2 gas. This volume of CO_2 was split into three fractions: *ca.* 2.0 mL for AMS ^{14}C analysis, 0.10 mL for ^{13}C analysis, and the remaining CO_2 was archived in a flame-sealed tube.

The reaction tube, now containing only the sinking POC fraction in an acid solution, was dried in a desiccator under vacuum for *ca.* 24 hr. CuO (wire form) and Ag foil were added to the sample tube, and a 9 mm OD quartz flanged-to-12.5 mm OD quartz tube was attached to the 12.5 mm OD sample tube. This step enabled us to use a #11 Ace threaded joint with a Teflon bushing at one end and an 18/9 O-ring glass ball joint at the other, to attach the sample tubes to a vacuum line for additional pumping to remove the last traces of water from the samples. Warm water was used to heat the tubes to aid the elimination of water, since a trace of water in the tube can cause it to explode during combustion. After *ca.* 36 hr of pumping, the sample tubes were flame-sealed at a pre-made constriction on the 9 mm tube and combusted at 850°C for a minimum of 1 hr. Within 3 days of combustion, the tubes were cracked on a vacuum line, and the CO_2 transferred through two U-shaped dry ice/isopropanol slush traps and collected into finger flasks. The CO_2 was split into three fractions as described above for the sinking PIC CO_2.

The CO_2 from sinking POC and PIC was converted to graphite targets using reduction of CO_2 onto cobalt at 615°C with H_2 gas (Vogel, Nelson and Southon 1987) at the University of California, Irvine (UCI). $\Delta^{14}C$ was measured at the Center for AMS Research at Lawrence Livermore National Laboratory. ^{14}C measurements are reported as $\Delta^{14}C$ (‰) for geochemical samples without a known age (Stuiver and Polach 1977). Total uncertainty (laboratory plus statistical) for individual AMS $\Delta^{14}C$ measurements range from ±6 to ±15‰. $\Delta^{14}C$ values are corrected for blank CO_2 added during acidification and combustion of the samples as well as blank CO_2 added during production of the graphite. The blank CO_2 volumes were obtained from individual "blanks" (empty sample apparatus prepared exactly as for a sample). Blank values generated from the acidification step were small (4.9 ± 2.4 μg C, N=54), an average of 0.6% of the average PIC sample. Combustion blanks ranged in size from 19–44 μg C (with an average of 26 ± 8 μg C, N=45), and comprised 1.3–1.9% of the POC sample CO_2 volumes. The acidification blanks were combined, as were the combustion blanks, to obtain enough CO_2 for AMS targets. A single acidification blank $\Delta^{14}C$ value of +350 ± 20‰ was used to correct the $\Delta^{14}C$ of the PIC samples. An average combustion blank $\Delta^{14}C$ value of −323 ± 100 ‰ (N=3) was used to correct the $\Delta^{14}C$ of the POC samples. $\delta^{13}C$ measurements were made on each sample at the Woods Hole Oceanographic Institution using a VG Micromass 602E isotope ratio mass spectrometer with an overall uncertainty of ±0.10‰.

RESULTS AND DISCUSSION

Yields of the POC and PIC samples (Table 1) were determined by comparing the manometric measurement of CO_2 obtained during the combustion and acidification steps with the amount of OC and IC, respectively, that were determined from the Carlo Erba CHN measurements.

Two sets of calcite standards were run, one set before and one set after the samples were run. The first set of calcite standards had a lower average yield (79 ± 11%, N=3) than that for the second set (103 ± 7%, N=3). This is likely the result of weighing inaccuracies in the first set. As it was difficult to obtain accurate weights for standards and samples, we have since changed our procedure by weighing the samples in a small Ag foil boats. The combined boat and sample are placed into the combustion tube. This decreases the amount of static electricity in and around the tube, which scatters the sample. It also helps prevent the very fine particles of sample from being pumped away during evacuation of the sample apparatus.

TABLE 1. $\Delta^{14}C$ and Related Data for Samples Analyzed as Part of This Study

Sample no.	UCID no.	CAMS no.	Duration (days)	Midpoint date of collection	Event cup number	Depth (mab)	% yield	Sinking POC $\Delta^{14}C$‰	Sinking PIC $\Delta^{14}C$‰	Calcite $\Delta^{14}C$‰	$\delta^{13}C$
	2220	37174			Calcite		88			−992	3.1
	2221				Calcite		83				2.8
	2222	37256			Calcite		67			−995	3.1
1	2144	37213	30	7/15/92	1216, 1	650	95	−24			−22.0
	2145	37214	30		1216, 1	650	83		6		2.2
2	2146	37215	30	8/15/92	1216, 2	650	101	−16			−22.0
	2147	37216	30		1216, 2	650	85		25		0.9
3	2148	37217	30	9/15/92	1216, 3	650	92	−23			−22.0
	2149	37218	30		1216, 3	650	96		3		1.6
4	2151	37178	30	10/15/92	1216, 4	650	*		-3		1.5
5	2152	37219	30	7/15/92	1216, 1	100	99	7			−22.0
	2153	37220	30		1216, 1	100	111		21		1.2
6	2154	37221	30	8/15/92	1216, 2	100	101	−8			−21.9
	2155	37179	30		1216, 2	100	*		-9		1.7
7	2156	37222	30	9/13/92	1216, 3 & 4	100	*	1			−21.9
	2157	37180	30		1216, 3 & 4	100	*		-5		1.2
8	2160	37224	10	3/30/93	1619, 4	650	93	12			−22.3
	2161	37225	10		1619, 4	650	102		40		0.5
9	2159	37223	10	4/20/93	1619, 6	650	*		38		1.0
10	2162	37226	10	5/20/93	1619, 9	650	103	11			−22.5
	2163	37227	10		1619, 9	650	85		41		1.0
	2253	37175			Calcite		111			−989	3.7
	2256	37176			Calcite		103			−991	3.8
	2257	37177			Calcite		97			−990	3.3

*Yields were very low due either to sample loss during transfer of sample to combustion tube or a loss of sample CO_2. These values were not included in the averages stated in the text.

The percent yields of the PIC samples (Table 1) for which there were values averaged 94 ± 11 (N=6). $\delta^{13}C$ values of the PIC (average = +1.3 ± 0.5‰, N=8) are typical of planktonic foram tests that lived in surface waters of the Sargasso Sea (Deuser and Ross 1989).

The percent yields of the POC samples for which there were values averaged 98 ± 4 (N=7). $\delta^{13}C$ results of the POC samples are remarkably similar (average = −22.1 ± 0.2‰ (N=8) and are equivalent to the values for marine sinking POC that had been measured at this site (−21.5 ± 0.7‰, N=31) during the 18-month period just prior to the collection of our samples (Druffel *et al.* 1996).

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$\Delta^{14}C$ results for the POC samples (range from –24 to 12‰) are lower overall than those for the PIC samples (–9 to 41‰) (Table 1 and Fig. 2). All of the samples collected from the 650 mab trap (#1–4, 8–10) had POC $\Delta^{14}C$ values that were lower by 26–41‰ than the PIC $\Delta^{14}C$ results. All POC and PIC $\Delta^{14}C$ values were lower than the surface dissolved inorganic carbon (DIC) $\Delta^{14}C$ values, which ranged from 49–85‰ over a 5-yr time period at Station "M" (Masiello *et al.* 1998).

The Gulf of Alaska data from a single 6-month deployment of a sediment trap at 400 mab showed POC $\Delta^{14}C$ values that were higher than the surface water DIC values and the PIC $\Delta^{14}C$ values. This indicated that there was a source of terrestrial (post-bomb) organic carbon to the deep sea in this region (Fig. 2; Druffel *et al.* 1986). At Station "M", however, the POC $\Delta^{14}C$ values are generally lower than the PIC and surface DIC $\Delta^{14}C$ values, indicating that there is a source of "old" organic carbon to the deep sea (Druffel *et al.* 1996). The lowering of PIC $\Delta^{14}C$ values with respect to the DIC $\Delta^{14}C$ values may reflect two processes: 1) the presence of fine particles of calcium carbonate that are resuspended from the sediment surface locally or at the shelf/slope region and laterally transported via jets and eddies, and/or 2) the source of carbon for the $CaCO_3$ tests is from depths deeper than the mixed layer from which DIC $\Delta^{14}C$ samples were collected (25 and 85 m).

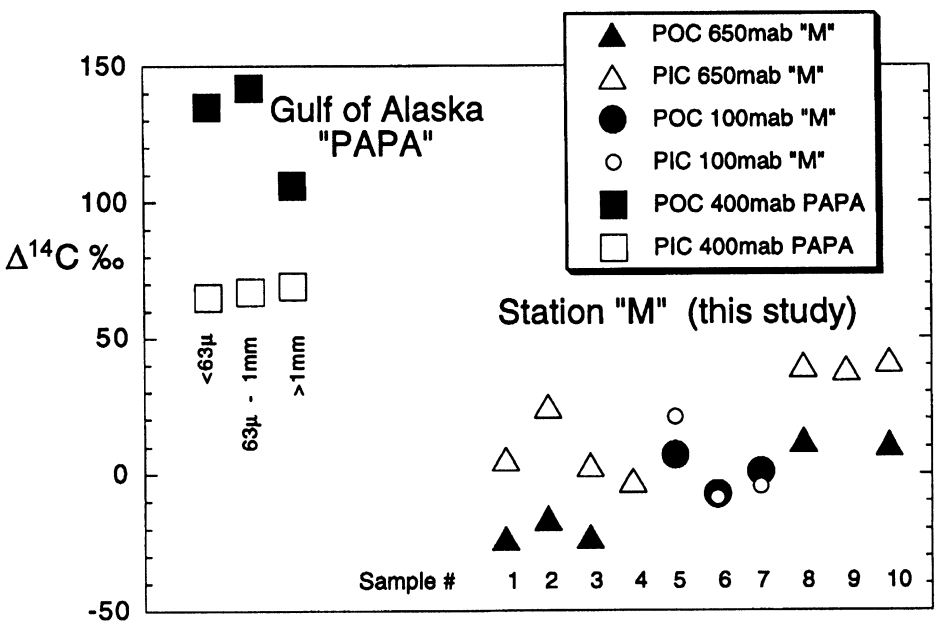

Fig. 2. $\Delta^{14}C$ results for the POC and PIC samples. $\Delta^{14}C$ results from the Gulf of Alaska (50°N, 145°W, 400 m depth, collected March 1984). Samples were wet-sieved into 3 size-fractions and are shown for comparison (Druffel *et al.* 1986).

Conclusion

This paper reports a new technique for extraction and analysis of ^{14}C in both the organic carbon and inorganic fractions of a single marine sample. This technique will be useful for studies that are limited in terms of sample size, time and materials. Reduced handling of these small samples is a distinct advantage of this technique as far as reducing blank levels.

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