SIMPLE, RAPID, AND COST EFFECTIVE: A SCREENING METHOD FOR ^{14}C ANALYSIS OF SMALL CARBONATE SAMPLES

Shari L Bush[1] • Guaciara M Santos[1,2] • Xiaomei Xu[1] • John R Southon[1] • Nivedita Thiagarajan[3] • Sophia K Hines[3] • Jess F Adkins[3]

ABSTRACT. We have developed a simple, rapid method to screen carbonates for survey applications, which provides radiocarbon dates with decreased precision at lower cost. The method is based on previous work by Longworth et al. (2011) and involves mixing pulverized $CaCO_3$ with Fe powder, followed by pressing into aluminum target holders for direct ^{14}C accelerator mass spectrometry (AMS) measurements. An optimum beam current averaging ~10% of those produced by >0.7 mg C graphite targets was obtained for carbonate samples of 0.3–0.5 mg (0.04–0.06 mg C). The precision of the method was evaluated by measuring triplicates of ^{14}C reference materials, as well as by comparing results from this rapid method with results from high-precision AMS measurements on graphite (typically 0.2–0.3%). Measurement reproducibility was ~1.8% (1σ) for samples <10 ka BP, and it increased drastically for older samples. However, *t* tests on paired samples resulted in *p* values greater than 0.05, indicating a good correlation between this survey method and the conventional one. An average blank (calcite) of 0.0075 Fm (~39 ka BP) was achieved. The simplicity of the technique allowed us to process and measure 72 deep-sea coral samples in less than 25 hr.

INTRODUCTION

Radiocarbon has been proven highly useful in paleoceanography and paleoclimate research. Studies on marine carbonates, including deep-sea coral skeletons, can help to evaluate past climate changes, ocean circulation, and carbon cycle dynamics. However, procedures of sample preparation and analysis by accelerator mass spectrometer (AMS) are usually optimized for high-precision measurements and can be time consuming and relatively expensive. For rapid screening large sets of samples to determine trends in age distributions or to identify individual samples for later U/Th dating, the procedures for high-precision sample preparation and measurement are not inappropriate but are clearly not ideal.

Current ^{14}C AMS methodology to produce filamentous graphite from carbonate samples requires several steps that can take 2–3 days in total; physical cleaning (if required), leaching, hydrolysis, graphitization, and pressing into target holders. Recently, 2 methods for rapid carbonate analysis have been developed, one based on combustion of carbonate in an elemental analyzer followed by sealed tube graphitization (Burke et al. 2010), and a second that uses hydrolysis in septum-sealed vials in an autosampler (Gas Bench) linked to a CO_2 gas ion source (McIntyre et al. 2011). These survey methods bypass some steps required for high-precision ^{14}C AMS sample processing but are still relatively complex and require ≥10 mg of carbonate material. Longworth et al. (2011) have recently developed a simpler, low-precision (2%) rapid screening method by directly loading mixtures of $CaCO_3$ and titanium powders into cathodes for a cesium sputtering ion source.

Here, we report a simple, rapid method to screen carbonate samples that provides dates with decreased precision at a lower cost. Our work is based on the Longworth et al. (2011) technique, but an iron catalyst is used in lieu of titanium, which can coat the ionizer surface and adversely affect ion source performance. Moreover, our method does not require an additional "cap" of metal powder to be placed over the sample. Both methods require ≤1 mg of $CaCO_3$ powder, with Longworth's need-

[1]Department of Earth System Science, University of California, Irvine, California 92697-3100, USA.
[2]Corresponding author. Email: gdossant@uci.edu.
[3]California Institute of Technology, Pasadena, California 91125, USA.

© 2013 by the Arizona Board of Regents on behalf of the University of Arizona
Proceedings of the 21st International Radiocarbon Conference edited by A J T Jull & C Hatté
RADIOCARBON, Vol 55, Nr 2–3, 2013, p 631–640

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

ing from 0.2–1.0 mg, while the optimal sample size for our procedure is just 0.3 mg. In addition, our method does not involve any chemical pretreatment prior to the measurements. The many steps of the traditional method are thus reduced to grinding the sample and pressing it into a target holder.

EXPERIMENTAL DESIGN AND RESULTS

In order to produce a rapid and effective survey method, we first optimized our procedures by measuring blanks (^{14}C-free carbonates), standards of known ^{14}C content, and samples previously measured by high-precision ^{14}C AMS. Then, the practicality of the rapid survey method was checked by measuring a large set of unknown-age deep-sea solitary corals.

Sample Selection

One blank and 3 standards were used. Their respective Fm values and ^{14}C ages are in-house calcite blank (Fm = 0 or ^{14}C-free); in-house coral standard (Fm = 0.945; ~450 yr BP); IAEA-C2 (chalk, Fm = 0.411; ~7135 yr BP); and FIRI-C (turbidite, Fm = 0.104; ~18,180 yr BP).

Table 1 Fraction modern values and uncertainties are shown for carbonate samples undergoing both high-precision ^{14}C dating (with UCIAMS#) and the optimized survey method (0.3 mg of $CaCO_3$ mixed with Sigma Aldrich -400 mesh Fe powder). Percent deviations in Fm are also shown to demonstrate how much the rapid method differs from the high-precision method and for what age range. Two samples (GeoB13728 117cm and GeoB13728 132cm) were selected to demonstrate the effects of alternative pretreatments. Measurement dates are displayed to emphasize the storage time for some of these samples.

Sample name	Lab code, prep method	Date run	Site	Fm ±1σ	% deviation	^{14}C age (BP)
GeoB13728 117cm	UCIAMS 96721	8/11/2011	Alboran Sea, Morocco	0.2447 ± 0.0006		11,310 ± 25
	Survey- not clean	8/16/2011		0.2512 ± 0.0049	2.7	11,100 ± 160
	Survey- Dremel	8/16/2011		0.2432 ± 0.0048	–0.6	11,360 ± 160
	Survey- Leached	8/16/2011		0.2446 ± 0.0060	0.0	11,310 ± 200
GeoB13728 132cm	UCIAMS 96722	8/11/2011	Alboran Sea, Morocco	0.2424 ± 0.0006		11,385 ± 25
	Survey- not clean	8/16/2011		0.2443 ± 0.0046	0.8	11,320 ± 160
	Survey- Dremel	8/16/2011		0.2277 ± 0.0055	–6.1	11,890 ± 200
	Survey- Leached	8/16/2011		0.2528 ± 0.0080	4.3	11,050 ± 260
HS4-33	UCIAMS 77473	5/19/2010	Heshang Cave, China	0.3548 ± 0.0009		8325 ± 20
	Survey	8/16/2011		0.3442 ± 0.0068	–3.0	8570 ± 160
HS4-5	UCIAMS 77413	5/18/2010	Heshang Cave, China	0.7908 ± 0.0012		1885 ± 15
	Survey	8/16/2011		0.7768 ± 0.0063	–1.8	2030 ± 70
Nodule 4-JPC323 powder	UCIAMS 22599	2/10/2006	Santos Basin, Brazil	0.0064 ± 0.0004		40,620 ± 530
	UCIAMS 22603	2/10/2006		0.0062 ± 0.0004		40,840 ± 540
	Survey	8/16/2011		0.0131 ± 0.0042	108.0	34,820 ± 2580
Nodule 5-ESS-71 powder	UCIAMS 22600	2/10/2006	Santos Basin, Brazil	0.0194 ± 0.0004		31,660 ± 180
	UCIAMS 22604	2/10/2006		0.0204 ± 0.0004		31,270 ± 180
	Survey	8/16/2011		0.0254 ± 0.0043	27.5	29,510 ± 1350
Banco 75-Dolomita powder	UCIAMS 22605	2/10/2006	Santos Basin, Brazil	0.0091 ± 0.0004		37,760 ± 380
	Survey	8/16/2011		0.0121 ± 0.0045	32.7	35,480 ± 3020
PS70-35-3GC-2 23cm	UCIAMS 96727	8/11/2011	Rost Reef, Norway	1.0616 ± 0.0014		–450 ± 15
	Survey	8/16/2011		1.0447 ± 0.0160	–1.6	–340 ± 130
PS70-35-3GC-2 67cm	UCIAMS 96731	8/11/2011	Rost Reef, Norway	0.8682 ± 0.0016		1135 ± 20
	Survey	8/16/2011		0.8518 ± 0.0138	–1.9	1290 ± 140

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

Previously measured samples included forams from the Labrador Margin in the North Atlantic; speleothems from Heshang Cave, China; carbonate concretions from the Santos Basin, off Brazil; and deep-sea corals (*Lophelia pertusa*) from the Alboran Sea, Morocco, and Rost Reef, Norway. These carbonate samples were selected from previous projects with high-precision ^{14}C results obtained as far back as February 2006 (Table 1).

For an age distribution of corals, we measured an unknown deep-sea solitary coral set consisting of 72 individual *Desmophyllum dianthus* aggregate corals from the North Atlantic, New England Seamounts. The corals were collected between 33–39°N and 60–67°W and at depths of 1500–1600 m. The ^{14}C survey data obtained here will help in selecting samples for further measurements, such as high-precision ^{14}C, U/Th, and clumped isotopes, with the ultimate aim of developing a $\Delta^{14}C$ and temperature record of intermediate waters in the North Atlantic for the past 40,000 yr.

Rapid Method Development

The purpose of this study was to simplify and improve the Longworth et al. (2011) technique. We substituted Fe powder for the Ti used previously, and focused on systematically investigating the $CaCO_3$ plus Fe mixture performance in our AMS system, following the criteria below.

A. Minimum Sample Size Coupled with Maximum Beam Current

Initial tests were done with pulverized $CaCO_3$ samples of 1–2 mg mixed with ~5.0 mg of either Alfa Aesar -325 mesh or Sigma Aldrich -400 mesh Fe powder, to determine what sample size and which Fe powder could provide the highest beam current. We found that as $CaCO_3$ sample size decreased, beam current intensity and precision improved (Figure 1). Later, the beam current was checked for samples in the 0.1 to 1.0 mg range. This second survey and all subsequent tests used Sigma Aldrich -400 mesh Fe exclusively, since it gave higher currents (Figure 1). Moreover, it was known from earlier work that the Sigma Aldrich -400 mesh Fe contained lower trace levels of carbon than the Alfa Aesar product (Santos et al. 2007a). An optimum beam current (i.e. the highest current for a given sample) averaging about 10% of those produced by >0.7 mg C graphite targets (~80 μA; $^{12}C^{+1}$) was obtained for samples of 0.3 mg of $CaCO_3$ (~0.04 mg C). Below this size, beam currents were the same or slightly lower. An intriguing observation is that for these and smaller $CaCO_3$ samples, the currents obtained from our ion source are similar (within a factor of 2) to those from graphite samples containing the same amount of carbon. We cannot explain why the beam currents from $CaCO_3$ mixed with the Alfa Aesar Fe (~2.5μA; $^{12}C^{+1}$) were systematically lower than when Sigma-Aldrich Fe (~8 μA; $^{12}C^{+1}$) was used (Figure 1). Note that this is not a contamination issue: beam currents from both iron powders without $CaCO_3$ were <0.3% of those from 0.7–1 mg C graphite samples (Santos et al. 2007a).

The addition of 0.5–1.0 mg of TiH_2 to the $CaCO_3$ plus Fe powder mixture was also tested, in an attempt to promote *in situ* graphite production by hydrogen reduction, but no improvement was observed in beam current intensities. The benefits of solely using Fe are simplicity and not having to coat the ionizer surface with undesirable Ti, which can lead to additional source servicing (Longworth et al. 2011).

B. Minimum Sample Processing, Spectrometry Measurement Time, and Data Analyses

The Alboran Sea deep-sea corals (GeoB13728 117cm and GeoB13728 132cm; Table 1) were used to determine if chemical pretreatment was required before AMS measurement. Chunks of corals (before powdering) were either left uncleaned, physically cleaned with a Dremel tool (to remove outer surface layer of the sample), or Dremeled plus chemically leached (~10% of the sample was

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

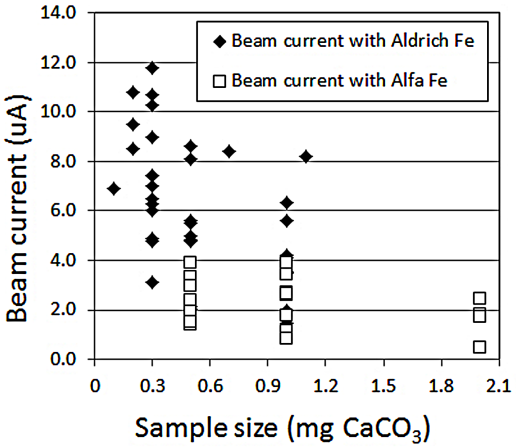


Figure 1 Ion beam currents ($^{12}C^{+1}$) versus $CaCO_3$ powder sample sizes for directly pressed carbonate samples mixed with Alfa Aesar -325 mesh and Sigma Aldrich -400 mesh Fe powders.

removed with 1N HCl). The cleaning test showed no statistical differences among alternative procedures within approximately ±2σ uncertainties. This may be due to the fact that ^{14}C ages obtained by the rapid method are less accurate than the high-precision ones (Table 1), and thus the method is less sensitive to precleaning procedures. More systematic tests remain to be performed, especially if corals have black crusts on them. Nevertheless, the removal of precleaning procedures is advantageous for a survey method, as it eliminates unnecessary sample processing steps and contributes to its low cost.

The KCCAMS facility operates a National Electrostatics Corporation compact spectrometer based on a 0.5MV accelerator (NEC 1.5SDH-1) coupled with an in-house modified ion source (Southon and Santos 2007 and references therein). For this survey method, we chose to limit the AMS measurement time for each sample to 4 runs of 150 s each, rather than 10 to 15 runs. We felt that a long measurement time for these very small samples with low beam currents was unnecessary for a survey method. Large individual uncertainties (in this case) are not just a product of reduced numbers of counts but are often dominated by uncertainties in background corrections (Santos et al. 2007b). However, for samples >>20 kyr BP, we extended the measurement time, typically to 5 or 6 runs, to allow for the removal of contamination from the sample target surface. If contamination was present, the initial 1 or 2 runs were discarded.

For data analysis, we typically use 6 primary standards (oxalic acid I; OX-I) of >0.7 mg C graphite to allow us to set up and tune the AMS system as well as to normalize the $^{14}C/^{12}C$ ratios after the removal of anomalous measurements (Santos et al. 2007b). For this survey method, we used just 2 >0.7 mg C graphitized OX-I targets per wheel, plus at least two 0.3-mg calcite blanks and 2 secondary standards (calcite and IAEA-C2 as $CaCO_3$ powder) for background corrections and quality control. The current integrators of our AMS system were carefully calibrated, with particular attention paid to the lowest 10% of the ^{12}C and ^{13}C current ranges to allow us to measure samples as small as a few µg using the same current ranges as full-sized samples (Beverly et al. 2010). All ^{14}C results shown were fractionation-corrected using the on-line AMS $\delta^{13}C$ values. A mass balance background correction was applied (except on ^{14}C-free samples), following the formulae shown in Santos et al (2007c).

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

C. Quality Assurance

Figure 2 shows the results of calcite blanks and secondary standards tested and their deviation from consensus values. Note that in this figure ^{14}C results are plotted for all combinations of sample sizes, Fe powders (prebaked and not prebaked), as well as the mixture of Fe powder and TiH_2. However, the largest group of measurements was performed using 0.3 mg of uncleaned $CaCO_3$ powder mixed with Sigma Aldrich Fe -400 mesh, presented as group A6 (solid black squares). As we continued to refine the method and came closer to the final version, we created a larger pool of measurements under similar conditions.

C.1 Background. Santos et al. (2007a) showed that the -400 mesh Fe powder from Sigma Aldrich has lower carbon content than the Alfa Aesar -325 mesh powder, and therefore can provide a better blank. Because this catalyst has a tendency to sinter before and during the graphitization process, it is not currently used for graphitization in our laboratory, but the sintering issue is irrelevant for the present experiments.

Figure 2a shows all ^{14}C results from the calcite blank. Under the conditions specified as A6, our calcite plus Fe mixture yielded an average age of 39,750 ± 800 BP (0.0074 ± 0.0008 Fm). This result indicates that the conditions (i.e. amount of material and type of metal reagent) used in the A6 group (solid black squares) seem superior to some of the other combinations shown in the Figure 2 legend.

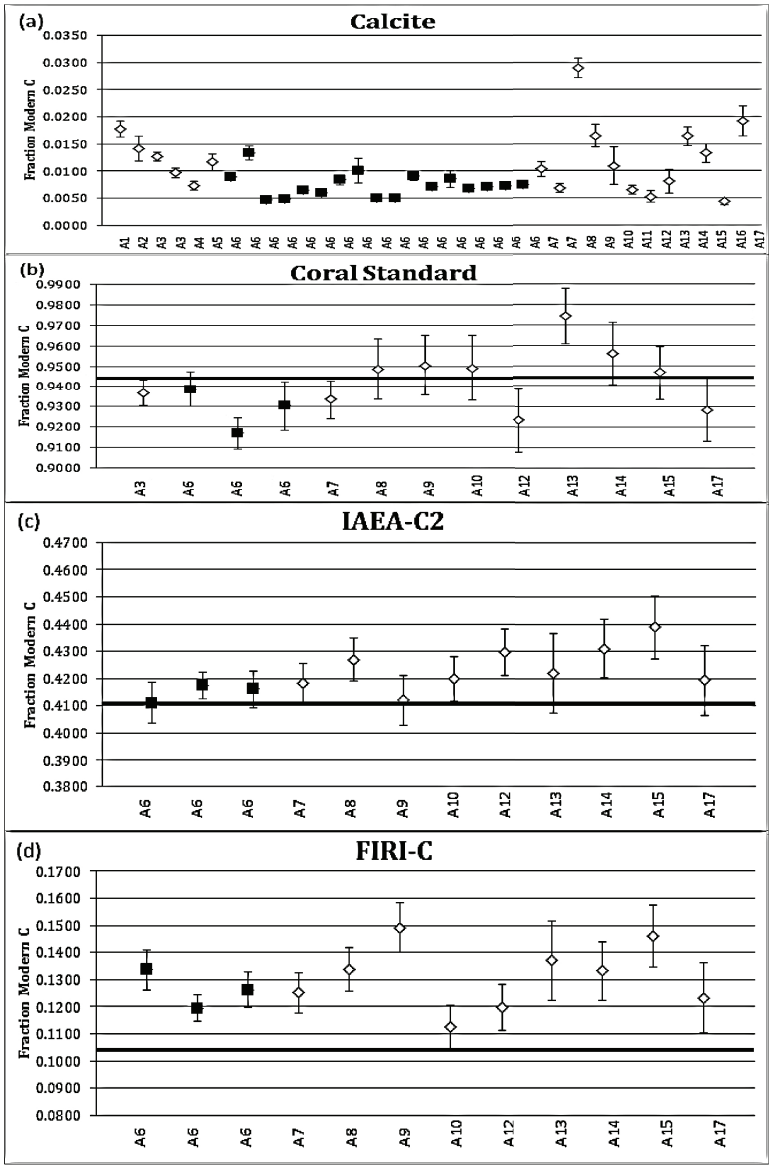
Since the blank is relatively constant for a given type of sample processing (Santos et al. 2010), background corrections should scale inversely with the mass of the samples. Therefore, it is not surprising that the blank tends to dominate when samples become smaller and/or older. Consequently, our survey method is limited by high blank values due to the small sample sizes. Moreover, untreated Fe powder is a known source of contamination (Santos et al 2007a), while adsorption of atmospheric CO_2 during pulverizing and mixing of $CaCO_3$ powder might also introduce some exogenous C.

C.2 Precision and Accuracy. The Holocene standard (coral and IAEA-C2) ^{14}C results are shown in Figure 2(b,c), and are consistent with the consensus values within $\pm 2\sigma$ uncertainty. To ascertain the correlation level of both methods (A6 method survey versus high precision), we performed *t* tests for the coral standard ($n = 3$, $t = -2.42$, $p = 0.10$) and IAEA-C2 ($n = 3$, $t = 1.77$, $p = 0.20$). Our rapid survey method is statistically indistinguishable from the conventional high-precision method (with $p > 0.05$).

^{14}C results on a deglacial turbidite standard (FIRI-C) sometimes differed from the consensus value (Fm = 0.104) by several standard deviations (Figure 2d). This may be due to the heterogeneous nature of the turbidite, which is a carbonate/clay mixture containing <50% carbonate. Any younger organics present in the material would not be oxidized by the hydrolysis procedure used for high-precision samples but could bias the ^{14}C values during direct sputtering. We subjected FIRI-C to prebaking in air at 500 °C (to remove organic C and adsorbed young C) followed by directly sputtering (Fm = 0.1332 ± 0.0022; $n = 2$; ~16,195 BP), and prebaking followed by cooling for 48 hr and sputtering (Fm = 0.1712 ± 0.0040; $n = 2$; ~14,180 BP). Our ^{14}C values confirmed this standard's isotopic heterogeneity as well as a tendency to adsorb atmospheric CO_2. Therefore, FIRI-C was not tested further or used in our discussions.

The optimized method (A6) was chosen by the combination of maximum beam current (Figure 1) and lower background (Figure 2a), as well as reproducibility coupled with accuracy, indicated by reasonably good agreement of the measured Fm values for secondary standards to their consensus

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press



Legend of Methods Tested on Standards (Sample Size; Powder Type)			
Marker	Methods Tested	Marker	Methods Tested
A1	0.1 mg; Sigma Aldrich Fe not baked	A10	0.5 mg; Alfa Aesar Fe +TiH_2
A2	0.1 mg; Sigma Aldrich Fe baked	A11	0.7 mg; Sigma Aldrich Fe
A3	0.2 mg; Sigma Aldrich Fe	A12	1.0 mg; Sigma Aldrich Fe
A4	0.3 mg; Sigma Aldrich Fe not baked	A13	1.0 mg; Sigma Aldrich Fe +TiH_2
A5	0.3 mg; Sigma Aldrich Fe baked	A14	1.0 mg; Alfa Aesar Fe
A6	**0.3 mg; Sigma Aldrich Fe**	A15	1.0 mg; Alfa Aesar Fe +TiH_2
A7	0.5 mg; Sigma Aldrich Fe	A16	1.1 mg; Sigma Aldrich Fe
A8	0.5 mg; Sigma Aldrich Fe + TiH_2	A17	2.0 mg; Alfa Aesar Fe
A9	0.5 mg; Alfa Aesar Fe		

Figure 2 Measured fraction modern values for calcite blanks and secondary standards (in-house coral standard, IAEA-C2 and FIRI-C). The legend indicates the sample size and the reagent powder used. The method chosen for the rapid survey is indicated by black squares (also indicated as A6). Consensus values are indicated by the thick horizontal black lines, except for calcite where 0 is assumed to be the true value.

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

values (Figures 2b,c). Further comparison between results from the rapid method on previously measured unknowns and those from high-precision also indicates good agreement. Figure 3 shows the % deviation of Fm rapid method versus the Fm of high-precision values, thus indicating that the rapid and high-precision graphite results are within ~1.8% (1σ) for most of the samples with Fm > 0.2 (or <10 ka BP). Note that in Figure 3 we plotted the triplicate analyses of the known-age standards with the optimized method (A6 in Figure 2) as well as the results of the "unknown" samples (previously measured by high-precision) shown in Table 1.

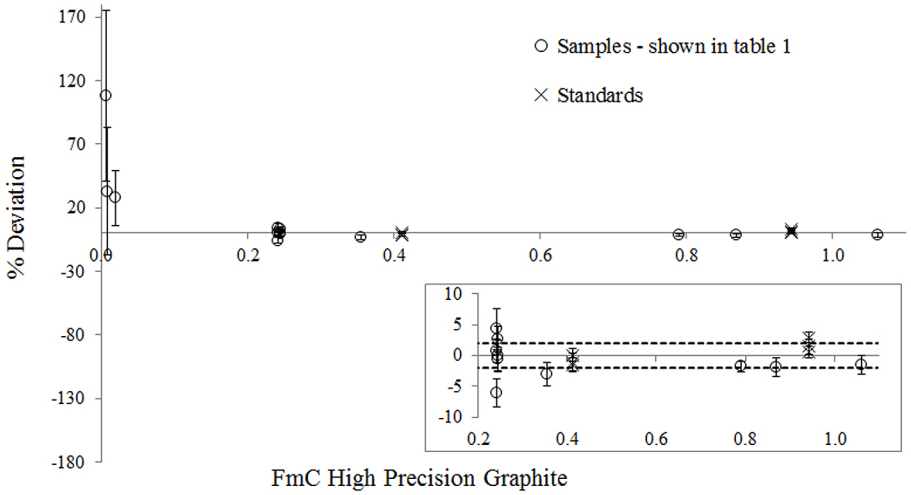


Figure 3 Percent deviations of fraction modern values (=ΔFm/Fm × 100) for standards (coral and IAEA-C2) and previously measured unknowns (Table 1) obtained by the rapid screening method (A6) versus Fm results from the high-precision method. FIRI-C ^{14}C results were not included due to its heterogeneous nature (see text). Thick dashed lines indicate ~1.8% (1σ).

The Optimized Survey Method

This method can be summarized as the following. First, grind <1.0 mg of $CaCO_3$ to a fine powder, weigh out 0.3 mg, mix it well with ~5.0 mg of unbaked Sigma-Aldrich -400 mesh, 99.9% pure Fe (Lot# 05406EA) in a 6 × 50 mm tube. Once the powder is mixed, it is poured directly into an aluminum cathode and pressed for AMS measurement. For samples within modern to 10 ka BP range, the average accuracy of the ^{14}C values produced by the rapid method (Group A6) is 1.8% (±1σ). Beyond 10 ka BP, it becomes relatively poor, and beyond 30 ka BP, the final ^{14}C results are limited by the blank value (Table 1).

AGE DISTRIBUTION OF CORALS BY RAPID METHOD

The 72 New England Seamounts corals were measured on 2 wheels over a period of 19 hr (Figure 4). The seamounts fall into 3 categories: 1) the Muir Seamount; 2) the NE Seamounts, Kelvin and Manning (MANN); and 3) the Corner Rise Seamounts, Corner (COR), Lyman (LYM), and Verrill (VER). Two calcite blanks per wheel were included to correct for modern carbon contamination, as well as secondary standards (in-house coral and IEAE-C2) prepared in the same fashion as the corals. A set of 26 corals of various age ranges were chosen for duplicate tests to verify the reproducibility of the method, and 14 coral samples also underwent high-precision measurements. These AMS ^{14}C results, along with duplicate results of standards, are presented in Table S1 (online Supplementary file).

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

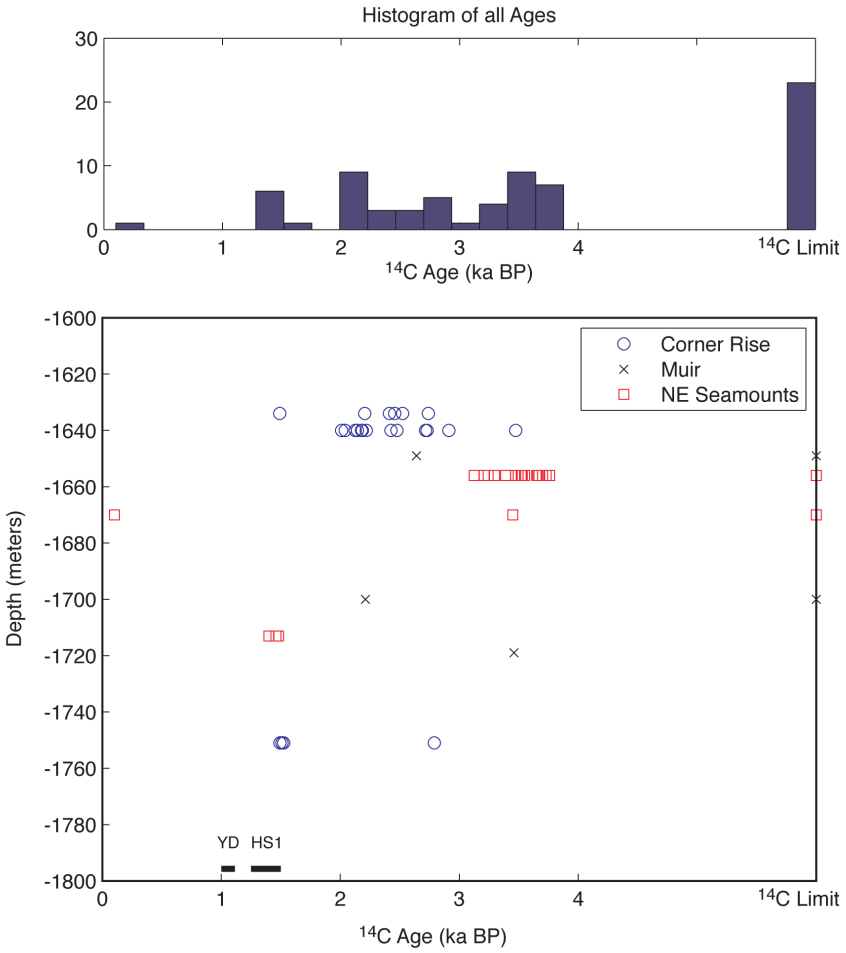


Figure 4 The age and depth distribution of the 72 deep-sea corals dated using the rapid method. Each point represents a single ^{14}C age result and/or mean age from duplicate and triplicate measurements produced from a single coral sample (Table S1, Supplementary file), except in the ^{14}C limit region where 2 or more corals for the same corresponding depth had overlapped and therefore are indistinguishable. The histogram represents the number of corals relative to age. Errors are smaller than the symbol sizes. ^{14}C ages that are above the detection limit for this method (~35 ka) are represented in the ^{14}C detection limit line (or "^{14}C-dead bin"). The Younger Dryas (YD) and Heinrich Stadial 1 (HS1) periods are represented by solid horizontal bars.

Duplicate values for 22 of the 26 corals measured fall within ±2σ of each other, but 4 showed larger deviations: SHIRI-D02 (11σ), SHIRI-E01 (14σ), SHIRI-F05 (4σ), and SHIRI-F09 (3σ). Some of those samples were remeasured by both methods (rapid and high-precision; Table S1). At the moment, we do not have an explanation for this discrepancy, except that all those samples are beyond 20 ka BP. Further tests are needed to clarify this issue.

Results from the 14 corals run as $CaCO_3$ + Fe mixtures and as high-precision graphite (Table S1) confirm that this method is most suitable for samples <30 ka BP. The average deviation of paired corals <20 ka BP was just 1.6% (lower than the tests with standards and known-age samples,

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

Figure 3), but again it increased drastically for older samples. However, *t* tests on paired corals resulted in *p* values greater than 0.05 (Table S2, online Supplementary file).

The ages of the calcite blanks run on separate wheels differed from each other, with average values of 36,300 ± 700 and 43,000 ± 730 BP for the 1st and 2nd wheels, respectively. Because blank values greatly influence older ^{14}C age results, we assigned errors of ±50% to all background subtractions for the rapid method (cf. ±30% for background corrections for graphite samples, based on observed long-term scatter in calcite blanks). We feel that pending further development, the low beam currents and reduced count rates, plus the possibility of unresolved contamination issues, justify the larger uncertainty on the blank correction for the survey method. Given this conservative estimate of uncertainty, no significant differences were observed in background-corrected data when the mean blank value was calculated from each wheel separately or as a combination of all blank values from both wheels.

The 72 North Atlantic corals dated by our rapid method show no noticeable trend between depth and age for the ~150-m-wide water column depth range considered here. However, several features that have been noted previously, and some that have not, can be seen in the data (Figure 4). There is a clear preference for glacial ages in the coral population (Robinson et al. 2007). Only 1 specimen has a Holocene age. Over half of the data are beyond 30 ka BP (Table S1), indicating a relatively old population of corals in the North Atlantic. Some of those samples are barely above the detection limit for the survey method developed here; therefore, they are represented in the "^{14}C-dead" bin (^{14}C limit, in Figure 4). A total of 23 corals fell within the ^{14}C-dead range: a) 17 corals from the New England (NE) Seamounts split between depths 1656 m (n = 5) and 1670 m (n = 12), and b) 6 from Muir at 1649 m (n = 4) and 1700 m (n = 2). Interestingly, there are no peaks at either the Younger Dryas or Heinrich Stadial 1. Separate, large modes of population growth have been seen previously in the NE Seamounts at these times (Thiagarajan et al. 2013). For the first time, we can identify a separation between the Corner Rise Seamounts, Muir Seamount, and the NE Seamounts populations in this data set. Muir clearly has the most ^{14}C-dead corals at ~1700 m depth. The Corner Rise has no very old specimens and the NE Seamounts show the greatest span of ages. All 3 of these conclusions are the result of using this new age screening method on a focused water column depth interval across several seamount types in the North Atlantic. This sort of biogeographical information is a major breakthrough for rapid, inexpensive, and relatively precise ^{14}C age analyses and should pave the way for many other studies of this type on a variety of marine calcifiers.

DISCUSSION AND CONCLUSION

The ^{14}C results from the first set of unknowns (Table 1) measured with the rapid and high-precision methods show that for samples <10 ka BP, the average deviation is 1.8%. The error greatly increases once ages exceed 10 ka BP. However, *t* tests on paired samples resulted in *p* values greater than 0.05, indicating a high correlation between methods (survey versus high precision). The largest deviation observed is for the Nodule 4-JPC323 sample, whose ^{14}C high-precision age yielded 40,840 yr BP while the rapid method date is 34,820 yr BP. The discrepancy between these dates is possibly due to a combination of heterogeneity in the sample powder and absorption of atmospheric carbon during the 5 yr of storage between the high-precision and rapid-method measurements.

Variation in ^{14}C values for the carbonate blanks was rather high in some cases; we believe it reflects a combination of low beam current and reduced count rates resulting from the nature of this non-graphite method, plus modern carbon contamination of the calcite powder during processing. This has a large effect on unknown samples with ages >30 ka BP: for this age range ^{14}C results are heavily dependent on the background corrections. However, while our rapid reconnaissance method

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press

is limited by the relatively high blank, it is still useful for identifying older samples for more precise dating.

In summary, we have developed a rapid survey method that allows us to process, run, and analyze up to 72 samples in 25 hr. This method is particularly useful for screening small samples (i.e. forams for preliminary sediment core chronologies), since we require only 0.3 mg of material. Our method is practical for survey applications, determining temporal distributions, and for identifying samples for high-precision measurements.

ACKNOWLEDGMENTS

We wish to thank the 2 anonymous reviewers for the very constructive and detailed suggestions and the editors Mark McClure and Tim Jull.

REFERENCES

Beverly RK, Beaumont W, Tauz D, Ormsby KM, von Reden KF, Santos GM, Southon JR. 2010. The Keck Carbon Cycle AMS Laboratory, University of California Irvine: status report. *Radiocarbon* 52(2):301–9.

Burke A, Robinson LF, McNichol AP, Jenkins WJ, Scanlon KM, Gerlach DS. 2010. Reconnaissance dating: a new radiocarbon method applied to assessing the temporal distribution of Southern Ocean deep-sea corals. *Deep-Sea Research I* 57(11):1510–20.

Longworth BE, Robinson LF, Roberts ML, Beaupre SR, Burke A, Jenkins WJ. 2013. Carbonate as sputter target material for rapid ^{14}C AMS. *Nuclear Instruments and Methods in Physics Research B* 294:328–34.

McIntyre CP, Roberts ML, Burton JR, McNichol AP, Burke A, Robinson LF, von Reden KF, Jenkins WJ. 2011. Rapid radiocarbon (^{14}C) analysis of coral and carbonate samples using a continuous-flow accelerator mass spectrometry (CFAMS) system. *Paleoceanography* 26: PA4212, doi:10.1029/2011PA002174.

Robinson LF, Adkins JF, Scheirer, DS, Fernandez DP, Gagnon A, Waller RG. 2007. Deep-sea scleractinian coral age and depth distributions in the northwest Atlantic for the last 225,000 years. *Bulletin of Marine Science* 81(3):371–91.

Santos GM, Mazon M, Southon JR, Rifai S, Moore R. 2007a. Evaluation of iron and cobalt powders as catalysts for ^{14}C-AMS target preparation. *Nuclear Instruments and Methods in Physics Research B* 259(1): 308–15.

Santos GM, Moore RB, Southon JR, Griffin S, Hinger E, Zhang D. 2007b. AMS ^{14}C sample preparation at the KCCAMS/UCI Facility: status report and performance of small samples. *Radiocarbon* 49(2):255–69.

Santos GM, Southon JR, Griffin S, Beaupre SR, Druffel ERM. 2007c. Ultra small-mass ^{14}C-AMS sample preparation and analyses at KCCAMS Facility. *Nuclear Instruments and Methods in Physics Research B* 259(1):293–302.

Santos GM, Southon JR, Drenzek NJ, Ziolkowski LA, Druffel E, Xu XM, Zhang D, Trumbore S, Eglinton TI, Hughen KA. 2010. Blank assessment for ultra-small radiocarbon samples: chemical extraction and separation versus AMS. *Radiocarbon* 52(3):1322–35.

Southon JR, Santos GM. 2007. Life with MC-SNICS. Part II: further ion source development at the Keck Carbon Cycle AMS facility. *Nuclear Instruments and Methods in Physics Research B* 259(1):88–93.

Thiagarajan N, Gerlach D, Roberts ML, Burke A, McNichol A, Jenkins WJ, Subhas AV, Thresher RE, Adkins JF. 2013. Movement of deep-sea coral populations on climatic timescales. *Paleoceanography* 28(2):227–36.

https://doi.org/10.1017/S0033822200057787 Published online by Cambridge University Press