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# HIGH-PRECISION AMS $^{14}C$ RESULTS ON TIRI/FIRI TURBIDITE

Thomas P Guilderson[1,2] • John R Southon[1,3] • Thomas A Brown[1]

**ABSTRACT.** Unleached aliquots of TIRI/FIRI turbidite were analyzed by accelerator mass spectronomy (AMS) over a timespan of 18 months. Individual analyses ranged from 18,090–18,245 yr BP with reported errors between 30–50 yr. The weighted average fraction modern (FM) of these 28 measurements is 0.10378 ± 0.00008 (which equates to 18,199 ± 8 yr BP) and the measurements show a 1 standard deviation scatter of 0.00044 (±35 yr). The fractional error of these results indicates reproducibility of individual measurements at the 4‰ (1σ) level, which is consistent with the quoted counting-statistics-based errors. Laboratories engaged in the determination of $^{14}C$ results at reasonably high precision should consider taking advantage of the TIRI and FIRI sample materials in the role of process standards. Additional suites of high-precision data are necessary to refine the accuracy of these sample materials.

## INTRODUCTION

The desire to predict future climate change is forcing us to look back into the past at increasingly finer temporal resolution to determine the regional leads and lags of the climate system as it responds to a myriad of external forces at decadal to centennial frequencies. The underlying goal of these studies is to develop a better understanding of the forces and responses that result in natural climate changes (e.g., sub-Milankovitch solar forcing, internal oscillations, and cryosphere processes). The determination of such leads and lags requires both more detailed and more robust chronological control than has routinely existed for paleoclimate studies and a better understanding of the inherent and implicit errors in calibrating ages from a variety of materials and locations to a common temporal timescale.

The Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory has contributed not only to the development of individual paleoclimate studies and the interaction of climate and human civilization (e.g., Weiss et al. 2002) but also to the definition of the radiocarbon calibration timescale (e.g., Hughen et al. 1998, 2000). As a consequence of our high-resolution coral-radiocarbon work and in concert with enhancements to, and advances in the understanding of, our ion source (Southon and Roberts 2000; Brown et al. 2000), we have modified our data acquisition scheme and are now building up representative datasets that validate reasonably high-precision AMS-$^{14}C$ that for older (late Pleistocene) samples is comparable to the capabilities available from high-precision liquid scintillation counting (e.g., McCormac et al. 1998). The TIRI/FIRI turbidite results presented here are part of an ongoing, high-precision, coral-based Th/U $^{14}C$ calibration project (e.g., Fairbanks et al. 2001) and were analyzed as unknowns concurrently with the coral samples to monitor/confirm the reported precision of the coral results.

## METHODS

An appropriate amount to yield 1.0 mg-carbon targets (~20 mg) of TIRI/FIRI turbidite was placed in individual vacutainers and evacuated to $\leq 1 \times 10^{-3}$ Torr with gentle heating. A 0.5 ml aliquot of 85% phosphoric acid was injected into the vacutainer, after which the vacutainer was placed on a heating block at 90 °C for 1 hr. The resulting $CO_2$ was cryogenically purified to remove water and transferred into individual graphite reduction reactors. The $CO_2$ was reduced to graphite at 570 °C in the presence of an iron catalyst and a stoichiometric excess of hydrogen using procedures similar

[1]Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California 94551, USA.
[2]also at Department of Ocean Sciences, University of California-Santa Cruz, Santa Cruz, California 94596, USA.
[3]now at Department of Earth System Sciences, University of California-Irvine, Irvine, California 92967, USA.

to those described in Vogel et al. (1987). The graphite/iron samples produced were then pressed into aluminum target holders for subsequent AMS analysis.

We have noticed an offset between acid-leached and non-acid-leached turbidite, whereby leached TIRI turbidite tends to be 100–200 yr older. This is undoubtedly due to the selective removal of finer carbonate particles (assumedly, coccolithophorids and planktonic foraminifera fragments). Similar results were observed as part of the TIRI intercomparison. The results presented within are from un-leached TIRI turbidite.

The prepared graphite targets were sputtered in a high-intensity cesium sputter source (Southon and Roberts 2000) with an equivalent $^{12}C^{-}$ current of 275–300 μA, which yields ~900 $^{14}C$ counts-second$^{-1}$ on a modern carbon sample. After mass selection via the low-energy injector magnet, the negative ion beam ($^{13}C^{-}$ or $^{14}C^{-}$ and molecular isobars) was injected into the accelerator (FN Tandem Van de Graff at CAMS), passed through a stripper foil, and on exiting the accelerator, was magnetically- and velocity-filtered, and subsequently measured in an off-axis faraday cup ($^{13}C^{4+}$) or analyzed in a gas ionization detector ($^{14}C^{4+}$) (Davis et al. 1990). The CAMS ion source sample wheel has slots for up to 64 targets and we normally load about 50 unknown samples in a routine sample wheel. Each wheel load is composed of a suite of about 10 aliquots of the primary (OX1) standard, plus secondary standards (OX2, ANU, TIRI B wood), the unknown samples, and blanks, and is broken into several groups. In general, a group is composed of 10–14 unknowns with intervening and bracketing primary standards. Samples are analyzed in such a fashion that a single group is completely analyzed prior to proceeding onto the next. A group is analyzed repeatedly such that a suite of bracketing primary standards and the secondary standards are analyzed in conjunction with the unknown samples. For "high-precision" samples, a single group of unknowns is cycled through at least 5 times. During each cycle, an individual target is analyzed for either 30,000 $^{14}C$ events or 200 seconds, whichever comes first. The turbidite samples were interspersed throughout the sample wheel and were analyzed as unknown samples. Because of their low $^{14}C$ concentration, the turbidite samples reached maximum time prior to obtaining 30,000 events. Cumulative $^{14}C$ events for the TIRI turbidite results presented here are between 90,000 and 100,000 events.

Raw data ($^{14}C/^{13}C$ ratios) are normalized to the average of 6 bracketing aliquots of the primary standard for each pass through a sample group. Counting errors (primary standard and unknown) are propagated through the analysis and are assumed to be Gaussian (cf., Bevington and Robinson 1992). The average of the n-measurement cycles of each unknown is then determined and for the final error, the larger of the counting error or the external error of the n-cycles is chosen. CAMS $^{14}C$ dates are based on $^{14}C/^{13}C$ atom ratios, not decay-counting, to obtain specific $^{14}C$ activities. The algorithms used at CAMS (Southon, unpublished) are similar to those developed at Arizona (Donahue et al. 1990). Data are presented according to the conventions of Stuiver and Polach (1977). Calculations include a background subtraction and inclusion of background error based on $^{14}C$-free calcite determined on multiple aliquots of acid-leached calcite for each wheel of unknowns (cf., Brown and Southon 1997). The average background subtraction for the 8 runs presented here was FM = 0.0011 (n = 26). On any given wheel, the scatter of the backgrounds varied between 5–35% and the appropriate scatter of the same blanks was used as the background uncertainty.

## RESULTS

The values obtained for the TIRI/FIRI turbidite samples are presented in Table 1, along with dates of AMS analysis and the preparation log-number (a unique log-number for samples prepared in our own graphite laboratory). These prep-log-numbers are reported because, historically, CAMS has not

Table 1 TIRI turbidite results from a high-precision $^{14}C$ calibration project

| Date | N-log # | Fmodern[a] | ±FM | $^{14}C$ age | ±yr |
|---|---|---|---|---|---|
| 18-Mar-01 | N36555 | 0.10346 | 0.00041 | 18220 | 40 |
| 18-Mar-01 | N36557 | 0.10406 | 0.00037 | 18180 | 30 |
| 18-Mar-01 | N36691 | 0.10365 | 0.00041 | 18210 | 40 |
| 18-Mar-01 | N36693 | 0.10380 | 0.00048 | 18200 | 40 |
| 2-May-01 | N37419 | 0.10347 | 0.00049 | 18220 | 40 |
| 2-May-01 | N37452 | 0.10452 | 0.00044 | 18140 | 40 |
| 5-Jun-01 | N37431 | 0.10389 | 0.00042 | 18190 | 40 |
| 5-Jun-01 | N37504 | 0.10364 | 0.00042 | 18210 | 40 |
| 5-Jun-01 | N37443 | 0.10427 | 0.00042 | 18160 | 40 |
| 5-Jun-01 | N37502 | 0.10430 | 0.00039 | 18160 | 30 |
| 5-Jul-01 | N38795 | 0.10410 | 0.00047 | 18170 | 40 |
| 5-Jul-01 | N38807 | 0.10399 | 0.00042 | 18180 | 40 |
| 17-Jul-01 | N38814 | 0.10402 | 0.00045 | 18180 | 40 |
| 17-Jul-01 | N38824 | 0.10446 | 0.00052 | 18150 | 50 |
| 17-Jul-01 | N38831 | 0.10387 | 0.00045 | 18190 | 40 |
| 17-Jul-01 | N38837 | 0.10382 | 0.00046 | 18200 | 40 |
| 6-Dec-01 | N42165 | 0.10311 | 0.00033 | 18250 | 30 |
| 6-Dec-01 | N42175 | 0.10355 | 0.00036 | 18215 | 30 |
| 6-Dec-01 | N42177 | 0.10351 | 0.00041 | 18220 | 35 |
| 8-Jan-02 | N42185 | 0.10330 | 0.00040 | 18235 | 35 |
| 8-Jan-02 | N42193 | 0.10373 | 0.00041 | 18205 | 35 |
| 8-Jan-02 | N42195 | 0.10391 | 0.00041 | 18190 | 35 |
| 12-Jun-02 | N45680 | 0.10364 | 0.00061 | 18210 | 50 |
| 12-Jun-02 | N45681 | 0.10358 | 0.00060 | 18215 | 50 |
| 12-Jun-02 | N45682 | 0.10506 | 0.00059 | 18100 | 50 |
| 2-Sep-02 | N47693 | 0.10297 | 0.00039 | 18260 | 35 |
| 2-Sep-02 | N47705 | 0.10357 | 0.00046 | 18215 | 40 |
| 2-Sep-02 | N47710 | 0.10380 | 0.00041 | 18195 | 35 |

[a]We present the Fmodern results with 5 significant digits to allow readers to manipulate the data in a similar fashion as ourselves and to minimize propagation of round-off errors.

assigned laboratory numbers to internal secondary or tertiary standards, backgrounds, test-samples, etc. As per Stuiver and Polach (1977), rather than using the reported ages in calculating a weighted mean, we report our results as the weighted mean of the measured Fraction Modern (FM) values of the TIRI turbidite samples. The weighted mean and weighted mean uncertainty (1σ) of the TIRI turbidite results are 0.10378 ± 0.00008 (n = 28), which equates to 18,199 ± 8 yr BP. Using the standard deviation of the TIRI/FIRI turbidite results, an external estimate of the uncertainty of the mean (SD/√N) is 0.00008 (±8 yr). The distribution of the measurements and their quoted uncertainties yields a reduced chi-squared of 0.93 (Table 2).

## DISCUSSION

We find that the external fractional uncertainty in the 28 individual measurements is ~4‰ (1σ). This implies that our measurements on these 18,000-yr-old samples are reproducible at the ±35-yr level. Because of the vagaries of radioactive decay, this is a more appropriate characterization of the relative error than the common practice in the stable isotope community, which would take the standard

Table 2 TIRI turbidite summary statistics (FM)

| | |
|---|---|
| Weighted mean | 0.10378 |
| Standard Deviation (1σ) | 0.00008 |
| Standard Dev in weighted mean (σ /√N) | 0.00044 |
| Error on wtd mean from individual measuring errors | 0.00008 |
| Reduced chi-squared | 0.93 |

deviation of the reported Fmodern or "D14C" (in per mil) and call this the reproducibility of the samples.

The reduced chi-squared value obtained for the results ($\chi^2 = 0.93$) shows that the scatter of the 28 measurements is consistent with the uncertainty estimates that have been derived from measurement error and background correction uncertainties. Taken with the above, this implies that our measurements are reproducible and precise within the quoted uncertainties. Graphical examination of the results (Figure 1) indicates that the distribution of the TIRI turbidites follow a Gaussian distribution. The scatter of these TIRI turbidite results is similar to recent results obtained on repeated analysis of a modern in-house coral standard (e.g., Guilderson et al. 2000).

Our individual numbers basically agree with the TIRI and FIRI "consensus" values within the uncertainties of the individual measurements. However, our weighted-mean value of 18,199 ± 8 BP is inconsistent with (slightly older than) the consensus TIRI (18,155 ± 34 BP) and FIRI (18,173 ± 11 BP) results. Yet, it is worth noting that the difference between the age obtained in this study and the FIRI C "consensus" value is smaller than the differences between the FIRI turbidite values obtained when the contributing laboratories were grouped by technique (i.e., AMS-based results: 18,183 ± 13 BP, n = 34; GPC-based results: 18,229 ± 28 BP, n = 17; LSC-based results: 18,140 ± 25 BP, n = 34). Whether this is due to systematic but small offsets between turbidite aliquots measured by different laboratories, or to a biasing of the consensus results to younger ages by a subset of data incorporating over-optimistic background estimates, or to some other cause, is unclear.

The increasing need for high-precision measurements in paleoclimate, archaeology, and modern-day $^{14}C$ geophysical tracer studies places high demands on the capabilities of the $^{14}C$ community to develop, validate, and maintain the ability to produce precise and accurate measurements that show appropriate levels of agreement. The utility of high-precision records produced at various $^{14}C$ laboratories will depend significantly on the demonstrated ability of the laboratories to produce precise and accurate measurements that show appropriate levels of agreement between the high-precision laboratories. The TIRI and FIRI sample suite provide a basis for such laboratory intercomparisons but it is apparent that accurate and precise ages of these materials may yet need to be determined. Further high-precision measurements of consistency samples, such at those provided by FIRI and TIRI, need to be made in order to ascertain which laboratories are capable of the reproducibility necessary for calibration quality measurements and to determine systematic laboratory offsets that may need to be accounted for when compiling results from different laboratories.

## SUMMARY

We have made reproducible measurements of an 18,000-BP sample over an 18-month period that scatter with a standard deviation equivalent to a ~4‰ fractional error. The scatter of these measurements is consistent with the counting-statistics-based estimates of the uncertainties in our measurements (i.e., we can do 4‰ on 18ka BP samples and see essentially nothing but counting statistics). Our measurements are accurate and consistent with the current knowledge of the $^{14}C$ content of the sample. Other laboratories should endeavor to perform reasonably high-precision analysis of the

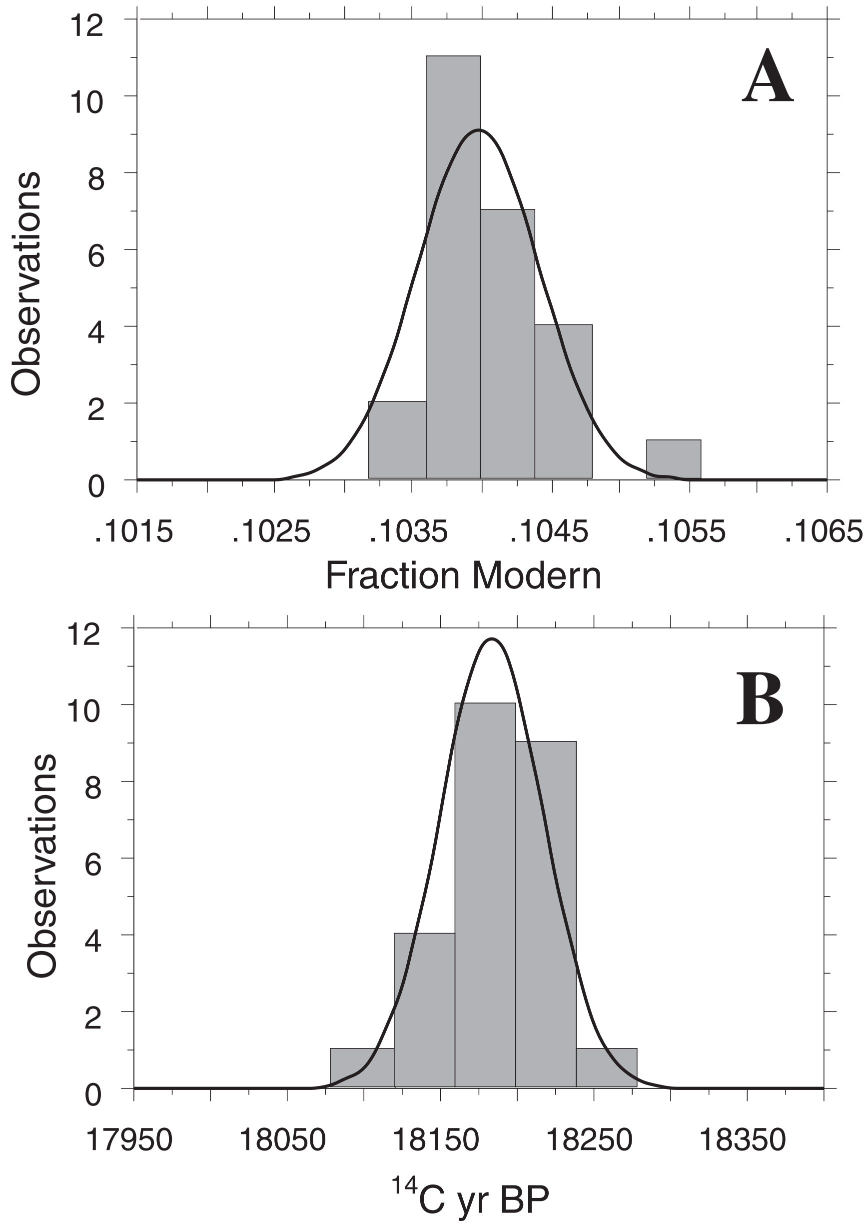


Figure 1 Distribution of TIRI turbidite results as a function of fraction modern (A) and conventional $^{14}C$ age. Respective curves are predicted Gaussian distributions determined from the mean and standard deviation of the turbidite results.

TIRI/FIRI sample suite so that a more accurate age determination of these materials is provided to the community. Additional sample materials, such as those provided by the TIRI/FIRI intercomparison projects, will be invaluable to constrain the accuracy and reproducibility of any individual suite of high-precision data.

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