

# REPRODUCIBILITY OF SEAWATER, INORGANIC AND ORGANIC CARBON $^{14}\text{C}$ RESULTS AT NOSAMS

KATHRYN L. ELDER, ANN P. McNICHOL and ALAN R. GAGNON

National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) Facility,  
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 USA

**ABSTRACT.** The majority of samples processed at the National Ocean Sciences AMS Facility (NOSAMS) thus far were collected as part of the World Ocean Circulation Experiment (WOCE). Due to the long storage time (2–3 yr) required to analyze thousands of samples on the accelerator mass spectrometer (AMS), a test was designed and implemented to determine the effects, if any, of storage time on  $^{14}\text{C}$  concentration. We find no systematic offsets in AMS measurements made over a 5-yr period between a total of 16 replicate sets from surface and deep water collected at the same locality. Furthermore, the average  $\Delta^{14}\text{C}$  value from the deepwater AMS replicates ( $-213.1\text{‰}$ , std. dev. 7.3) agrees very closely with the conventional  $^{14}\text{C}$  results published for GEOSECS ( $-212.7\text{‰}$ ) from station 320 taken 20 yr earlier.

A total of 73 WOCE shipboard replicate sets (162 AMS measurements) were analyzed with a mean precision of 4.3‰. AMS results from 20 more shipboard replicate sets (44 AMS measurements) submitted as  $\text{CO}_2$  from the Stable Isotope Laboratory (SIL) at the University of Washington were analyzed with a mean precision of 3.4‰. These results suggest no significant difference between water stripping methods used in each preparation lab.

To assess reproducibility, we calculate a pooled estimate of  $\sigma$  for replicates called  $s$ , which we use as an approximation of  $\sigma_{\text{TOT}}$  for a given sample type. The  $s$  for WOCE seawater replicates is 4.9‰ and 5.8‰ for SIL gas replicates. These numbers demonstrate an overall reproducibility of seawater AMS results at NOSAMS that is in line with reported errors. We take the difference between total error  $s$  and machine error as the overall standard deviation of combined uncertainties associated with preparation of samples and with AMS. For seawater samples processed at NOSAMS,  $\sigma_{\text{SPL}}$  is calculated to be 2.4‰, and for the SIL gas replicates it is 4.8‰.

Reproducibility of samples prepared with an acid hydrolysis technique is demonstrated using 24 coral samples submitted in triplicate by Dr. R. G. Fairbanks of Lamont Doherty Earth Observatory. Seventy-two replicates were prepared and analyzed at NOSAMS with a mean reported precision of 1.2‰. The pooled estimate  $s$  for the Fairbanks triplicates is 2.6‰. We calculate a laboratory reproducibility uncertainty for coral hydrolysis samples of 2.2‰.

In 1993, NOSAMS participated in the Third International Radiocarbon Intercomparison (TIRI) Study. We report here 60 AMS analyses of the six TIRI test materials, five of which are organic carbon samples, to validate sample-processing methods for organic carbon sample AMS analyses at NOSAMS.

## INTRODUCTION

In 1991, the Sample Preparation Laboratory (SPL) at NOSAMS was established to produce graphite targets for analysis on the NOSAMS accelerator and to develop methods to achieve routine  $\pm 3\text{--}4\text{‰}$  precision for AMS  $^{14}\text{C}$  analysis of deepwater samples collected as part of the World Ocean Circulation Experiment (WOCE). To date, the SPL has produced >16,000 graphite targets that have been AMS-analyzed. *Ca.* 70% of reported results thus far are from WOCE seawater samples; 13.5% are from organic carbon and 12.5% are from inorganic carbon ( $\text{CaCO}_3$ ) samples.

Since 1993, we have routinely analyzed seawater samples with a machine precision of  $\pm 3\text{‰}$  (von Reden *et al.* 1997). However, there is little point in achieving a very precise measurement if it is not reproducible. When replicate analyses of the same material agree closely within the quoted precision of the individual analyses, then the quoted precision is meaningful. This paper reports on AMS analyses of replicate seawater and coral samples to give evidence that supports our quoted precision. We use the error of replicate analyses to estimate total error and, in turn, to place limits on the component of that error due to sample processing.

We also present results of our periodic analysis since 1992 of samples sent to us as participants in the Third International Radiocarbon Intercomparison (TIRI) study. Analyses of internationally

accepted standards demonstrate accuracy and validate methods used to produce  $^{14}\text{C}$  results by demonstrating that there is no systematic offset from the consensus values.

## METHODS

*Ca.* 13,400 seawater samples were collected during the WOCE program for AMS analysis at NOSAMS. The samples were poisoned with mercuric chloride at the time of collection and then stored at ambient conditions until processed further. Since storage time is typically on the order of several years before the  $\text{CO}_2$  is stripped from the seawater, a test was designed to determine the effects of long-term storage on the dissolved inorganic carbon (DIC) in poisoned seawater samples.

For the test, a site was chosen from a location in the Pacific (WOCE transect P06C, station 97,  $32^\circ 30.40'\text{S}$ ,  $127^\circ 59.45'\text{W}$ ) to coincide with one occupied 20 years previously as part of the Geochemical Ocean Sections Study (GEOSECS). In June 1992, 24 replicate samples were collected at both 20 m and 2500 m water depths (total 48 samples) at the reoccupation site. Since February 1993, replicates from each depth interval have been analyzed at NOSAMS on roughly a six-month cycle for a total of 8 replicate sets over the 5 years since the date of collection. The results are compared to assess the variation with time, if any, due to storage. The test also allows us to compare our results with the conventional  $^{14}\text{C}$  results published for the same location from a GEOSECS deepwater sample taken at the same depth (2450 m) 20 years earlier.

“Seawater replicates” are defined as two or more 500 mL aliquot subsamples taken from the same Niskin™ bottle or from Niskin™ bottles fired simultaneously that collect from the same depth in the water column. There are 73 WOCE replicate sets analyzed thus far that were processed entirely at NOSAMS, and 20 sets that were processed to convert DIC to  $\text{CO}_2$  (water stripping) at the Stable Isotope Laboratory (SIL), in the School of Oceanography, University of Washington. “Coral replicates” are samples that span the same intervals in a coral, *i.e.*, the same growth. Each replicate referred to in this paper was processed individually from start to finish according to methods previously described for collection, handling, processing and analyzing AMS samples (McNichol and Jones 1991; McNichol *et al.* 1994; Vogel, Southon and Nelson 1987; Cohen *et al.* 1994) with the exception of water stripping for the seawater  $\text{CO}_2$  SIL replicates.

Routine quality control procedures in the SPL assure us that all graphite samples meet stringent quality checks and that the carbon (graphite) produced is both homogeneous and isotopically non-fractionated (Osborne *et al.* 1994). Graphite samples that are submitted to the AMS are pressed into aluminum target cartridges and loaded into 59 positions on a sample carousel. In the AMS, each target is typically analyzed in three cycles over a 2-day period. The first 2-min exposure is part of the cleaning cycle, followed by two 20-h acquisition cycles that sputter each target *ca.* eight separate times totaling roughly 40 min of analysis time per sample. The deviation between repeated measurements of a target over time is used in a data-flagging scheme together with several other monitored system parameters to filter out the time-dependent instabilities in sample and AMS performance (Schneider *et al.* 1994). The reported error for any sample is the larger of the error computed from counting statistics (internal error) or the standard error computed from the variance between repeated measurements of a target (external error) (Schneider *et al.* 1994).

From two to five seawater replicates per set have been analyzed over the past 6 years on many different wheels. Replicates within a set are not necessarily run concurrently or on the same wheel. Each of the coral triplicates was run on a separate wheel in the AMS during the months of August, September and October 1995, respectively.

## RESULTS AND DISCUSSION

## WOCE Seawater Samples

Results from the test to determine the effects of storage time on  $\Delta^{14}\text{C}$  are plotted in Figure 1. AMS results from 8 replicate sets for each of the 20 m and 2500 m water depths show no systematic change with increasing storage time. The 15 analyses of surface water samples have an average  $\Delta^{14}\text{C}$  value of 127.0‰ with a standard deviation of 5.0. The 17 measurements from the deeper 2500 m depth have an average  $\Delta^{14}\text{C}$  value of -213.1‰ with a standard deviation of 7.3. At the deep station, the data collected on day 578 appear anomalously low. The  $\delta^{13}\text{C}$  values measured for this replicate are also low (unpublished data) and suggest that the data for this sample are less accurate than values measured for others in the suite. If we reject this sample, the average and standard deviation are -211.3 and 5.3‰, respectively, corresponding to the precision observed for the surface samples. This  $\Delta^{14}\text{C}$  value agrees very closely with the GEOSECS reported conventional value of -212.7 from station 320, 2450 m (Östlund *et al.* 1987). These findings indicate that there is no offset in AMS measurements due to storage time since collection and confirm that our water stripping, graphitization and target preparation methods do not bias AMS results as compared to the GEOSECS data.

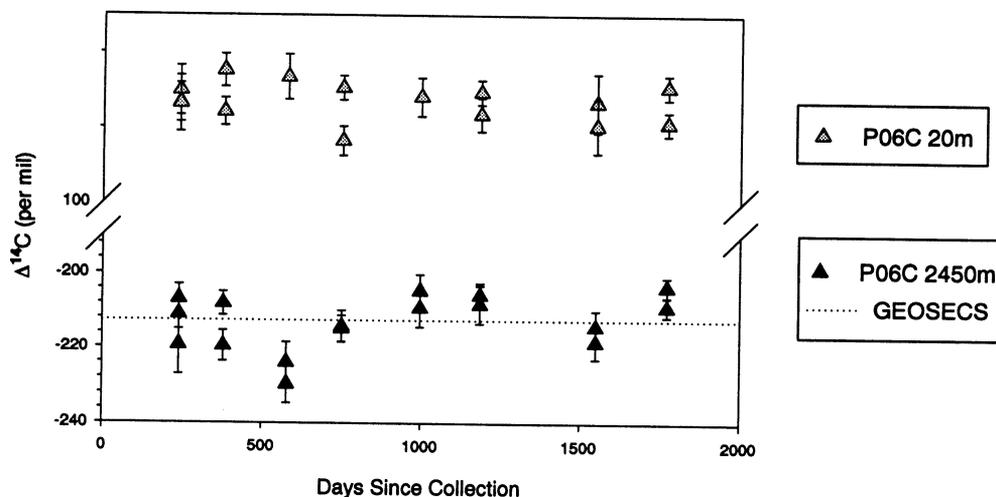


Fig. 1. P06C Station 97, GEOSECS Reoccupation Site. Results from a total of 48 analyses in 8 replicate sets over the 5 yr since the date of collection are plotted as  $\blacktriangle$  (20 m) and  $\triangle$  (2500 m).  $\cdots$  = conventional  $^{14}\text{C}$  results published for the same location from a GEOSECS deepwater sample taken at 2450 m 20 yr earlier.

During the 40-min AMS analysis time for each seawater target, an average of 200,000 to 300,000  $^{14}\text{C}$  atoms are detected, yielding a Poisson statistic of  $\pm 1.8$ – $2.2$ ‰. After incorporating blank corrections, normalization to  $\delta^{13}\text{C}$  and referencing to the NBS Oxalic Acid I and II standards, we would predict a theoretical overall machine precision of  $\pm 3.1$ ‰ for one analysis. However, since January 1997, 90% of WOCE seawater AMS analyses have a reported precision of  $\leq 5.1$ ‰; 50% are  $\leq 3.5$ ‰; and 10% are  $\leq 2.6$ ‰. This higher precision than the theoretical reflects the increased uncertainty introduced during sample processing and may include other random indeterminate errors. Here we use our analyses of replicates to place limits on the error contribution of sample processing and that of AMS analysis.

The standard deviation of replicates,  $\sigma$ , is an assessment of the reproducibility of the techniques used to produce an AMS measurement. AMS  $^{14}\text{C}$  analyses of seawater samples is time-consuming

and therefore a large number of replicate analyses is not feasible. However, a good approximation of  $\sigma$  can be made using a pooled estimate  $s$  from discrete replicate sets. We can assume the same sources of indeterminate error for the sets since they are of the same composition and have been analyzed using identical methods.

We calculate  $s$ , or the theoretical  $\sigma$  of seawater replicates using the following formula (Skoog and West 1976: 58–59):

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{\text{DOF}}} \quad (1)$$

Deviations from the mean for each replicate set are squared; the squares for all of the subsets are then summed and divided by the number of degrees of freedom. The pooled  $s$  is obtained by taking the square root of this quotient. The number of degrees of freedom (DOF) is obtained from the total number of measurements minus the number of subsets, or replicate sets.

We have 162 individual AMS measurements of seawater samples from 73 replicate sets; therefore the number of DOF is 89. Since the DOF is >20, we can consider the estimate of  $s$  to be a good approximation of  $\sigma$ . The pooled  $s$  of seawater replicates is calculated to be 4.9‰. A histogram of the differences between individual AMS analyses and replicate means ( $x_i - \bar{x}$ ) is shown in Figure 2A with a superimposed Gaussian-fit curve. The half-width for the curve is 5.1‰, agreeing well with both the calculated  $s$  and the mean reported machine precision for the group of 4.3‰ (Table 1).

TABLE 1. Replicate Analyses Performed at NOSAMS

Sample type (process)*	No. of analyses	No. of replicated sets	DOF	Mean reported precision ( $\sigma_{\text{AMS}}$ )	Pooled estimate $s$ ( $\sigma_{\text{TOT}}$ )	$\sigma$ associated with sample processing ( $\sigma_{\text{SPL}}$ )
Seawater DIC (WS)	162	73	89	4.3	4.9	2.4
Seawater CO <sub>2</sub> (GS)	46	21	25	3.4	5.8	4.8
Coral CaCO <sub>3</sub> (HY)	72	24	48	1.2	2.6	2.2

\*WS = water stripping samples; GS = gas samples; HY = acid hydrolysis samples.

To date, 20 replicate sets of seawater CO<sub>2</sub> from 44 individual samples (DOF = 24) prepared at SIL have been run at NOSAMS. These replicates were stripped of CO<sub>2</sub> and sent to us in flame-sealed tubes to be further reduced to graphite and run on the AMS. The gas replicate samples have a pooled  $s$  value of 5.8‰. These results suggest no significant difference between the water stripping methods used. A histogram of the differences between individual AMS analyses and the replicate means ( $x_i - \bar{x}$ ) for the 20 gas replicate sets is shown in Figure 2B.

Because contributions to error are theoretically the same for all replicates, we can assume  $s$  is a good approximation of the combined error of collection, water stripping, graphitization, target preparation and AMS analysis. It then follows that the difference between  $s$  ( $\sigma_{\text{TOT}}$ ) and machine error (mean reported precision) is an estimation of the overall standard deviation of combined uncertainties associated with preparation of samples, and with AMS analysis ( $\sigma_{\text{TOT}}^2 = \sigma_{\text{SPL}}^2 + \sigma_{\text{AMS}}^2$ ). The term  $\sigma_{\text{AMS}}$  used here is simply the mean reported error of all replicates, *e.g.*, the larger of the error computed from counting statistics (internal error) or the standard error computed from the variance between repeated measurements of a single target (external error) per carousel or wheel. Thus,  $\sigma_{\text{AMS}}$  incorporates some short-term component of noncounting statistical error over the period of wheel analysis (~2 days). And since *ca.* 40% of the replicate pairs were not analyzed on the same wheel,  $s$  ( $\sigma_{\text{TOT}}$ )

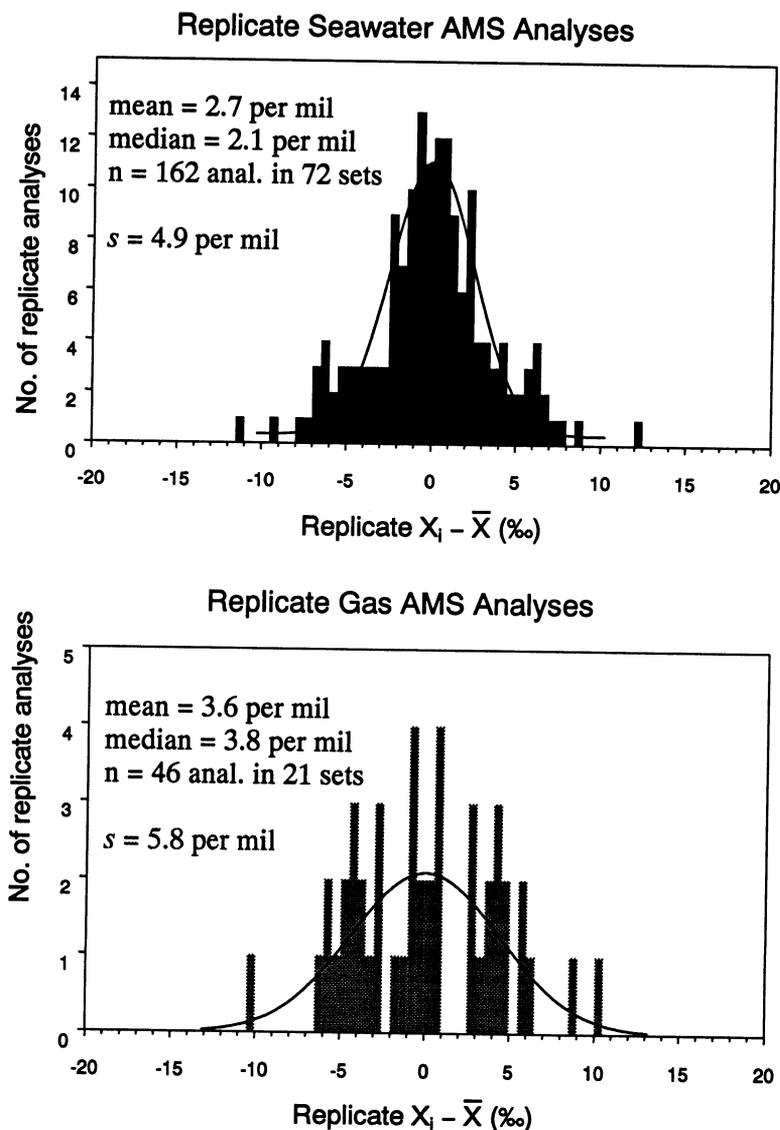


Fig. 2. Differences between individual AMS results and their replicate mean ( $x_i - \bar{x}$ ) with a superimposed Gaussian-fit curve. A. Seawater samples processed in entirety at NOSAMS. B. Seawater samples submitted by SIL as  $\text{CO}_2$ .

must incorporate some component of noncounting statistical error over periods from days to months. Although we are not able to independently measure either  $\sigma_{\text{SPL}}$  or  $\sigma_{\text{AMS}}$ , we can use these replicate analyses to place overall limits on these components. For seawater samples processed at NOSAMS,  $\sigma_{\text{SPL}}$  is calculated to be 2.4‰ and for the SIL gas replicates it is 4.8‰.

#### Fairbanks Coral Replicates

In 1995, 24 Barbados coral samples were submitted to NOSAMS in triplicate by Dr. R. G. Fairbanks of Lamont Doherty Earth Observatory. High-precision  $^{14}\text{C}$  analyses of these corals were used to calibrate  $^{14}\text{C}$  with U/Th measurements.

Using the same method described above to calculate a pooled estimate of  $s$ , we obtain a value of 2.6‰ for the replicate coral samples with 48 DOF (Table 1). A histogram of the differences between 72 individual coral AMS measurements and the replicate means is shown in Figure 3. The laboratory reproducibility uncertainty for coral replicates is 2.2‰, very close to that for the seawater replicates.

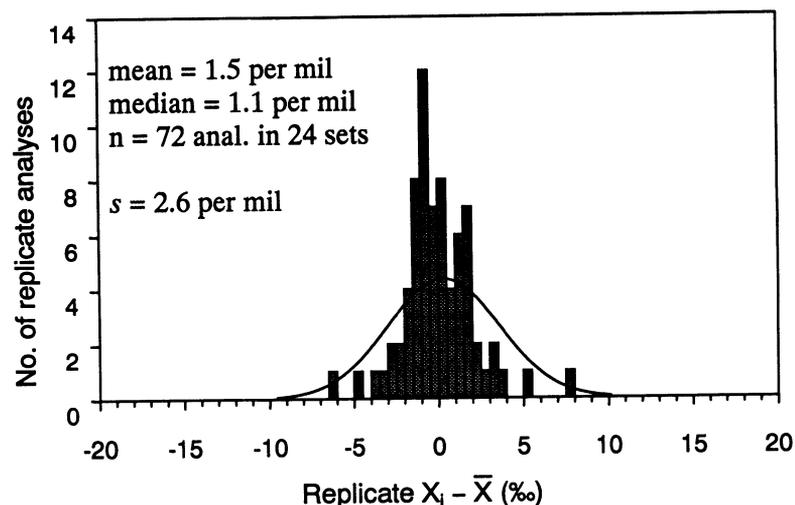


Fig. 3. Fairbanks Coral replicate  $\text{CaCO}_3$  analyses. Differences between 72 individual coral AMS measurements made at NOSAMS and their replicate means.

### TIRI Samples

In 1992, NOSAMS participated in the TIRI study. Since then, we have performed periodic analysis of the six TIRI test materials, five of which are organic carbon samples (Table 2). Figure 4 shows the preliminary results from participating laboratories together with 60 AMS analyses made at NOSAMS to date of the same materials. These results validate sample-processing methods for organic carbon sample AMS analyses at NOSAMS by demonstrating no systematic offset between our measurements and the preliminary consensus values.

TABLE 2. Measurements of TIRI Quality Assurance Materials

Sample	Preliminary consensus		NOSAMS		
	Value	Est. $\sigma$	Mean value	no.	$s^*$
A: Barley mash	157.74 $\Delta^{14}\text{C}$	0.084	156.77 $\Delta^{14}\text{C}$	7	8.78
B: Belfast pine	4503 BP	6	4476 BP	9	63
C: IAEA cellulose	290.58 $\Delta^{14}\text{C}$	0.8	293.96 $\Delta^{14}\text{C}$	7	8.09
D: Hekla peat	3810 BP	7	3780 BP	5	107
E: Ellanmore humic	11,129 BP	12	11,046 BP	6	43
F: Icelandic doublespar	46,750 BP	208	54,276 BP†	26(3)†	3140†

\* $s$  = standard deviation of population, not standard deviation of the mean

†Includes only 1997 data

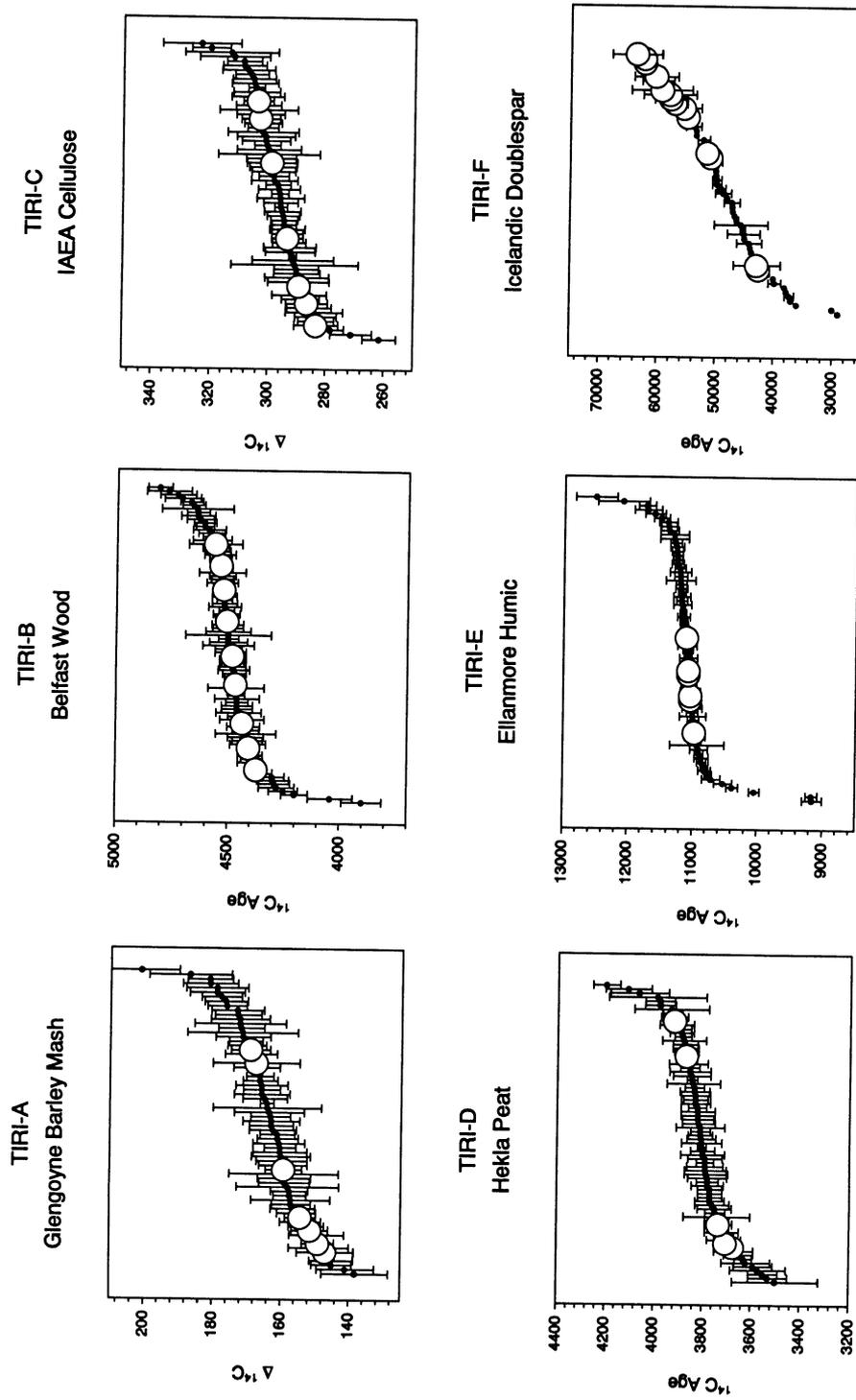


Fig. 4. Results from analysis of samples included in the TIRI study. Preliminary results from other participating laboratories (●) and 60 AMS analyses made at NOSAMS (○).

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