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## INTRA-ANNUAL VARIABILITY OF THE RADIOCARBON CONTENT OF CORALS FROM THE GALAPAGOS ISLANDS<sup>1</sup>

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**ABSTRACT.** We report AMS <sup>14</sup>C measurements on subannual samples of coral from the Galapagos Islands that span the period, 1970–1973. Both the major 1972 El Niño/Southern Oscillation event and intra-annual changes in regional upwelling of <sup>14</sup>C-depleted waters associated with alternation of surface-ocean current patterns are evident in the record. Our data show that the corals preserve a detailed record of past intra-annual variations of the <sup>14</sup>C content of surface ocean water.

### INTRODUCTION

Radiocarbon concentrations in aragonite skeletons of hermatypic (reef-building) corals record the <sup>14</sup>C concentrations of dissolved inorganic carbon (DIC) in local sea water at the time of skeletal accretion. Annual density bands in corals from the Galapagos Islands (and many other locations) enable the independent determination of the growth year of particular bands. Thus, we can reconstruct the past variations of <sup>14</sup>C concentration in local sea water by measuring <sup>14</sup>C concentrations in annual bands of coral skeletons. In previous studies, several researchers (Druffel & Linick 1978; Druffel 1981, 1987, 1989; Druffel & Suess 1983; Nozaki *et al.* 1978) have used <sup>14</sup>C measurements on annual bands in corals from tropical and temperate locations to investigate the incorporation of <sup>14</sup>C-depleted “Suess-effect” carbon and bomb-produced <sup>14</sup>C into the surface layers of the Atlantic and Pacific Oceans, and variations of surface ocean currents and mixing processes.

Druffel (1981) measured the <sup>14</sup>C content of Galapagos corals using gas proportional β-counting systems and, for the most part, measured complete annual band couplets. The results showed the incorporation of bomb-produced <sup>14</sup>C into surface ocean waters from 1961 to 1977, and possible effects of incorporation of <sup>14</sup>C-depleted “Suess-effect” carbon into surface ocean waters between 1929 and 1954. Druffel also suggested that annual average Δ<sup>14</sup>C values from coral samples from the years of El Niño/Southern Oscillation events (ENSO) were significantly higher than the values obtained for adjacent non-ENSO years due to diminished upwelling of <sup>14</sup>C-depleted waters during these events. To investigate this effect further, Druffel measured the <sup>14</sup>C content of pairs of six-month-average coral samples from a weak ENSO year, 1969, a strong ENSO year, 1972, and a non-ENSO year, 1974. Whereas the values obtained from the 1969 “seasonal” samples were compatible with decreased upwelling during the first part of the year, the values for the 1972 “seasonal” samples were not significantly different from each other, and their average was incompatible with the annual average value obtained for that same year. The values obtained for

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<sup>5</sup>We regret the passing of our friend and colleague, Professor Emeritus Fred H. Schmidt, who died on 17 January 1991.

the “seasonal” samples from the non-ENSO year, 1974, did not differ significantly. Druffel concluded that the  $^{14}\text{C}$  levels of the summer and winter waters in the Galapagos Islands during non-ENSO years were not significantly different.

In this study, we have used the small-sample capability of  $^{14}\text{C}$  accelerator mass spectrometry (AMS) to measure subannual samples of coral from the Galapagos Islands. The goal of these measurements was to use the increased time resolution attainable through these smaller samples to search for intra-annual variations in  $^{14}\text{C}$  levels of surface waters of the region. The details of variations in the  $^{14}\text{C}$  levels of the surface waters of this region in the years preceding, during and following an ENSO event were of particular interest to us. To ensure that we had sufficient sensitivity to detect the variations of interest in the  $^{14}\text{C}$  content of the corals, we made repeated measurements of a secondary standard during the course of this study; these measurements show that our  $^{14}\text{C}$  AMS system is capable of precise and accurate ( $\pm 4\%$ ) measurements. Our coral data show sharp intra-annual variations in the  $^{14}\text{C}$  concentration of the local surface waters of the Galapagos region and a distinct ENSO signal.

We present below a brief, simplified description of the surface ocean currents in the Galapagos Islands region and the possible influences of these currents on the  $^{14}\text{C}$  content of Galapagos waters.

#### GALAPAGOS ISLANDS

The Galapagos Islands lie on the equator off the coast of Peru at  $90^\circ\text{W}$  longitude. The influence of the major surface ocean currents on the waters of the Galapagos Islands has been described by Glynn and Wellington (1983) and by Enfield (1989) in an extensive review of ENSO phenomena.

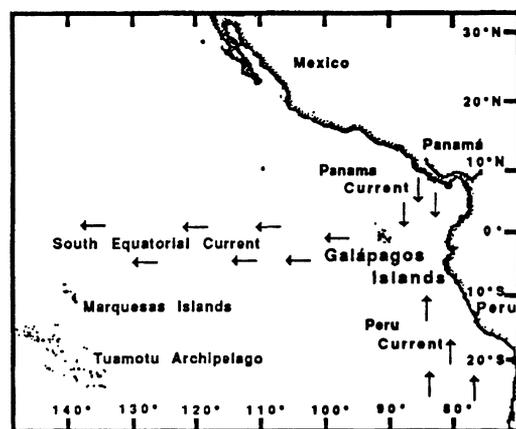


Fig. 1. Map of Galapagos Islands area that indicates the major surface ocean currents influencing the  $^{14}\text{C}$  content of the Galapagos Islands waters, i.e., the Peru, Panama and South Equatorial Currents

Briefly, during non-ENSO years, two surface currents alternate as the major source of surface ocean waters in the Galapagos Islands region. From about April to December, the Peru Current is the dominant source of the waters that flow through the Galapagos region as the South Equatorial Current (Fig. 1). The waters of the Peru Current are relatively cool ( $18^\circ\text{--}22^\circ\text{C}$ ) due to the upwelling and mixing of subsurface waters during the northward, offshore movement of the current along the coast of Chile and Peru. From January to about March, southeast tradewinds weaken, and relatively warm ( $25^\circ\text{--}28^\circ\text{C}$ ) tropical surface waters of the Panama Current flow from the north and become a major source of the waters in the Galapagos Islands region. This annual intrusion of warm northern waters is evident in the sea-surface-temperature (SST) record that has been obtained at Academy Bay in the Galapagos Islands (Fig. 2). Because the upwelled waters in the Peru Current

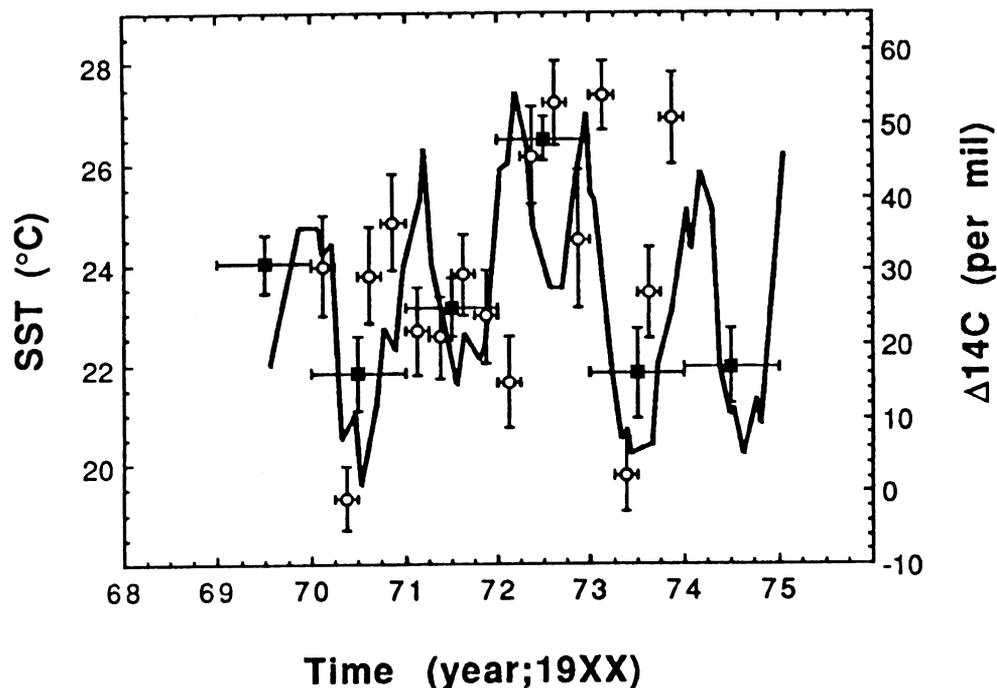


Fig. 2.  $\Delta^{14}\text{C}$  data obtained on Galapagos Island corals and Galapagos SST, 1969–1974.  $\circ$  = our preliminary  $\Delta^{14}\text{C}$  data obtained on “three-month” samples of coral from Punta Pitt, San Cristóbal Island (1970–1973);  $\blacksquare$  = annual average  $\Delta^{14}\text{C}$  data (Druffel 1981) on coral taken from Gardner Bay, Española (Hood) Island; — = SST recorded at Academy Bay, Santa Cruz Island (data from Heinrich Sievers as presented by McConnaughey (1986)). The horizontal error bars on the  $\Delta^{14}\text{C}$  data show the approximate time span each sample represents; the vertical error bars show the  $1\sigma$  uncertainty in the determination of the  $^{14}\text{C}$  content of each coral sample.

are depleted in  $^{14}\text{C}$  relative to the surface waters of the Panama Current, the intra-annual variation between these two sources should be evident in variations of the  $^{14}\text{C}$  content of the corals.

In addition to the other oceanographic and atmospheric effects associated with ENSO events, the alternation between these two sources of surface waters is disturbed during ENSO years. Surface waters that have been influenced by strong upwelling of relatively cool subsurface waters do not return in the April-to-December period following the onset of an event. SST in the Galapagos Islands stays anomalously high during this period, and the diminished influence of  $^{14}\text{C}$ -depleted upwelled waters should result in the suppression of the annual return to lower  $^{14}\text{C}$  content for coral growth during this April-to-December period. Thus, a sustained period of high  $^{14}\text{C}$  content, characteristic of surface waters from the Panama Current, should be evident in the coral growth during the ENSO periods.

## METHODS

We obtained coral samples from a coral core collected by T. A. McConnaughey (Quaternary Isotope Laboratory, University of Washington) from Punta Pitt, San Cristóbal Island in the Galapagos (89.5°W, 1°S). McConnaughey (1986) described the core collection and initial processing methods. For this study, we divided each annual band for the years 1970–1973 into four equal sections to produce a total of 16 samples for measurement, each representing about a three-month growth period. Variations in coral growth rate in response to changes in local water

temperature and light levels complicate the establishment of accurate subannual time scales for corals (Glynn & Wellington 1983; McConnaughey 1986). In light of this, it is clear that the actual time periods represented by our “three-month” coral samples probably vary somewhat. In this initial report, we have treated each of our coral samples as representative of an approximately three-month period, but we recognize the uncertainties introduced by growth-rate variations.

We extracted the carbon in each of the coral samples as CO<sub>2</sub> by carbonate dissolution in 100% phosphoric acid at *ca.* 75°C. Typically, the coral samples weighed 8–25 mg and produced 1–3 mg of carbon as CO<sub>2</sub> (chemical yields for this preparation step were >95%). The CO<sub>2</sub> was then converted to graphite by iron-catalyzed hydrogen reduction (Vogel *et al.* 1984) and prepared for <sup>14</sup>C measurement as described previously (Balsley *et al.* 1987; Brown *et al.* 1990). Typical ion-source targets prepared for measurement by our Ta encapsulation method contain 200–300 μg of carbon; hence, we were able to prepare several ion-source targets from each coral sample.

We measured the <sup>14</sup>C content of the coral samples using the AMS <sup>14</sup>C system that we developed at the University of Washington Nuclear Physics Laboratory (Grootes *et al.* 1986; Brown *et al.* 1990; Schmidt *et al.* 1990). We discuss below the current precision and accuracy of our <sup>14</sup>C AMS measurements.

#### PRECISION AND ACCURACY

We demonstrated previously (Brown *et al.* 1990) that the distribution of our measurements having a counting statistics precision of *ca.* 1% is consistent with a Gaussian distribution with a 1 σ variance of 1% (*i.e.*, for measurements with 1% counting statistics, uncertainties in counting statistics are the only significant source of scatter in our data). In this analysis, we also showed, through the measurement of approximately contemporary standards, that our measurement system can attain an accuracy of at least 4‰ (*i.e.*, any systematic bias introduced into our data by our measurement system is <4‰).

As part of our continuing evaluations of the precision and accuracy of our measurement system, we have measured an approximately one-half-life-old secondary standard previously measured by high-precision β-counting. Figure 3 shows the <sup>14</sup>C/<sup>13</sup>C data we obtained on this sample from June to November, 1990. These data are normalized with respect to our Chinese Sucrose <sup>14</sup>C laboratory standard. The 1 σ scatter of the measurements is essentially equal to the typically 1.7% counting statistics uncertainties of the individual measurements. From the weighted mean of our normalized <sup>14</sup>C/<sup>13</sup>C data, we calculated a <sup>14</sup>C age for the sample of 6150 ± 30 BP (this calculation includes an estimated uncertainty of ± 1‰ in the δ<sup>13</sup>C of the AMS sample due to fractionation during graphitization); this agrees, at the 1 σ level, with the high-precision β-counting age for the sample of 6120 ± 35 BP (QL-11658) (based on the uncertainties of these dates, the 1 σ uncertainty in the expected difference between the dates is ± 46 yr; the difference between the dates is only 30 yr). These results confirm that, for measurements with counting statistics precisions of 1–2%, counting statistics uncertainties are the only significant source of scatter in our measurements, and that our measurement system introduces no systematic bias into our data >4‰.

#### RESULTS AND DISCUSSION

Figure 2 shows the preliminary Δ<sup>14</sup>C results of our measurements of the “three-month” coral samples for the years 1970–1973 (the data are also given in Table 1). Each data point represents an average of at least four <sup>14</sup>C/<sup>13</sup>C determinations, each having a counting statistics uncertainty of *ca.* ± 1% (except for the 4th sample of 1972, which was measured only twice). These measurements were made on at least two separately prepared ion-source targets (except for the 4th sample of 1972 and the 3rd and 4th sam-

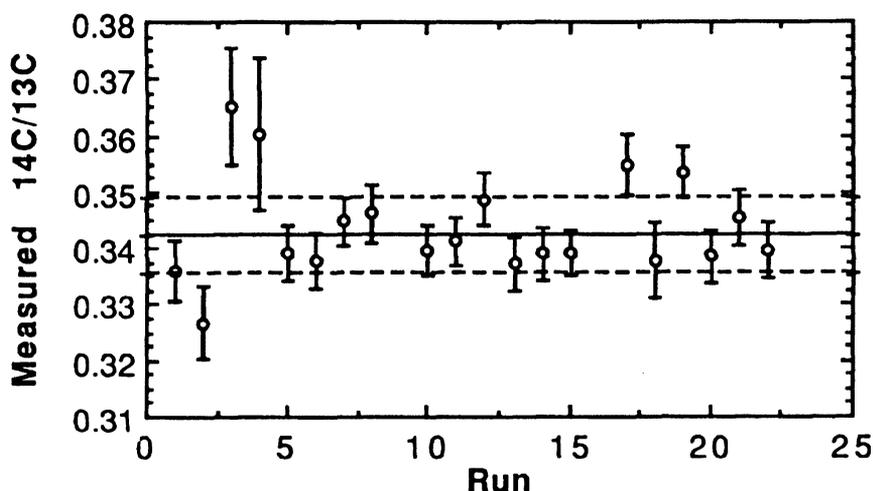


Fig. 3. Normalized  $^{14}\text{C}/^{13}\text{C}$  data obtained on the secondary standard, QL-11658.  $\circ$  = measured  $^{14}\text{C}/^{13}\text{C}$  ratios for runs between June and November 1990, on targets prepared from QL-11658 (these measurements are normalized with respect to our Chinese Sucrose  $^{14}\text{C}$  laboratory standard). The error bars represent  $1\sigma$  uncertainties in the  $^{14}\text{C}/^{13}\text{C}$  ratios derived from counting statistics; — = the weighted mean of all of the data; --- =  $\pm 1$  standard deviation calculated from the data. This distribution is important as it clearly indicates the method used to calculate the quoted values, *i.e.*, as opposed to error estimate propagation. (The values from runs 3 and 4, while included in the calculation of the weighted mean, have been excluded from the standard deviation calculation because the format of this calculation does not allow these values, which are relatively far from the weighted mean and have unusually large  $\sigma$ s, to be given appropriately lesser weights than the other, more precise values.)

TABLE 1. Measured  $\Delta^{14}\text{C}$  values for “three-month” coral samples from Punta Pitt, San Cristóbal Island, Galapagos Islands

Year	Months represented by sample (approx.)	$\Delta^{14}\text{C}$ (‰)
1970	January–March	+31 $\pm$ 7
	April–June	-1 $\pm$ 4
	July–September	+29 $\pm$ 7
	October–December	+37 $\pm$ 7
1971	January–March	+22 $\pm$ 6
	April–June	+21 $\pm$ 6
	July–September	+30 $\pm$ 6
	October–December	+24 $\pm$ 6
1972	January–March	+15 $\pm$ 6
	April–June	+46 $\pm$ 6
	July–September	+53 $\pm$ 6
	October–December	+34 $\pm$ 9
1973	January–March	+54 $\pm$ 5
	April–June	+2 $\pm$ 5
	July–September	+27 $\pm$ 6
	October–December	+51 $\pm$ 6

ples of 1973). We calculated these preliminary age-corrected  $\Delta^{14}\text{C}$  values following the conventions of Stuiver and Polach (1977), and using  $\delta^{13}\text{C}$  values estimated for the samples from previously published  $\delta^{13}\text{C}$  data (McConnaughey 1986). Analysis of the scatter of individual measurements of each sample about the mean for that sample confirms that the  $1\sigma$  error bars (derived from counting statistics uncertainties and typically *ca.*  $\pm 6\%$ ) accurately represent the variance in our data. These data clearly show significant variations in the  $^{14}\text{C}$  content of the coral on time scales shorter than one year.

Figure 2 also shows the SST record obtained at Academy Bay over the same period. Notwithstanding the uncertainty in the actual time period that each of the “three-month” coral samples represents, the similarity between our  $\Delta^{14}\text{C}$  results and the SST variations is striking. The correlation coefficient,  $r$ , for these two data sets as shown is 0.39 ( $n$ , the number of data points, = 16, and  $P$ , the probability that this correlation coefficient value could be obtained from two uncorrelated data sets, = 0.2). In light of evidence that the growth rates of Galapagos corals in the cooler waters of April to December may drop to less than half the rates in the warmer waters of January to March (Glynn & Wellington 1983), we made appropriate adjustments to the length of time that each sample represents in a preliminary attempt to compensate for coral growth-rate variations due to changes in water temperature. Keeping in mind the limitations of the data presented by Glynn & Wellington (1983) and the uncertainties in these preliminary adjustments, we found that the correlation between the SST and adjusted  $\Delta^{14}\text{C}$  data sets is significant ( $r = 0.74$ ,  $n = 16$ ,  $P < 0.002$ ). We believe that this correlation clearly shows the effects of variations in the surface-ocean currents that flow into the Galapagos Islands on both the temperature and  $^{14}\text{C}$  content of the surface waters of the region.

Figure 2 also shows the annual average  $\Delta^{14}\text{C}$  values obtained by Druffel (1981) on corals collected from Gardner Bay, Española (Hood) Island. In general, these annual average data are consistent with annual averages of the “three-month” average  $\Delta^{14}\text{C}$  values that we obtained. Note that the locations within the annual bands chosen to mark the beginning of each year may have been slightly different in these two studies. Because of the significant intra-annual  $\Delta^{14}\text{C}$  variations evident in our data, such differences could be the source of small disagreements between the annual average  $\Delta^{14}\text{C}$  values obtained by Druffel and those calculated from our data. Some differences may also exist in local upwelling that could cause the  $^{14}\text{C}$  content of the waters at our Punta Pitt collection site to differ slightly from that at Druffel’s Gardner Bay site. The  $\Delta^{14}\text{C}$  values that Druffel obtained for the “six-month” average coral samples from 1972 ( $28 \pm 3\%$  and  $32 \pm 4\%$ ) are clearly incompatible with Druffel’s annual average and our “three-month” average  $\Delta^{14}\text{C}$  values obtained for that same year.

## CONCLUSIONS

At this initial stage of our study of the intra-annual variability of the  $^{14}\text{C}$  content of Galapagos Islands corals, we emphasize two points. First, it is evident from the preliminary “three-month” average  $\Delta^{14}\text{C}$  values that intra-annual variations exist that are significant both statistically and oceanographically. These intra-annual variations reflect subannual changes in the sources of the surface waters that flow through the Galapagos region. Second, the 1972 ENSO event is reflected in the  $^{14}\text{C}$  content of the surface waters in the Galapagos Islands, and the ENSO signal preserved in the coral is consistent with expected changes in the surface waters due to variations in surface-ocean currents during such events.

Clearly, the magnitude of the subannual variations (35–50‰ during the period that we studied) is such that one must use caution in attempting to identify the origin of upwelled waters in the Galapagos region using average annual  $^{14}\text{C}$  content data. We believe that further subannual measurements on Galapagos and other corals will help us understand the current structure of the tropical Pacific, and help to constrain ocean-circulation models of the region. The ENSO signal in our  $\Delta^{14}\text{C}$  data suggests that more detailed measurements of the coral record of the 1972 and other ENSO events will provide information on the

variations of the surface-ocean currents in the Galapagos region during similar events throughout the available coral record.

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#### REFERENCES

- Balsley, D. R., Farwell, G. W., Grootes, P. M. and Schmidt, F. H. 1987 Ion source sample preparation techniques for carbon-14 AMS measurements. *In* Gove, H. E., Litherland, A. E. and Elmore, D., eds., *Proceedings of the 4th International Symposium on AMS. Nuclear Instruments and Methods in Physics Research B29*: 37–40.
- Brown, T. A., Farwell, G. W., Grootes, P. M., Quay, P. D. and Schmidt, F. H. 1990  $^{14}\text{C}$  AMS at the University of Washington: Measurements in a shared facility at the 1% level on 0.4 mg samples. *In* Yiou, F. and Raisbeck, G. M., eds., *Proceedings of the 5th International Conference on AMS. Nuclear Instruments and Methods in Physics Research B52*: 351–356.
- Druffel, E. R. M. 1981 Radiocarbon in annual coral rings from the eastern tropical Pacific Ocean. *Geophysical Research Letters* 8(1): 59–62.
- \_\_\_\_\_ 1987 Bomb radiocarbon in the Pacific: Annual and seasonal timescale variations. *Journal of Marine Research* 45: 667–698.
- \_\_\_\_\_ 1989 Decade time scale variability of ventilation in the North Atlantic: High-precision measurements of bomb radiocarbon in banded corals. *Journal of Geophysical Research* 94(C3): 3271–3285.
- Druffel, E. M. and Linick, T. W. 1978 Radiocarbon in annual coral rings of Florida. *Geophysical Research Letters* 5(11): 913–916.
- Druffel, E. M. and Suess, H. E. 1983 On the radiocarbon record in banded corals: Exchange parameters and net transport of  $^{14}\text{CO}_2$  between atmosphere and surface ocean. *Journal of Geophysical Research* 88(C2): 1271–1280.
- Enfield, D. B. 1989 El Niño, past and present. *Reviews of Geophysics* 27: 159–187.
- Grootes, P. M., Stuiver, M., Farwell, G. W., Leach, D. D. and Schmidt, F. H. 1986 Radiocarbon dating with the University of Washington Accelerator Mass Spectrometry System. *In* Stuiver M. and Kra, R. S., eds., *Proceedings of the 12th International  $^{14}\text{C}$  Conference. Radiocarbon 28(2A)*: 237–245.
- Glynn, P. W. and Wellington, G. M. 1983 *Corals and Coral Reefs of the Galápagos Islands*. Berkeley, University of California Press: 330 p.
- McConnaughey, T. A. (ms) 1986 Oxygen and carbon isotope disequilibria in Galapagos corals: Isotopic thermometry and calcification physiology. Ph.D. dissertation, University of Washington, Seattle: 340 p.
- Nozaki, Y., Rye, D. M., Turekian, K. K. and Dodge, R. E. 1978 A 200 year record of carbon-13 and carbon-14 variations in a Bermuda coral. *Geophysical Research Letters* 5(10): 825–828.
- Schmidt, F. H., Brown, T. A., Farwell, G. W. and Grootes, P. M. 1990 The University of Washington AMS system: A six-year technical update. *In* Yiou, F. and Raisbeck, G. M., eds., *Proceedings of the 5th International Conference on AMS. Nuclear Instruments and Methods in Physics Research B52*: 229–232.
- Stuiver, M. and Polach, H. A. 1977 Discussion: Reporting of  $^{14}\text{C}$  data. *Radiocarbon* 19(3): 355–363.
- Vogel, J. S., Southon, J. R., Nelson, D. E. and Brown, T. A. 1984 Performance of catalytically condensed carbon for use in accelerator mass spectrometry. *In* Wöflli, W., Polach, H. A. and Andersen, H. H., eds., *Proceedings of the 3rd International Symposium on AMS. Nuclear Instruments and Methods in Physics Research B5*: 289–293.