Marine04: Marine radiocarbon age calibration, 26 – 0 ka BP

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Abstract

New radiocarbon calibration curves, IntCal04 and Marine04, have been constructed and internationally ratified to replace the terrestrial and marine components of IntCal98. The new calibration datasets extend an additional 2000 years, from 0 –26 ka cal BP (Before Present, 0 cal BP = AD 1950), and provide much higher resolution, greater precision and more detailed structure than IntCal98. For the Marine04 curve, dendrochronologically dated tree-ring samples, converted with a box-diffusion model to marine mixed-layer ages, cover the period from 0 – 10.5 ka cal BP. Beyond 10.5 ka cal BP, high-resolution marine data become available from foraminifera in varved sediments and U/Th-dated corals. The marine records are corrected with site-specific ¹⁴C reservoir age information to provide a single global marine mixed-layer calibration from 10.5 – 26.0 ka cal BP. A
substantial enhancement relative to IntCal98 is the introduction of a random walk model, which takes into account the uncertainty in both the calendar age and the radiocarbon age to calculate the underlying calibration curve (Buck and Blackwell, this issue). The marine datasets and calibration curve for marine samples from the surface mixed layer (Marine04) are discussed here. The tree-ring datasets, sources of uncertainty, and regional offsets are presented in detail in a companion paper by Reimer et al. (this issue).

Introduction

Radiocarbon dates must be converted to calendar ages for greatest utility in comparison, for example, to known historical ages in archeology or calendric ice cores and layer-counted marine sediments as well as U/Th chronologies in paleoceanographic studies. Tree-ring dendrochronologies provide the most accurate and highest resolution calibration data for terrestrial \(^{14}\)C ages, but currently are limited to the past 12.4 ka cal BP (Friedrich et al., this issue). In addition, for applications to calibration of marine dates, tree-ring \(^{14}\)C ages must be modeled to derive equivalent ocean mixed-layer ages. High-resolution measurements of the marine \(^{14}\)C calibration curve beyond tree rings have been obtained from planktonic foraminifer in layer-counted varved sediments, extending detailed calibration back to 14.7 ka cal BP (Hughen et al., 2000). Additional marine data parallel to and beyond the varved sediment record are available through extensive measurements from U/Th-dated corals around the world (Edwards et al., 1993; Bard et al., 1998; Burr et al., 1998; Cutler et al., this issue; Fairbanks et al., this issue).

In this paper we describe the data sets and methods used to construct the Marine04 portion of the new IntCal04 calibration curve. Details concerning the original tree-ring data used for the younger portion of Marine04, 0-10.5 ka cal BP, are given in a companion paper by Reimer et al. (this issue). Because high-resolution marine data are lacking from 0 to 10.5 ka cal BP, the calibration curve for surface mixed layer marine samples, Marine04, is constructed over this period from tree-ring measurements (Figure 1). The tree ring data are combined using a random walk model (RWM) described in detail in Buck and Blackwell (this issue). The smoothed IntCal04 tree-ring curve output from the random-walk model is then used as input into a global ocean-atmosphere box diffusion model (Stuiver and Braziunas, 1993). The model is used to deconvolve the \(^{14}\)C production rate from the tree-ring data and calculate the ‘global’ ocean mixed layer radiocarbon ages. Beyond tree-rings, \(^{14}\)C measurements of foraminifera from Cariaco Basin varved sediments and U-series dated corals are used to construct the calibration curve. The high-resolution Cariaco basin data set begins at 10.5 ka cal BP, and the tree ring-based data set is therefore only used back to that time. The coral and foraminiferal \(^{14}\)C data sets are converted to ‘global’ ocean mixed layer values by subtracting the difference (\(\Delta R\)) between the regional reservoir age and the mixed layer reservoir age R (Stuiver et al., 1986) calculated from the box-diffusion model. The normalized coral and foraminiferal \(^{14}\)C data are then combined via the RWM into a single smooth curve and added to the end of the tree-ring based modeled mixed-layer curve.

The IntCal04 working group, which met at Queen’s University Belfast, in April 2002 and at Woods Hole Oceanographic Institution in May 2003, established criteria for
acceptance of data into the IntCal04 calibration dataset including general limitations on analytical errors and acceptable scatter and specific record-dependent criteria (Reimer et al., 2002). The criteria for acceptable tree-ring records are discussed in brief in Reimer et al. (this issue). For corals, criteria were established to detect alteration of the original aragonite, including X-ray diffraction measurements to show $\leq 1\%$ calcite, initial $\delta^{234}$U within $\pm 5\%$o of accepted seawater values, and concordant protactinium ages where available, especially where diageneric is most likely due to sub-aerial exposure. Numerous data from corals with pristine aragonite, and in several cases concordant Pa ages, have led to a revision in our understanding of the history of seawater $\delta^{234}$U (see Cutler et al., this issue and references therein), and adoption of new criteria for coral initial $\delta^{234}$U values. These criteria are discussed in greater detail in a later section. For layer counted chronologies, such as those based on varve counting, acceptance criteria include the need for multiple-core chronologies to confirm that no sections are missing from core-breaks or erosion. In addition, independent radiometrically dated tie points should be employed whenever possible to validate and assess the quality of the layer chronology. For all marine records, site-specific reservoir corrections should be measured, and a “reasonable” error should be reported with the reservoir age (Reimer et al., 2002).

The calibration datasets for terrestrial and marine samples were presented for consensus ratification at the 18th International Radiocarbon Conference in Wellington, New Zealand in Sept. 2003. Suggestions from conference participants have been incorporated into the final product. We do not make a recommendation for calibration beyond 26 ka at this time due to large disparities between the available datasets (van der Plicht et al., this issue).

The Marine04 Datasets

The datasets used in the IntCal04 and Marine04 calibrations are given in full as supplemental material on the radiocarbon website (www.radiocarbon.org) and are also available at www.calib.org. Uncertainties are given for the radiocarbon ages and the calibrated or cal timescales in order that they may be combined properly, since in some cases the cal timescale errors are not independent. Replicate $^{14}$C measurements within a laboratory or made by two or more laboratories are given separately, when available. These data are not necessarily completely independent estimates of the underlying calibration curve since they are derived from the same samples but have been included for completeness.

Tree-ring datasets (0-10.5 ka cal BP)

The Holocene part of the Marine04 radiocarbon calibration is based on several millennia-long tree-ring chronologies providing an annual, nearly absolute time frame, which was rigorously tested by internal replication of many overlapping sections. Whenever possible, chronologies were crosschecked with independently established chronologies of adjacent regions. Details of individual tree-ring data sets are provided by Reimer et al. (this issue).
Marine Datasets (10.5-26 ka cal BP)

Marine calibration older than 10.5 ka cal BP is provided by data from Cariaco basin and coral U/Th ages. Cariaco and coral data are combined from 10.5 to 14.7 ka cal BP, and coral data alone are used to extend calibration back to 26 ka cal BP. We calculated site-specific reservoir corrections from the weighted mean difference of marine and tree-ring \(^{14}\)C ages using data overlapping from 500-12,500 BP (Table 1), not including recent pre-bomb data pairs used in previous publications. This was done in order to avoid uncertainty in the degree of fossil fuel influence on reservoir calculations from recent samples, and also to assess changes in reservoir age due to different climatic states (e.g., Younger Dryas). In addition, the increased number of marine-terrestrial age comparisons provides more realistic error estimates on calculated reservoir corrections. For each marine sample the difference in \(^{14}\)C age was calculated for the nearest point in the tree-ring derived portion of IntCal04. For this comparison, no error was included for the calendar age of the marine samples. However, the IntCal04 curve was smoothed with a 20-point (100-year) average to diminish the influence of calendar age uncertainty. The error in the difference was calculated from the square root of the errors of the marine and the IntCal04 \(^{14}\)C ages added in quadrature. The weighted mean of all the differences was calculated for each location and the square root of the variance (observed standard deviation or scatter sigma) was taken as the uncertainty (Table 1). For the Vanuatu corals a decadal average of the Burr et al. (1998) single year data was used for the comparison in addition to the Cutler et al. (this issue) data. For Mururoa there are no overlapping tree-ring data points so we use the value calculated for Tahiti, which is within a reasonable proximity. The calendar chronology for Cariaco Basin is based on a wiggle-match with the tree-rings, so there is obvious circularity in using this difference although the calculated value overlaps with measurements from the core top (Hughen et al. 1996) and from corals from Isla Tortugas (Guilderson et al., in review). For all sites, the reservoir corrections calculated here agree well within errors with previous measurements (Table 1). For sites where we have compiled modern “pre-bomb” data (<100 BP), the inclusion of a fossil fuel correction (Bard et al., 1988; Southon, 2002; Guilderson et al., in review) may change calculated reservoir ages by up to 100 years, although generally still in agreement with the new values.

The current state of knowledge dictates that, for construction of a global marine \(^{14}\)C calibration curve, site-specific reservoir and \(\Delta R\) values are assumed to be constant with time. Although there is evidence for large (factor of two) reservoir age shifts in the past, for example during deglaciation in the high-latitude North Atlantic (Bard et al., 1994; Austin et al., 1995; Björk et al., 1998; Bondevik et al., 1999; Eiriksson et al., 2000; Waelbrook et al., 2001), Mediterranean Sea (Siani et al., 2001), and New Zealand region (Sikes et al., 2000), all marine data sets used in Marine04 come from low latitude tropics where the fluctuations in reservoir correction may not be as great. For example, Cariaco basin \(^{14}\)C ages agree closely with anchored tree-ring ages from 10.5 to 12.4 ka cal BP across the large climatic shifts of the Younger Dryas (Hughen et al., this issue), exhibiting no evidence of significant reservoir variability. Nevertheless, Cariaco comparison to floating tree-ring sections indicate the possibility that reservoir age
increased by up to 50% during the Allerød (Kromer et al., this issue). Therefore, both within single locations and between regions, some changes in reservoir correction through time may be apparent—either as slight trends or increased/decreased variability (Figure 2). Many of these changes reflect real shifts in regional or local oceanography, such as surface circulation and advection, meridional overturning, or local upwelling, rather than analytical uncertainties due to sample diagenesis or laboratory error. For example, the large variability in the Papua New Guinea and Vanuatu reservoir calculations are probably indications of changes in the amount of Eastern Equatorial water reaching these sites and local upwelling at Papua New Guinea.

Quantifiable records of changes in regional oceanographic conditions adequate for predicting and correcting such reservoir variability are presently lacking. Thus a certain degree of scatter in site-specific reservoir values through time cannot be avoided, and must instead be characterized as reservoir uncertainty. This uncertainty incorporates all sources of error in reservoir measurement and calculation, and is likely an overestimation of true oceanic variability. Increased data density in the future may allow us to identify spatial and temporal patterns of reservoir variability, increasing precision for calibration as well as our understanding of ocean circulation change.

Table 1. New and previously determined site-specific reservoir corrections.

<table>
<thead>
<tr>
<th>Location</th>
<th>Reservoir correction (tree ring overlap)</th>
<th>Uncertainty</th>
<th>N</th>
<th>Previous value (known age, “pre-bomb”)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbados</td>
<td>360</td>
<td>80</td>
<td>22</td>
<td>400⁰</td>
</tr>
<tr>
<td>Cariaco Basin</td>
<td>430</td>
<td>30</td>
<td>196</td>
<td>420⁰</td>
</tr>
<tr>
<td>Kirimati</td>
<td>330</td>
<td>80</td>
<td>27</td>
<td>300</td>
</tr>
<tr>
<td>Mururoa</td>
<td>Same as Tahiti</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Papua New Guinea</td>
<td>490</td>
<td>150</td>
<td>17</td>
<td>407⁰</td>
</tr>
<tr>
<td>Tahiti</td>
<td>280</td>
<td>120</td>
<td>22</td>
<td>300⁰</td>
</tr>
<tr>
<td>Vanuatu Espiritu Santu Tasmaloum</td>
<td>530</td>
<td>105</td>
<td>41</td>
<td>494&lt;sup&gt;d&lt;/sup&gt; 500&lt;sup&gt;de&lt;/sup&gt;</td>
</tr>
<tr>
<td>Vanuatu Urelapa</td>
<td>350</td>
<td>120</td>
<td>14</td>
<td>400⁰</td>
</tr>
</tbody>
</table>

<sup>a</sup>Bard et al. (1998); <sup>b</sup>Hughen et al. (1996); <sup>c</sup>Edwards et al., 1993; <sup>d</sup>Burr et al. (1998); <sup>e</sup>Cutler et al. (this issue).

U/Th-dated Corals

Mass spectrometric techniques have been used to measure paired <sup>14</sup>C and <sup>230</sup>Th (as well as <sup>231</sup>Pa) ages on fossil corals for <sup>14</sup>C calibration. A plot of coral initial δ<sup>234</sup>U versus calendar
age for corals which pass the <1 % calcite criteria shows a distinct decline back in time (Figure 3). Adopting a screening criteria based on modern seawater $\delta^{234}$U of 145.8 ± 5‰ (Cheng et al., 2000) as originally proposed would eliminate approximately half of the data between 17 and 26 ka cal BP. Many of the older coral data show concordant $^{231}$Pa ages (Cutler et al., this issue; Fairbanks et al., this issue), and thus the lower value for initial $\delta^{234}$U is probably a reflection of true changes in seawater $\delta^{234}$U through time. We set the acceptance criteria to be within three standard deviations of the mean value for the two groups of corals before and after 17 ka cal BP. For corals that grew from 0-17 ka cal BP, initial $\delta^{234}$U must lie within ± 7.2‰ (3σ) of 145.2‰ (n = 171), close to our original criteria of accepted seawater values. However, for older corals between 17 and 26 ka cal BP in age, initial $\delta^{234}$U appears to be lower and a new value has been adopted for screening, 140.6 ± 7.2‰ (3σ, n = 80) (see Figure 3). Although the data in Figure 3 could also accommodate a gradually changing seawater $\delta^{234}$U, it is possible that seawater $\delta^{234}$U may have changed abruptly following input of high $^{234}$U/$^{238}$U glacial flour during deglaciation (e.g., Robinson et al., 2004). Thus a two-step model is used here for simplicity.

The data sets of Bard et al. (1990, 1998), Edwards et al. (1993) and Burr et al. (1998) were used in IntCal98 (Stuiver et al., 1998) and have been updated for inclusion in IntCal04 and Marine04. Extensive new coral data sets have been included from Cutler et al. (this issue) and Fairbanks et al. (this issue).

[Bard et al., (1998) collected samples from boreholes drilled off the islands of Tahiti and Mururoa, French Polynesia, in order to complement the database previously obtained on Barbados corals (Bard et al. 1990, 1993). 19 dates from Barbados cover an age span from 0.7 to 22 ka cal BP; 27 dates from Tahiti cover 9.5 to 13.8 ka cal BP; 4 dates from Mururoa span 15.5 to 23.5 ka cal BP.

Edwards et al., (1993) measured paired $^{14}$C and $^{230}$Th ages on uplifted fossil corals from the Huon Peninsula, Papua New Guinea. 17 age pairs cover an age span from 7.6 to 13.1 ka cal BP. Revised $^{234}$U and $^{230}$Th half-lives for $^{230}$Th-age and $\delta^{234}$U (Cheng et al., 2000) have been applied.

Burr et al., (1998) analyzed a single Diploastrea heliopora coral from Vanuatu. Growth bands in the coral were used to identify individual years of growth. $^{14}$C measurements were made on each year and are updated here to the original annual resolution. 352 dates over four discrete intervals cover an age span between 11.7 and 12.4 ka cal BP.

Cutler et al. (this issue) analyzed fossil corals in drill cores from Papua New Guinea and Vanuatu, obtaining calendar ages using both $^{230}$Th and $^{231}$Pa dating techniques. 6 samples from Papua New Guinea span an age range from 12.4 to 25.3 ka cal BP; 48 samples were obtained from Vanuatu–25 dates from Tasmaloum spanning ages of 11.0 to 24.6 ca ka BP, and 23 dates from Urelapa covering ages from 5.4 to 19.6 ka cal BP. $^{231}$Pa was measured for eleven samples from Papua New Guinea (eighteen measurements) and eight
of those samples were found to be concordant. These measurements are shown as solid triangles in Figure 3.

Fairbanks et al. (this issue) recovered drill cores from Barbados and Kirimati in the Caribbean and central Pacific. Dating with $^{238}$U/$^{234}$U/$^{230}$Th used a multi-collector magnetic sector ICP mass spectrometer. 190 dates from Barbados cover an age range from 0.7 to 25.8 ka cal BP; 64 dates from Kirimati span ages from 7.0 to 13.7 ka cal BP. $^{231}$Pa was measured for a number of samples with low initial $\delta^{234}$U (R. Fairbanks, this issue).

Cariaco Basin varved sediments

For the previous IntCal98 data set (Stuiver et al., 1998), high-resolution calibration data older than tree rings were provided by Cariaco basin piston core PL07-PC56 (Hughen et al., 1998). Core 56PC was sampled every 10 cm, yielding approximately 100-200 year resolution. For this IntCal04 curve, data are used from Cariaco piston core PL07-58PC, with ~25% higher deposition rate than 56PC. Core 58PC was sampled every 1.5 cm, providing $^{14}$C calibration at 10-15 year resolution throughout the period of deglaciation (Hughen et al., 2000). The floating Cariaco varve chronology was anchored to the revised and extended German pine chronology (Friedrich et al., this issue) by wiggle-matching detailed $^{14}$C structure over a 1900-year window (Hughen et al., this issue). 388 dates span an age range from 10.5 to 14.7 ka cal BP.

Sources of Uncertainty

For corals, it has been customary to report the uncertainty at the 2 $\sigma$ level (Edwards et al., 1993; Bard et al., 1998). In cases where replicate $^{14}$C analyses have been made it is possible to examine the actual variability in sample preservation, preparation and measurement. We compared the replicate analyses of Polynesian corals measured at the Gif-sur-Yvette AMS facility (Bard et al., 1998; Paterne et al., in press; Bard et al., this issue). The average standard deviation in the difference for 9 replicates (calculated from the uncertainties in the paired measurements added in quadrature) was 95 $^{14}$C years, whereas the observed standard deviation (square root of the variance) was 142 $^{14}$C years. Therefore an error multiplier of 1.5 appears to be more appropriate than the conventional 2.0. We also compared replicate measurements of Barbados and Kirimati corals measured at CAMS (Fairbanks et al., this issue). For 118 replicates, individual samples of coral were leached, graphitized and analyzed. The average standard deviation in the difference was 19 $^{14}$C years and the observed standard deviation was 38 $^{14}$C years, which gives an error multiplier of 0.5, rounded up to 1.0. The coral data measured at the NSF-Arizona AMS Laboratory were previously determined to have a multiplier k=1.0 (Donahue et al., 1997) and this value was used for all Arizona AMS coral measurements. For the remaining coral data an error multiplier of 2.0 was used.

For Cariaco basin forams, 80 replicate samples were picked, cleaned and analyzed. The average standard deviation in the difference was 28 $^{14}$C years and the observed standard deviation was 42 $^{14}$C years, which gives an error multiplier of 0.66, rounded up to 1.0.
Another representation of $^{14}$C reproducibility for Cariaco samples can be obtained by the results of 28 measurements of the foram-rich TIRI/FIRI turbidite sample made at the CAMS laboratory where the Cariaco samples were measured (Guilderson et al., 2003), and from the comparison of $^{14}$C measurements between Cariaco foraminifera and tree rings (Hughen et al., this issue). In both of these cases, the measurements resulted in a low reduced chi-square value ($\chi^2/\text{Ndeg}$) of around 0.9, showing that the scatter in these data sets are consistent with the uncertainty estimates derived from measurement error and background correction uncertainties.

**Calibration curve construction**

The Marine04 curve is constructed in two parts, using a combination of tree-ring and marine data sets (Figure 1). From 0-10.5 ka cal BP, where high-resolution marine data are lacking, Marine04 uses the dendrochronology based curve of IntCal04. The tree ring data are combined using a random walk model (RWM) into a single smooth curve. This curve is then converted with an ocean-atmosphere box diffusion model to yield ocean mixed-layer $^{14}$C ages. The output of the box diffusion model is slightly smoothed and attenuated due to mixing and decay time of $^{14}$C in the oceans, and offset from the atmospheric IntCal04 curve by a global mixed-layer reservoir age $R$ (Figure 4a). The ‘global’ reservoir $^{14}$C age of the surface ocean, $R(t)$, is the time-dependent difference between the modeled or measured ‘global’ surface ocean and atmospheric $^{14}$C ages. From 0-12.4 ka cal BP, where both tree ring and calculated mixed-layer ages exist, $R$ varies with time as a result of rapid shifts in atmospheric $\Delta^{14}$C being attenuated in the surface ocean (Figure 4b). Beyond 10.5 ka cal BP, Marine04 relies on direct measurements of marine $^{14}$C ages from corals and foraminifera. Individual marine data sets were corrected to a consistent global mixed-layer $^{14}$C data set by subtracting $\Delta R$. $\Delta R$ is defined as the difference between the regional surface ocean $^{14}$C age and the ‘global’ surface ocean $^{14}$C age (Stuiver et al., 1986). Because atmospheric forcing of the regional part of the ocean and the world ocean are approximately parallel, $\Delta R$, for a given region, can, as a first approximation, be assumed to be constant. However, changes in oceanic circulation patterns or regional upwelling of deep (older) water may cause $\Delta R$ to vary with time. Whether or not $\Delta R$ for a given region is constant through time is thus an important issue when establishing a chronology for marine records or calibrating marine radiocarbon ages. A global $R$ value for the period 10.5-26 ka cal BP was determined by the results of box diffusion model simulations for 500 years from AD 1350-1850 (described below), and equaled 405 ± 22 years. After combining the corrected ‘global’ marine data with the RWM, the curve transitions smoothly into the box diffusion model mixed-layer $^{14}$C ages at 10.5 ka cal BP (Figure 5). [NOTE: Preliminary RWM model run.]

To calibrate marine $^{14}$C ages, one must know $\Delta R$, the site-specific offset from the global ocean reservoir. Although global $R$ in Marine04 changes from 0-10.5 ka cal BP (but remains constant from 10.5-26 ka cal BP), it is assumed that $\Delta R$ for any given marine location remains constant to a first approximation. To calculate $\Delta R$, the site-specific marine $^{14}$C age is compared to the Marine04 mixed-layer $^{14}$C age for any known calendar age. For modern pre-bomb measurements, the calendar age is usually known or can be
estimated accurately. A database of ΔR values calculated for known age marine samples is maintained at www.calib.org/marine. To evaluate the assumption of constant ΔR further back in time, terrestrial-marine pairs may be dated, however great care must be taken to ensure that they are indeed contemporaneous. In those cases, ΔR can be calculated either by calibrating the terrestrial 14C age and comparing the difference between the equivalent marine age and the measured marine age (Southon et al., 1995) or by directly comparing the terrestrial 14C age and the marine age using the combined IntCal04-Marine04 dataset following the method of Stuiver and Braziunas (1993) and Reimer et al. (2002b). ΔR and its estimated uncertainty is then used in conjunction with the marine calibration curve in most calibration software.

Random Walk Model

For IntCal04 and Marine04, the calendar age span (e.g., number of tree-rings, varves or coral growth bands) and calendar age uncertainty of the samples is taken into account through a stochastic random walk model (RWM) that estimates the underlying radiocarbon calibration curve (Buck and Blackwell, this issue). This model assumes that the changes in the curve from one year to the next can be represented by a Gaussian distribution with a mean of β and variance per year of r². Because there are usually multiple observations relevant to the estimated radiocarbon age for a given calendar year, the covariance is included within a window of 50 observations. The value for the parameter r = 8.5 for IntCal04 was derived from sensitivity tests on single year tree-ring measurements of the past 500 years (Stuiver et al., 1998b). The single year tree-ring measurements were initially selected for the model parameterization in order to retain as much signal as possible, but essentially the same value for r was obtained using decadal measurements in selected portions of the tree-ring dataset. The RWM variance parameter for Marine04 r = 6.5, and was calculated using a Monte Carlo simulation on pre-industrial coral measurements from the Florida Keys and Abraham Reef spanning the period 315 – 100 cal BP with the error in the radiocarbon age doubled (error multiplier = 2) (Druffel, 1982; Druffel and Griffin, 1993, 1999). The parameter selection details are given in Buck and Blackwell (this issue). The Marine04 radiocarbon calibration curve is generated by the model at intervals of 5 years for the range 0-10 ka cal BP, 10 years for 10-15 ka cal BP, and 50 years for 15-26 ka cal BP.

Ocean-Atmosphere Box Diffusion Model

The ocean-atmosphere box diffusion model is based on the work of Oeschger et al. (1975). The model was parameterized to produce a pre-industrial marine mixed layer Δ14C of -46.5 ‰ and a deep ocean value of -190‰ at AD 1830 for the 1998 marine calibration dataset, Marine98 (Stuiver et al., 1998b). This resulted in a reservoir age of 390 14C yrs for AD 1830 and an average reservoir age of 360 for the period 7050 BC to AD 1850 when compared to the atmospheric values from IntCal98. For Marine04, we used IntCal04 from 0 – 12.4 ka for input and allowed the model to spin up with the initial conditions for 2000 years to bring the system to equilibrium. The air-sea gas exchange coefficient F and eddy diffusivity K_z were varied slightly (Table 2) to achieve the Marine98 Δ14C values for the mixed layer over the last 500 years. Initial atmospheric
$\Delta^{14}C$ was set to 100 $‰$, the average value at the beginning of the tree-ring dataset. Pre-industrial atmospheric CO$_2$ concentration was set slightly lower at 270 ppm based on measurements of CO$_2$ trapped in ice from Law Dome, Antarctica (Indermuhle, 2000); however the model is relatively insensitive to changes in atmospheric CO$_2$ concentration of this order of magnitude. All other parameters were unchanged from Marine98. A representative section of the atmospheric $^{14}C$ record and box diffusion model mixed layer are shown in Figure 4.

Table 2. Box diffusion model parameters for Marine98 versus Marine04.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Marine98</th>
<th>Marine04</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-gas sea exchange</td>
<td>19 moles/m$^2$/yr</td>
<td>18.8 moles/m$^2$/yr</td>
</tr>
<tr>
<td>Eddy diffusivity</td>
<td>4000 m$^2$/yr</td>
<td>4220 m$^2$/yr</td>
</tr>
<tr>
<td>Pre-industrial atmospheric [CO$_2$]</td>
<td>280 ppm$^a$</td>
<td>270 ppm</td>
</tr>
<tr>
<td>Biosphere residence time and reservoir size (fraction of the atmosphere)</td>
<td>2.7 yrs; 0.34 atm</td>
<td>80 yrs; 2.86 atm$^b$</td>
</tr>
<tr>
<td>Ocean CO$_2$ concentration</td>
<td>2.31 mol/m$^3$c</td>
<td>same</td>
</tr>
<tr>
<td>Initial atmospheric $\Delta^{14}C$</td>
<td>90 $‰$</td>
<td>100 $‰$</td>
</tr>
</tbody>
</table>


In Marine98, the uncertainty in the marine calibration dataset was taken from the atmospheric dataset with no added uncertainty due to the choice of model parameters. We investigated the uncertainty in box diffusion model by varying F and $K_z$ by reasonable estimates. Using a simulation with 40000 random normal deviates of F between 18.8 ± 1 moles/m$^2$/yr and of $K_z$ between 4220 ± 500 m$^2$/y, the model produced a distribution for the offset between the surface mixed layer and the atmosphere of -50.4 ± 2.7 $‰$ or reservoir correction of 405 ± 22 years from AD 1350-1850. We use this value of 22 years for the uncertainty on the box diffusion model portion of Marine04.

**Comparison to Marine98**

The new Marine04 calibration curve shows many improvements over the previous Marine98 curve. Substantial new data sets provide additional calibration back to 26 ka cal BP (Cutler et al., this issue; Fairbanks et al., this issue), and higher resolution coverage for the interval beyond tree rings >10.5 ka cal BP (Hughen et al., this issue). As a result, Marine04 defines a great deal of structure beyond 15 ka cal BP, whereas Marine98 essentially followed a straight line (Figure 6). Despite the increased $^{14}C$ uncertainty used here, resulting from included uncertainty in reservoir corrections, the increased data resolution and RWM compilation algorithm create a much smaller error envelope in the final curve (Figure 6). During the deglacial interval of rapid climate change, large uncertainties and $^{14}C$ reversals primarily the result of the Marine98 splining procedure resulted in a curve of little practical use. In contrast, the Marine04 curve shows more monotonic behavior and a smaller error envelope, much more useful for calibration during this important time period.
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Figure captions:

Figure 1. Schematic diagram of IntCal04 and Marine04 calibration dataset construction. Tree-ring data extend from 0 to 12.4 ka cal BP. Beyond the end of the tree rings, coral and foraminifera data are converted to the atmospheric equivalent by subtracting a site-specific reservoir correction R. These data are input into the Random Walk Model (RWM) to produce IntCal04. Marine data from 10.5 – 26.0 ka cal BP are normalized to the “global” ocean by subtracting the regional difference from the model ocean (∆R). The “global” marine data are combined via the RWM and connected to the marine model output from 0 – 10.5ka cal BP to produce Marine04.

Figure 2. Site-specific reservoir corrections for the locations used in Intcal04 and Marine04. Sites include Cariaco Basin (Hughen et al., this issue); Vanuatu (Burr et al., 1998; Cutler et al., this issue); Barbados (Bard et al., 1998; Fairbanks et al., this issue); Tahiti (Bard et al., 1998); Kirimati (Fairbanks et al., this issue); and Papua New Guyinea (Edwards et al., 1993; Cutler et al., this issue). a) Reservoir corrections from 0-12.5 ka cal BP. Marine04 reservoir “R” changes from 0-10.5 due to shifts in atmospheric $^{14}$C production, but is held constant beyond 10.5. b) Blow-up of interval of greatest marine-terrestrial data overlap. Slight but coherent changes in reservoir age through time are likely due to real changes in oceanographic conditions (see text).

Figure 3. Initial $\delta^{234}$U calculated from coral calibration data from 0-26 ka cal BP. Symbols and references for sites are the same as in Figure 2. The data show a general decrease in initial $\delta^{234}$U for the earlier interval, 17-26 ka cal BP, although some data points possess concordant $^{231}$Pa ages (solid symbols). A lower value for initial $\delta^{234}$U,
140.6 ± 7.2‰, (3σ) has therefore been adopted as part of the acceptance criteria for corals older than 17 ka cal BP, and a value of 145.2 ± 7.2‰ (3σ) for corals younger than 17 ka cal BP.

Figure 4. Global marine reservoir age “R” for the past 3000 years. Atmospheric \( ^{14}C \) changes quickly following production spikes, but is muted in the ocean mixed layer. As a result, R calculated by the difference between Intcal04 and box-diffusion model output (curve a), shows large variability (curve b). Beyond 10.5 ka cal BP, when the Marine04 curve relies entirely on marine \( ^{14}C \) data sets, the global reservoir R is held constant at 405 years (see Figure 2).

Figure 5 Close-up of transition between tree-ring based and marine-based sections of Marine04 curve. Although global R (for calculating marine data \( \Delta R >10.5 \) ka cal BP) is taken from box-diffusion model output between 1300-1800 AD, the box-diffusion model output of tree ring data also shows a smooth transition to RWM output of marine data sets at 10.5 ka cal BP.

Figure 6. Comparison of Marine98 and Marine04 curves for interval beyond tree rings. Major improvements are evident during interval of deglaciation 15-10 ka cal BP, and Glacial period beyond 15 ka cal BP (inset).

Figure A1-A13: The Marine04 Marine calibration curve (1 σ envelope) and data with 1 σ error bars increased by the laboratory error multipliers described in the text. [NOTE: Preliminary RWM output]

References


Bard et al., 1988
Bard et al., 1990
Bard et al., 1993
Bard et al., 1994
Bard et al., 1998
Bard et al., this issue
Buck and Blackwell, this issue
Burr et al., 1998
Cheng et al., 2000
Cutler et al., this issue
Donahue et al., 1997
Druffel and Griffin, 1993
Druffel and Griffin, 1999
Druffel, 1982
Edwards et al., 1993
Emmanuel et al., 1984
Fairbanks et al., this issue
Friedrich et al., this issue
Guilderson et al., 2003
Guilderson et al., in review
Hughen et al., 1996
Hughen et al., 1998
Hughen et al., 2000
Hughen et al., this issue
Indermühle et al., 2000
Kromer et al., this issue
Neftel et al., 1985
Oeschger et al., 1975
Paterne et al., in press
Reimer et al. 2002a
Reimer et al. 2002b
Reimer et al. this issue
Robinson et al., in press
Sikes et al., 2000
Southon et al., 1995
Southon, 2002
Stuiver and Braziunas, 1993
Stuiver et al, 1984
Stuiver et al., 1986
Stuiver et al., 1998a
Stuiver et al., 1998b
Takahasi et al, 1981
van der Plicht et al., this issue).
Figure 1

Random Walk Model

Data Marine Model

Output

Random Walk Model Output

INTCAL04

MARINE04

26ka

12.4ka

0ka

26ka

0ka

10.5ka

12.4ka

0ka

26ka

0ka

10.5ka

10.5ka

Global R = 370

marine data - regional R

tree ring data

marine data + global R

Data

Random Walk Model Output

Marine Model Output
Figure 2
Figure 3a
Figure 3b
Figure 3c
Figure 3e