

# Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{14}\text{C}$ dates on pristine corals

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## Abstract

Radiocarbon dating is the most widely used dating technique in the world. Recent advances in Accelerator Mass Spectrometry (AMS) and sample preparation techniques have reduced the sample-size requirements by a factor of 1000 and decreased the measurement time from weeks to minutes. Today, it is estimated that more than 90 percent of all measurements made on accelerator mass spectrometers are for radiocarbon age dates. The production of  $^{14}\text{C}$  in the atmosphere varies through time due to changes in the Earth's geomagnetic field intensity and in its concentration, which is regulated by the carbon cycle. As a result of these two variables, a radiocarbon age is not equivalent to a calendar age. Four decades of joint research by the dendrochronology and radiocarbon communities have produced a radiocarbon calibration data set of remarkable precision and accuracy extending from the present to approximately 12,000 calendar years before present. This paper presents high precision paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  age determinations on pristine coral samples that enable us to extend the radiocarbon calibration curve from 12,000 to 50,000 years before present. We developed a statistical model to properly estimate sample age conversion from radiocarbon years to calendar years, taking full account of combined errors in input ages and calibration uncertainties. Our radiocarbon calibration program is publicly accessible at: <http://www.radiocarbon.LDEO.columbia.edu/> along with full documentation of the samples, data, and our statistical calibration model.

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## 1. Introduction

The records of the  $^{14}\text{C}$  content of the atmosphere and oceans contain a remarkable array of information about Earth history (Arnold and Libby, 1949; Libby, 1955; Suess, 1970; Damon et al., 1978; Stuiver, 1982; Stuiver and Pearson, 1986; Damon, 1988; Bard, 1998). Pro-

duced by cosmic rays in the upper atmosphere (Lal and Peters, 1962; Suess 1968; Lal, 1988),  $^{14}\text{CO}_2$  rapidly mixes throughout the troposphere and exchanges with the reactive carbon reservoirs of the oceans and biosphere, where it decays (Suess, 1955; Craig, 1957; de Vries 1958, 1959). For the past 11,000 years, fluctuations in the atmospheric  $^{14}\text{C}$  have been largely produced by changes in the solar magnetic field (de Vries, 1958, 1959; Stuiver, 1961; Stuiver and Quay, 1980). Most recently, Goslar et al. (2000a) concluded that variations in solar activity were the primary cause

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of the larger atmospheric  $^{14}\text{C}$  fluctuations for the period 11,000 to 14,500 years before present, although many researchers believe that carbon cycle changes tied to deep ocean circulation are a significant cause of atmospheric  $^{14}\text{C}$  fluctuations in this time interval (Edwards et al., 1993; Mikolajewicz, 1996; Stocker and Wright, 1996; Hughen et al., 2000; Muscheler et al., 2000; Delaygue et al., 2003). On longer time scales, changes in the Earth's magnetic field intensity impact the  $^{14}\text{C}$  content of the atmosphere, producing positive  $^{14}\text{C}$  anomalies during intervals of weaker geomagnetic field strength (Elsasser et al., 1956; McElhinny and Senanayake, 1982; Damon, 1988; Beer et al., 1988; Bard et al., 1990; Guyodo and Valet, 1999; Laj et al., 2000, 2004; Voelker et al., 2000). Of practical importance to a wide range of scientific disciplines is the radiocarbon calibration, which is used to convert radiocarbon ages to calendar years and to compute changes in atmospheric  $^{14}\text{C}$  ( $\Delta^{14}\text{C}$ ) through time (Stuiver, 1982; Damon, 1988; Bard et al., 1990, 1993; Edwards et al., 1993; Stuiver et al., 1986, 1998a, b; Burr et al., 1998; Hughen et al., 2000; Goslar et al., 2000c; Schramm et al., 2000; Voelker et al., 2000; Beck et al., 2001). Accurate calibration of radiocarbon ages to calendar years is essential for measuring time and rates of change for numerous scientific fields. According to Kutschera (1999), nearly 90% of all measurements made at the more than 50 active accelerator mass spectrometry laboratories are radiocarbon analyses.

The widely accepted tree ring radiocarbon calibration data set and resulting calibration curve are based on radiocarbon measurements of wood that has been absolutely dated by counting annual growth rings in overlapping tree chronologies (Stuiver, 1982; Damon, 1988; Stuiver et al., 1998a, b; Reimer et al., 2004). The continuous tree ring radiocarbon calibration spans from the present to nearly 12,000 yr BP. Suitable trees older than 12,000 yr BP are rare, but efforts continue to extend the tree ring calibration curve (Friedrich et al., 1999, 2001, 2004). In this study, we have overlapped and extended the tree-ring radiocarbon calibration from 0 to 50,000 yr BP using coral samples from our offshore coral reef core collection from Barbados (13.10°N; 59.32°W) in the western tropical Atlantic and Kiritimati Atoll (1.99°N, 157.78°W) in the central equatorial Pacific, and from the uplifted reefs of Araki Island (15.63°S; 166.93°E) in the western Pacific (Chiu et al., 2004, 2005a). Using new pretreatment and analytical techniques and state-of-the-art instrumentation at higher precision, we have reanalyzed the radiocarbon and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age dates from our original calibration work (Fairbanks, 1989, 1990; Bard et al., 1990, 1993, 1998), all of which were included in INTCAL98 (Stuiver et al., 1998a). These new results are reported in Appendix A.

In this paper, we present paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  (Lamont) and  $^{14}\text{C}$  age determinations (Lawrence Livermore National Lab and Leibniz-Labor for Radiometric Dating and Isotope Research Christian-Albrechts University Kiel) that span the entire range of the radiocarbon dating technique and present a radiocarbon calibration curve based on a Bayesian statistical model with rigorous error estimations. Our radiocarbon calibration curve is a stand-alone alternative to existing radiocarbon calibration data sets that infer calendar ages based on interpolations and correlations of local climate proxies in deep sea cores to the chronology of ice core proxies or assumptions about sedimentation rates (Voelker et al., 2000; Kitagawa and van der Plicht, 2000; Hughen et al., 2004a). Our calibration meets the requirements that each data point in the calibration has a measured calendar age ( $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ) and radiocarbon age with known errors that are independent of each other. We have chosen not to include coral data from other studies (Yokoyama et al., 2000; Paterne et al., 2004; Cutler et al., 2004; Hughen et al., 2004b) because coral samples reported in the literature typically contain between 1% and 5% calcite, a contaminant which is significantly concentrated during the sample-etching step prior to radiocarbon analyses, thereby corrupting the radiocarbon data (Chiu et al., 2005). In addition, we choose not to include coral samples that reported calcite detection limits above 0.2% (Bard et al., 1998), even if no calcite was reported in a sample, because samples contaminated by more than 0.2% are generally unsuitable for calibration purposes (Chiu et al., 2005), particularly for older samples. Finally, we have reanalyzed all of our previous radiocarbon calibration measurements on our Barbados samples (Fairbanks 1989, 1990; Bard et al., 1990, 1993, 1998; Stuiver et al., 1998a, b) at higher precision and with many replicates for both radiocarbon and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ , so we have not included these earlier measurements in our calibration curve. In the following sections, we outline our sample selection criteria, pretreatment procedures, analytical methods, Bayesian statistical model, and present our calibration curve.

## 2. Radiocarbon age calibration

### 2.1. Paired $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{14}\text{C}$ age dating of corals

Radiocarbon ages must be converted to calendar ages via an independent chronometer for accurate dating applications. Radiocarbon ages spanning the last 11,900 years are calibrated by making radiocarbon age determinations on tree rings of known age (Damon and Long, 1962; Damon et al., 1963; Stuiver et al.,

1998a,b; Spurk et al., 1998; Friedrich et al., 1999; Reimer et al., 2002, 2004). For the age interval between 12,000 years and 50,000 years before present, radiocarbon ages are calibrated by less precise and less accurate methods, such as varved sediments (Hughen et al., 1998, 2000, 2004b; Schramm et al., 2000; Goslar et al., 2000a,c; Kitagawa and van der Plicht, 2000; Hughen et al., 2004b; van der Plicht et al., 2004), correlation of distinct fluctuations in ocean/climate proxies dated by radiocarbon with similar features in the Greenland ice cores dated by layer counting and flow models (Hughen et al., 2000, 2004a; Voelker et al., 2000),  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  dating of speleothems (Vogel and Kronfeld, 1997; Goslar et al., 2000b; Beck et al., 2001) and corals (Fairbanks, 1990; Edwards et al., 1993; Bard et al., 1990, 1998a, b; Burr et al., 1998; Yokoyama et al., 2000; Cutler et al., 2004; Paterne et al., 2004; van der Plicht et al., 2004).

Each calibration approach has unique advantages and disadvantages. For example, it is possible that varved sediments can be dated precisely but not accurately due to missing or indistinct layers that lead to accumulating errors. Speleothems provide long records and are very useful for identifying general trends and maybe large  $^{14}\text{C}$  production anomalies, but speleothems are potentially limited by the dating errors due to variable groundwater uranium-series and carbon chemistry.  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  dating of corals can be reasonably precise and accurate, but samples of appropriate age are hard to acquire and the coral  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages can be altered by freshwater diagenesis (Hamelin et al., 1991; Henderson et al., 1993; Gallup et al., 1994, 2002; Ribaud-Laurenti et al., 2001), and in some locations by marine cements (Ribaud-Laurenti et al., 2001; Paterne et al., 2004). Even trace amounts of diagenetic calcite deposited in subaerially exposed corals will bias the radiocarbon measurements (Chiu et al., 2005a). In addition, ancient coral samples must be used for radiocarbon blanks because biogenic carbonate blanks are generally higher than spar calcite typically used in AMS laboratories. Attempts to develop a radiocarbon calibration curve by making radiocarbon measurements of microfossils in cores that contain proxies that can be correlated to ice core proxies have compounded errors due to proxy interpretations, correlation errors, and large uncertainties in ice-core chronologies (Hughen et al., 2000, 2004a; Voelker et al., 2000). Over the radiocarbon calibration interval, there are generally fewer than thirty tie points correlating deep sea core ocean/climate proxies to ice core proxies, thereby assigning calendar age estimates to most calibration points by interpolation. Differences between the various Greenland ice core chronologies are due to age model assumptions, inherent subjectivity in discerning annual bands in ice or layered sediments in general, the fidelity of proxies to record an annual signal, occasional wind

erosion or scouring of some snow layers, and compacting and degrading annual signals deeper in the ice cores (Dansgaard et al., 1989, 1993; Johnsen et al., 1992, 1995, 1997, 2001; Meese et al., 1994, 1997; Taylor et al., 1993; Stuiver et al., 1995; Andersen et al., 2004). Intervals where the annual signal is weak or missing entirely would not be counted by any of the proxies and therefore not included in Meese et al.'s (1997) error assessment. Another reason to avoid calibrating the radiocarbon timescale to ice core chronologies is the fact that many paleoclimate studies reference marine or terrestrial proxies to the ice core records of atmospheric gas chemistry, and these chronologies must remain independent for reliable interpretations.

All radiocarbon ages are readily subject to contamination by modern carbon during sample handling and processing of samples. In many cases, the different calibration archives are complementary and atmosphere and ocean calibration data sets from different locations and different archives are necessary to improve the accuracy and precision of ongoing international calibration efforts such as INTCAL98 (Stuiver et al., 1998a) and newer calibration data sets (e.g. IntCal04, Reimer et al., 2002, 2004; Marine04, Hughen et al., 2004b).

Unfortunately, combining published radiocarbon calibration data greater than 12,000 yr BP results in a confusing and inaccurate calibration data set (Fig. 1). Offsets and contradictions are the norm among these various calibration data sets, in stark contrast with the remarkably high quality tree ring calibration set for the present to 11,900 yr BP. Our contributions to the international radiocarbon calibration effort are the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  analyses of a suite of unusually high quality coral samples. Importantly, overlapping tropical Atlantic and Pacific calibration data sets are particularly helpful in constraining the uncertainties in the  $^{14}\text{C}$  reservoir age and validating fine details in those instances where the signals are coherent between oceans. It is our goal to construct a complete calibration data set using only pure aragonite coral samples, applying our rigorous pretreatment procedures outlined below, and measured with high precision mass spectrometry for  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  measurements with abundant replicate analyses.

Another important reason to develop a stand alone coral calibration curve is the fact that  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  ages have independent errors that can be measured and therefore, we can compute a rigorous error estimate for our radiocarbon calibration curve and calibrated radiocarbon ages. In contrast, radiocarbon calibration curves developed from floating varved sequences do not permit a rigorous error estimate of the calendar year due to the potential for an accumulation of errors in these sequences and inherent uncertainties in the age models. In addition, the accuracy and precision of our calibration data set can be tested by:

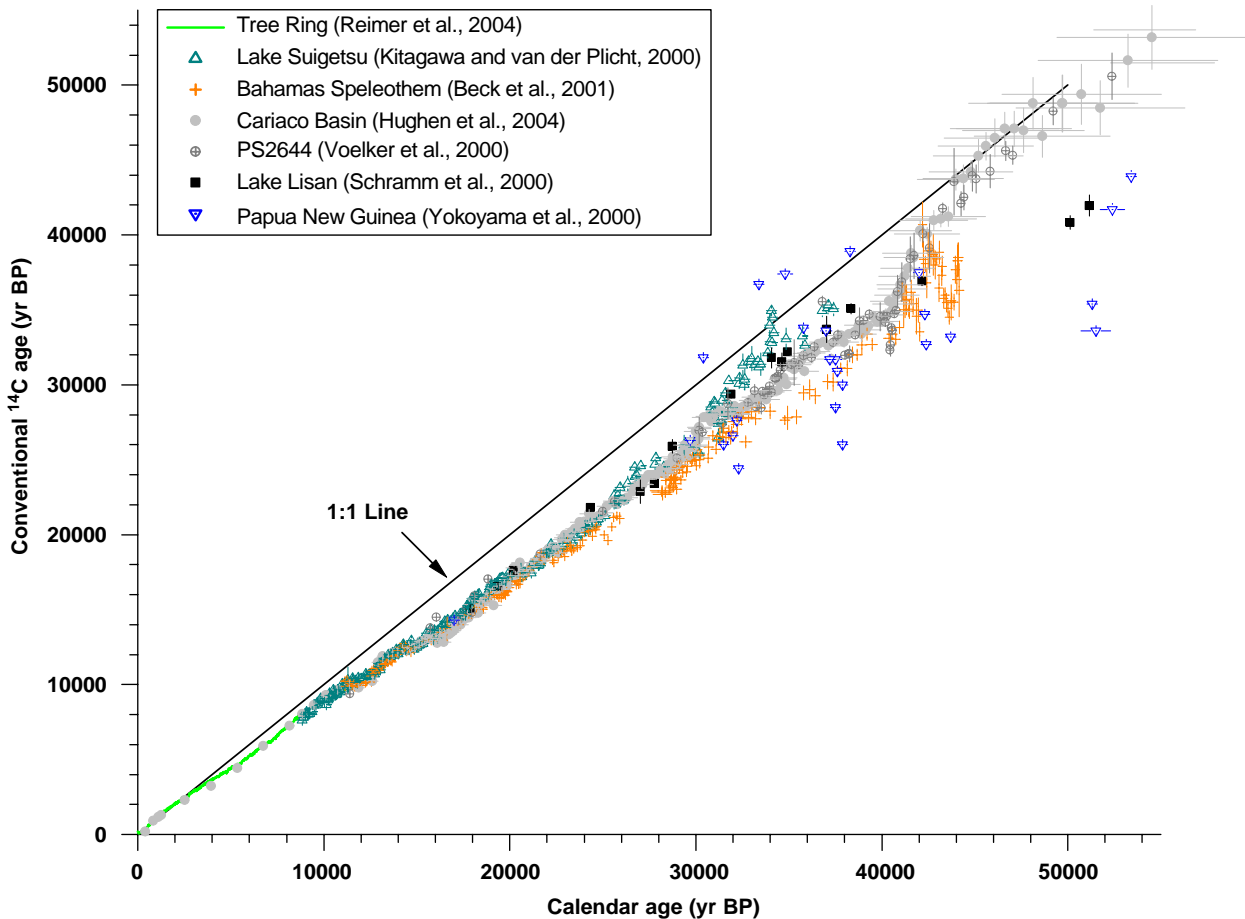


Fig. 1. Composite figure showing the range of radiocarbon calibration data from a variety of archives, including Bahamian speleothems (Beck et al., 2001), marine sediments (Hughen et al., 2000, 2004a; Voelker et al., 2000); lake sediments (Schramm et al., 2000; Kitagawa and van der Plicht, 2000), corals (Yokoyama, 2000), and tree rings (Reimer et al., 2004; Friedrich et al., 2004).

(a) measuring samples that overlap the tree ring calibration (Fig. 2); (b) making paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  ages on select samples (Pickett et al., 1994; Edwards et al., 1997; Cutler et al., 2004; Mortlock et al., 2005); and (c) through  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ,  $^{231}\text{Pa}/^{235}\text{U}$  and  $^{14}\text{C}$  measurements of our inter-laboratory calibration samples that are a subset of our calibration data. These calibration samples range from the modern to 50,000 yr BP at 10,000-year increments and are distributed to interested laboratories.

The direct determination of  $^{230}\text{Th}$ ,  $^{234}\text{U}$ , and  $^{238}\text{U}$  abundances by Thermal Ionization Mass Spectrometry (TIMS) opened a wide range of dating applications that were previously out of reach of the classical alpha-counting technique (Chen et al., 1986; Edwards et al., 1987a, b; Edwards, 1988; Bard et al., 1990; Gallup et al., 2002). The typical  $2\sigma$  precision of a mass spectrometry  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  date is better than 1% of the age (Chen et al., 1986; Edwards et al., 1987a, b; Mortlock et al., 2004). An early application of high precision  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  dating was paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  age dating of coral samples, thereby extending

the radiocarbon calibration beyond that based on tree rings (Bard et al., 1990; Fairbanks, 1990; Edwards et al., 1993) to approximately 20,000 yr BP.

In addition to measuring new samples from Barbados, we have reanalyzed all of our original Barbados samples presented in Fairbanks (1989, 1990), Bard et al. (1990, 1993, 1998), and Stuiver et al. (1998a, b) at higher  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  precision using our Fisons Plasma 54, and paired these data with new higher precision  $^{14}\text{C}$  analyses measured at the Lawrence Livermore National Lab (LLNL) Center for Accelerator Mass Spectrometry (CAMS) and Leibniz-Labor for Radiometric Dating and Isotope Research at Christian-Albrechts University Kiel. We have adopted the new half-life estimates for  $^{230}\text{Th}$  and  $^{234}\text{U}$  reported by Cheng et al. (2000) and report all data using these new values. Improvements to the sample pretreatment and quality control have been implemented (Chiu et al., 2005) and many of our new measurements include replicate analyses. In addition, we made 80 paired (including many replicates)  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  measurements from our Kiritimati cores collected in an offshore wire-line

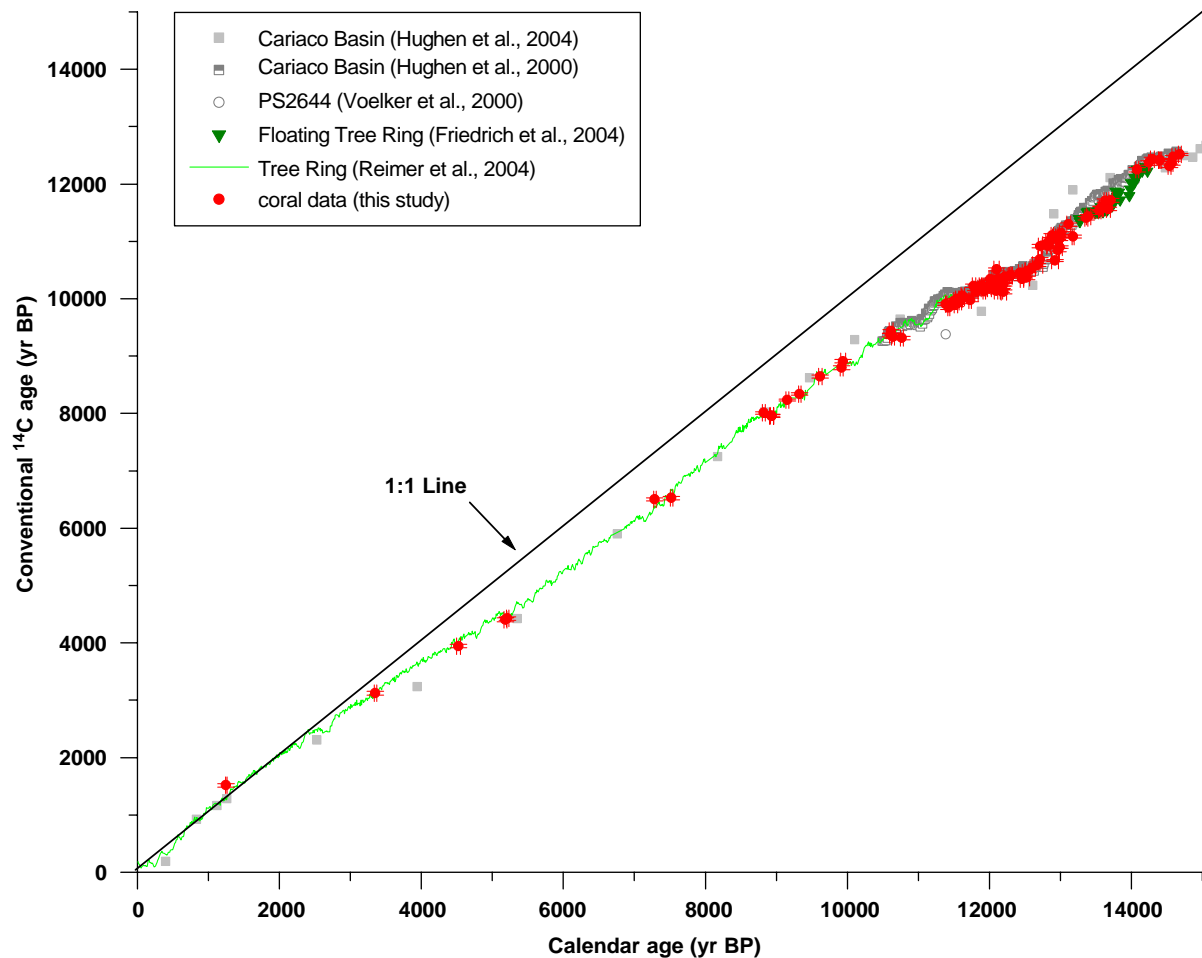


Fig. 2. Comparison of our coral data to the tree ring records of Reimer et al. (2004) and Friedrich et al. (2004) and the marine sediment data with calendar chronologies based on overlap with the tree ring data set and correlation to the oxygen isotope record in Greenland ice cores (Hughen et al., 2000, 2004a; Voelker et al., 2000). Note the consistency of our coral data with Friedrich et al.'s (2004) floating tree ring chronology, and where both diverge from the Cariaco (Hughen et al., 2000, 2004b) varved sequence between 13,300 and 14,000 yr BP. Figure zoom feature available at: <http://www.radiocarbon.ldeo.columbia.edu>.

drilling program in 1998/99 from the central Pacific. Samples dated older than 34,000 yr BP are from the uplifted reefs of Araki Island (15.63°S; 166.93°E) located in the southwest Pacific. These new results are presented and discussed in this paper (Fig. 3). A subset of our paired dates younger than 26,000 yr BP are included in the IntCal04 calibration papers (Reimer et al., 2004; Hughen et al., 2004b).

During the next 3 years, we plan to make approximately 400 new  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  measurements to fill in the gaps and details of the radiocarbon calibration from 0 to 50,000 yr BP. Our goal is to provide samples at approximately 100-year resolution or better. Our unique advantage is the quality of our coral samples from our offshore coring programs, combined with high precision  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and radiocarbon age measurements, and the suitable range of sample ages available in our cores. Our offshore core collections from Barbados, Kiritimati, and other Caribbean sites

contain hundreds of meters of core and thousands of pristine coral specimens between 4000 and 50,000 yr BP. Although it is our intention to quadruple the number of paired radiocarbon and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  measurements over the next 3 years, the broad utility of our existing calibration data and the many active research programs spanning the past 50,000 yr BP years justifies their publication at this time.

## 2.2. Sample and data quality control

The Barbados and Kiritimati samples that are younger than 30,000 yr BP resided exclusively in the marine environment and are remarkably well preserved. There is little microscopic (petrographic, scanning electron microscope, or binocular) or mineralogical evidence of aragonite or high magnesium marine cements in the coral pore spaces, as is occasionally reported at other reef core sites (Ribaud-Laurenti et al., 2001; Paterne

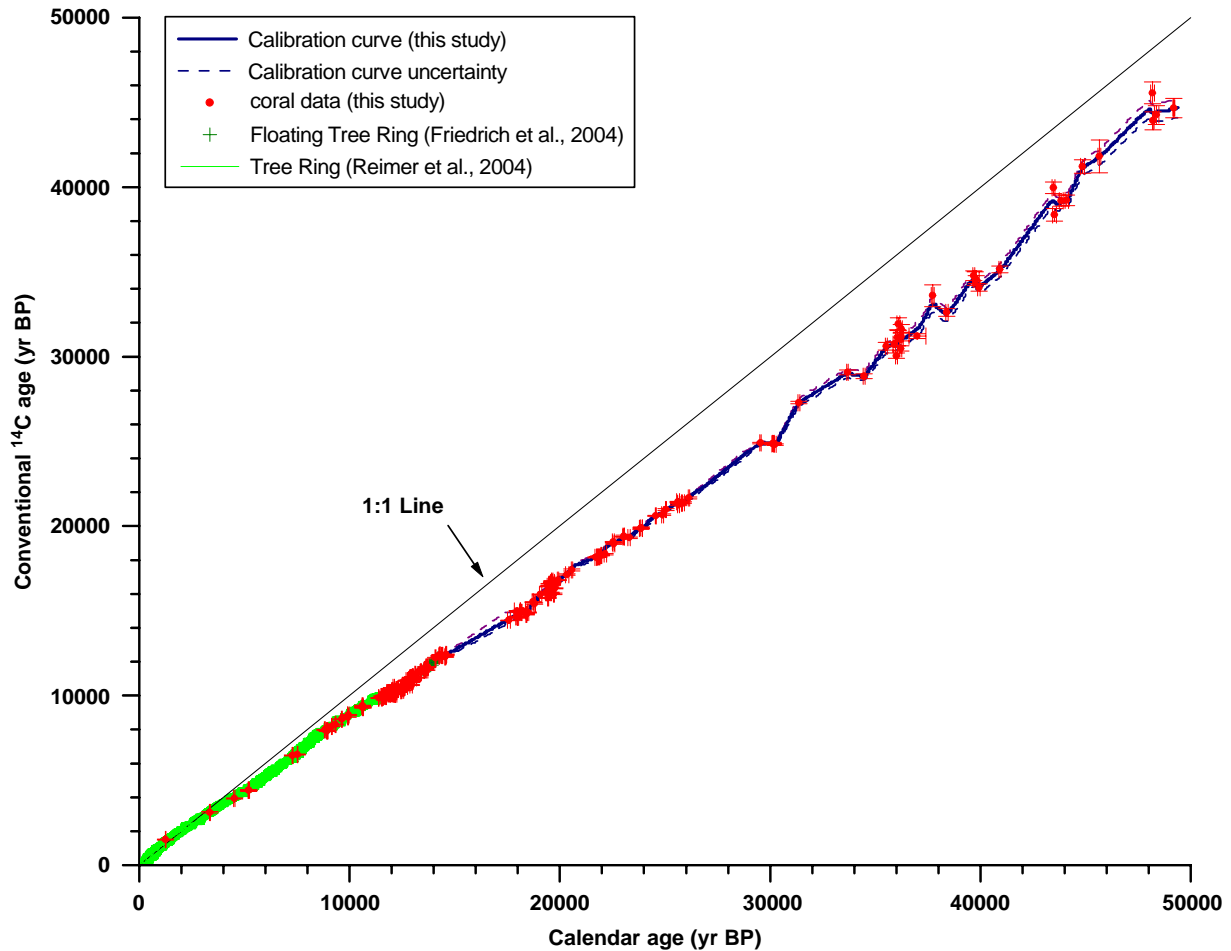


Fig. 3. Our coral calibration curve plotted with 1% confidence limits (corresponds to  $3\sigma$  uncertainties for normal distributions) and coral data plotted with  $1\sigma$  error bars. Calibration curve is compared to the tree ring chronologies (Reimer et al., 2004; Friedrich et al., 2004).

et al., 2004). The general lack of marine cements is probably due to the well ventilated locations of the Barbados and Kirimatiti core sites, which are removed from tidal or evaporative tidal conditions. Any sample showing even trace amounts of marine cement was not analyzed. For all of our samples, we use a “less than 0.2% calcite” quality control criterion. Calcite content is measured using an X-ray diffraction instrument with a calibrated detection limit of 0.2% calcite in an aragonitic coral. These pristine drill core samples and rigorous quality control criteria for vadose (zone exposed to percolating rain water) exposed samples are especially essential to the accuracy of the older radiocarbon dates, where a trace amount of calcite (i.e., greater than 0.2%) can result in unacceptably large offsets in radiocarbon ages (Chiu et al., 2004, 2005). The “less than 0.2% calcite” is the single most important screening criterion we have adopted, and it explains many of the differences between our calibration curve and published coral data that typically use 1% calcite detection limits and measure between 1% and 5% calcite in their samples (Yokoyama et al., 2000; Paterné et al., 2004).

The rapid burial of these corals minimizes the potential for microboring and encrusting organisms to degrade the sample quality, such as has occurred with dredged samples that resided on the sea floor for tens of thousands of years (Paterné et al., 2004). Most Barbados samples older than 30,000 yr. were subaerially exposed during the last glacial maximum lowstand, but have remained below sea level for the past 14,000 yr. A few samples older than 30,000 yr grew in deep water and were not subaerially exposed during the subsequent glacial maximum lowstand. In addition to these samples, we analyzed surface outcrop samples from interstadial uplifted reefs on Araki Island (15.63°S; 166.93°E) in the southwest Pacific for the time interval from 33,000 to 50,000 yr BP (Urmos, 1985). All Araki samples were subaerially exposed and were rigorously examined for signs of diagenesis based on criteria described later in this paper. Importantly, none of the samples has been exposed to the corrosive effects of a freshwater (phreatic) lens that is deleterious to  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  dating accuracy (Hamelin et al., 1991).

The following is a list of specific sample screening and data quality control criteria that we use for the construction of our radiocarbon calibration. The detailed analytical methods, acceptable precision, and accuracy of U-series and radiocarbon analyses for inclusion in the calibration data set will be discussed in the methods sections.

- X-ray diffraction (XRD) measurements on each sample must indicate less than 0.2% calcite based on a documented 0.2% calcite or better detection limit. Calibration standards of varying percentages of calcite in an aragonite sample are run with each batch of samples.
- The [U] of corals must be within the range of living/modern samples taking into consideration the species and the correlation of [U] and calcification temperature (Min et al., 1995).
- The  $\delta^{234}\text{U}_{\text{initial}}$  of coral samples must be between 138 and 150 per mil. Although the  $\delta^{234}\text{U}$  of modern seawater and corals averages 146 (Delanghe et al., 2002; Cutler et al., 2004), the glacial  $\delta^{234}\text{U}_{\text{initial}}$  estimates are slightly lower than this value (Cutler et al., 2004; Hughen et al., 2004a, b) and therefore, we have skewed the acceptable range toward lower values. Cutler et al. (2004) provides an analysis of the shifting  $\delta^{234}\text{U}$  over time.
- After ultrasonic cleaning, samples are examined microscopically for any evidence of foreign particles or aragonite cements. Samples are rejected if they show aragonite cements or visible contamination that cannot be ultrasonically removed.
- U-series and radiocarbon samples are taken from 2 concentric cores drilled into 4 mm thick slabs of the coral samples with the radiocarbon sample taken from the inner core. This assures systematic sampling and cleaning procedures and the proximal location of the two age determinations. X-ray diffraction samples are taken from the outer “donut” sampled for the U-series dates and the remainder of the sub-sample is archived. For samples older than 20,000 yr BP, the inner core is subjected to an extended hydrogen peroxide pretreatment step in order to remove organic matter (Chiu et al., 2005).
- Radiocarbon measurements are made with a relative precision better than or equal to +0.4% (one sigma) for samples less than 30,000 years old.
- $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age determinations are measured with a precision of better than +3.0 per mil (one sigma) over the entire calibration.
- A representative sampling of corals older than 30,000 yr BP that have been exposed to the vadose freshwater environment during the last glacial maximum low sea level, are analyzed for  $^{231}\text{Pa}/^{235}\text{U}$  ages, in addition to  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages, and  $^{14}\text{C}$  ages in order to validate the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age

determinations (Mortlock et al., 2004; Chiu et al., 2005c).

- Coral samples are ranked according to the following scale, and we strive to obtain the highest Category samples available for a given interval. Our ultimate goal is to construct a calibration curve that utilizes only Categories I thru IV samples, with as many Category I & II samples as possible. Category III samples are used only where sea-level variations limit the possibility of collecting Category I & II samples.

*Category I.* This category is reserved for samples that resided exclusively in the marine environment and have replicate radiocarbon and replicate  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age measurements that fall within  $2\sigma$  error respectively. Sample  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages are in stratigraphic order with respect to relative depth in core.

*Category II.* Samples that resided exclusively in the marine environment and are either not replicated or not replicated to within  $2\sigma$ . Sample  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages are in stratigraphic order with respect to their depth in core.

*Category III.* Samples that were exposed to vadose (rainwater percolating zone) freshwater and have  $^{231}\text{Pa}/^{235}\text{U}$  and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages that agree within  $2\sigma$  error.

*Category IV.* Samples that were that exposed to vadose freshwater and dated by  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  only.

*Category V.* Samples that were exposed to the freshwater table (phreatic lens) and have  $^{231}\text{Pa}/^{235}\text{U}$  and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages that agree within  $2\sigma$  error.

*Category VI.* Samples that were exposed to the phreatic lens and are not validated by concordant  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  dates.

### 2.3. $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ dating methods

We have developed techniques to determine the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  ages in a single coral fragment by Multi-Collector Inductively Coupled Mass Spectrometry (MC-MS-ICPMS) (Mortlock et al., 2004) using fragments as small as 0.5 g. In the case where only U and Th measurements are required, the procedure is modified from the version presented in Edwards et al. (1987a). Only samples exposed to vadose freshwater will likely benefit from the redundant  $^{231}\text{Pa}/^{235}\text{U}$  measurement (Mortlock et al., 2004). Although the details of the U-series methodology are presented elsewhere (Mortlock et al., 2004), we repeat some of the important features of the instrumentation and methods here.

#### 2.4. Mass spectrometry

U and Th isotopic measurements are made using our Fisons PLASMA 54 multi-collector magnetic sector double focusing Inductively Coupled Mass Spectrometer (MC-MS-ICPMS). A detailed description of the instrument design can be found elsewhere (Walder and Freedman, 1992; Halliday et al., 1995, 1998). In general, the instrument combines a double focusing magnetic sector mass spectrometer with an ICP source. Only a few of these instruments were manufactured, generally for the nuclear industry, and they varied in their configurations. Our instrument is equipped with a nine-collector Faraday array and is configured with an additional 30-cm radius Electro Static Analyzer (ESA) filter and a Daly detector with ion-counting capability. The abundance sensitivity achieved with the additional ESA energy filter is less than 0.3 ppm (measured as the contribution of mass 238 to mass 237 signal).

The sample injection into an ICP source is markedly simpler than loading a sample onto a filament and coaxing its ionization in a TIMS instrument. We employ either a MCN6000 desolvating nebulizer (CETAC) fitted with a PFA spray chamber or the ARIDUS 1 (PFA), fitted with a 50  $\mu$ l/min PFA micro nebulizer (Elemental Scientific Inc.) Typical sensitivity for our instrument is about 0.4 pA per ppb for  $^{238}\text{U}$ . Ionization efficiencies (the ratio of atoms detected to atoms introduced) for U, Th, and Pa are about a factor of 5–10 lower than those reported by TIMS. However, the routine precision in isotope ratios by MC-MS-ICPMS is comparable to the most precise measurements made by TIMS and the simplified sample injection and resulting increase in sample throughput present distinct advantages for the MC-MS-ICPMS technique. Fortunately in the case of corals, sample size is never a limitation.

The precise determination of isotopic ratios of U, Th, and Pa requires that mass fractionation (bias) and gain efficiency (calibration of the Daly detector) be known. Since the ion beam produced by a plasma source is relatively unstable, both fractionation and gain corrections must be made during the analyses. In order to make real-time corrections for mass bias, gain correction, and beam instability, we employ a multi-static routine for each U, Th, and Pa analysis. This approach is similar to that described in Luo et al. (1997) where it was demonstrated that multi-static routines yielded superior analytical precision for U and Th isotopic analyses. All measurements of the minor abundance isotopes ( $^{229}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{233}\text{Pa}$ ,  $^{233}\text{U}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ) are made with the Daly Detector and are accompanied by simultaneous measurement of  $^{238}\text{U}$  using one of the Faraday cups. Accurate gain corrections of the  $^{233}\text{U}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  isotope ratios require that the Daly detector operate without intensity biasing. Gain corrections of the  $^{229}\text{Th}/^{230}\text{Th}$ ,

$^{229}\text{Th}/^{232}\text{Th}$ , and  $^{233}\text{Pa}/^{231}\text{Pa}$  ratios are eliminated because the individual isotopes measured on the Daly detector are all normalized to  $^{238}\text{U}$ . Measurement precision of the U and Th isotope ratios (about 75 and 60 ratio measurements, respectively) are generally better than  $\pm 0.08\%$  and  $\pm 0.3\%$  (2 RSD) respectively. This translates to an average uncertainty of about 0.5% (2 RSD) of the age for the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ .

#### 2.5. Radiocarbon methods

At LLNLs subsamples of fossil corals are coarsely crushed, sonicated in Milli-Q water, the Milli-Q is decanted, the samples are dried, and weighed. An appropriate amount of 0.1 N HCl is added to the coral sample to remove 50–60% of the material (Yokoyama et al., 2000). Samples older than 30,000 yr receive a 60% leach. The neutralized acid and related salts are decanted, and the coral material is rinsed repeatedly with Milli-Q water and subsequently dried on a heating block. All radiocarbon samples older than 32,000 yr BP were ultrasonically cleaned in 30% hydrogen peroxide for seven days in order to oxidize any mold or other extraneous organic matter (including possible soil contamination) and analyzed at Leibniz-Labor for Radiometric Dating and Isotope Research at Christian-Albrechts University Kiel. In the Leibniz-Labor, the samples were subjected to a 60% leach with 1% HCl at room temperature overnight, followed by washing with Milli-Q water and a 15 min treatment with 15% hydrogen peroxide. The peroxide was siphoned off and the dampened samples were loaded directly into the vacuum extraction system to shield the sample from contamination with atmospheric  $\text{CO}_2$ .

At LLNL, approximately 20 mg samples, an appropriate amount to yield 1.0 mg-carbon targets, are placed in glass tubes and evacuated to  $1 \times 10^{-3}$  Torr with gentle heating. A 0.5 ml aliquot of 85% phosphoric acid is injected into the glass tubes, and the tubes are placed on a heating block at 90 °C. The  $\text{CO}_2$  that is released via this process is extracted through an offline manifold, cryogenically purified to remove water, and transferred into individual graphite reduction reactors. Similar to the procedure of Vogel et al. (1987), the  $\text{CO}_2$  is reduced to graphite at 570 °C in the presence of an iron catalyst and a stoichiometric excess of hydrogen. The graphite is then transferred and pressed into aluminum target holders for subsequent analysis by accelerator mass spectrometry.

At Leibniz-Labor, the procedure is largely the same as at LLNL (Nadeau et al., 2001), except that 100% phosphoric acid is used, and is evacuated separately during heating, and then vented with nitrogen. Carbonate and acid are then evacuated together, sealed in a glass ampoule and reacted overnight in a water bath at 90 °C. The reduction is done at 600 °C.



At LLNL, the prepared graphite targets are sputtered in a high-intensity cesium sputter source (Southon and Roberts, 2000) with an equivalent  $^{12}\text{C}^-$  current of 275–300  $\mu\text{A}$ , which yields 900–1000  $^{14}\text{C}$  counts/second on a modern carbon sample. After mass selection via the low energy injector magnet, the negative ion beam ( $^{13}\text{C}^-$  or  $^{14}\text{C}^-$  and molecular isobars) is injected into the accelerator (FN Tandem Van de Graaff at CAMS), passed through a stripper foil and, on exiting the accelerator, is magnetically and velocity filtered and subsequently measured in an off-axis Faraday cup ( $^{13}\text{C}^{4+}$ ) or analyzed in a gas ionization detector ( $^{14}\text{C}^{4+}$ ) (Davis et al., 1990). The CAMS ion source sample wheel has slots for up to 64 targets and normally about 50 unknown samples are loaded in a routine sample wheel. Each wheel load is composed of a suite of primary (OX1) and secondary (OX2, ANU, TIRI wood) standards and the unknown samples, and is broken into several groups. In general, a group is composed of two sub-groups containing 5–7 targets with intervening and bracketing primary standards. Samples are analyzed in such a fashion that a single group is completely analyzed prior to proceeding on to the next group. A group is analyzed repeatedly such that a suite of bracketing blanks, primary standards, and secondary standards are analyzed in conjunction with the unknown samples. A single group of unknowns is cycled through at least five times. During each cycle, an individual target is analyzed for either 30,000  $^{14}\text{C}$  events or 200 s, whichever comes first.

At LLNL, raw data ( $^{14}\text{C}/^{13}\text{C}$  ratios) are normalized to the average of the bracketing six primary standards for each pass through a sample group. Counting errors (primary standard and unknown) are propagated through the analysis and are assumed to be Gaussian (Bevington and Robinson, 1992). The average of the  $n$ -measurement-cycles of each unknown is then determined and for the initial error, the larger of the counting error or the external error of the  $n$ -cycles is chosen. CAMS  $^{14}\text{C}$  dates are based on  $^{14}\text{C}/^{13}\text{C}$  atom ratios, not decay counting to obtain specific  $^{14}\text{C}$  activities. The algorithms used at CAMS (Southon, unpublished) are similar to those developed at Arizona (Donahue et al., 1990). Radiocarbon age data are presented according to the conventions of Stuiver and Polach (1977) using the Libby half-life (5568 yr.). The  $\Delta^{14}\text{C}$  calculations are made based on the more recent  $^{14}\text{C}$  half-life of  $5730 \pm 40$  years (Godwin, 1962). Calculations include a background subtraction based on measurements of a fossil coral and inclusion of background error based on  $^{14}\text{C}$ -free calcite determined on multiple aliquots of acid leached calcite for each wheel of unknowns (cf. Brown and Southon, 1997).

Twenty-eight unleached aliquots of TIRI turbidite were analyzed with our LLNL AMS  $^{14}\text{C}$  measurements over a time span of 18 months. Individual analyses

ranged from 18090 to 18245 yr BP with reported one standard deviation errors between 30 and 50 years. The weighted average Fraction Modern of these 28 measurements shows a one standard deviation scatter of 0.00044 ( $\pm 35$  years). The weighted mean and weighted mean uncertainty (one-sigma) of the TIRI turbidite results are  $0.10378 \pm 0.00008$  ( $n = 24$ ) that equates to  $18,199 \pm 8$  years. The fractional error of these results indicates reproducibility of individual measurements at the 4 per mil (one sigma) level, which is consistent with the quoted counting statistics errors.

Samples older than 32,000 years were measured at the Leibniz-Labor for Radiometric Dating and Isotope Research at the Christian-Albrechts University Kiel (Nadeau et al., 1997, 1998). The model 846B HVEE cesium sputter ion source was run at moderate outputs around 30  $\mu\text{A}$  equivalent  $^{12}\text{C}^-$  beam for optimal stability, giving around 60 counts/s for a modern sample. The separator/recombinator selects masses 12, 13, and 14, attenuates mass 12 by a factor 100, and injects the three masses simultaneously into the HVEE 3 MV tandem accelerator at 2.5 MV.  $^{12}\text{C}^{+3}$  and  $^{13}\text{C}^{+3}$  are measured simultaneously in two off-center Faraday cups, and  $^{14}\text{C}^{+3}$ , after electrostatic deflection and a  $90^\circ$  magnet, in a gas ionization detector, yielding both  $^{14}\text{C}/^{12}\text{C}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios simultaneously. These ratios are largely insensitive to fluctuations in ion source output or transmission. The 846B wheel loads about 40 unknowns together with 8 OXII standards, backgrounds and reference materials spaced evenly between the unknowns. Stable and reproducible target preparation and measuring conditions make it possible to use the average of all OXII targets for comparison with the unknowns in each cycle. Comparison of the scatter statistics between cycles with Poisson statistics indicates Poisson statistics is the main cause of the measuring uncertainty (Nadeau et al., 1998). “Old” coral samples are used to provide the optimum background subtraction (Nadeau et al., 2001). The blank value for Araki coral AK-H-2 was  $0.1334 \pm 0.0114$  pMC (average of 5 targets). This scatter-based uncertainty is unusually small, so we adopted a more conservative and conventional value of 1/8 of the blank (0.0167) as its uncertainty. The  $^{230}\text{Th}/^{234}\text{U}$  age of AK-H-2 is 97,000 yr BP.

## 2.6. Barbados, Kiritimati and Araki reservoir age estimates

The radiocarbon content of tropical surface water is depleted in  $^{14}\text{C}$  compared to the atmosphere due to incomplete isotopic equilibration and mixing with subsurface waters of older ages. This  $^{14}\text{C}$  offset between surface water and atmosphere is known as the “reservoir age” and in recent times ranges between 300 and 500 years in the western tropical and subtropical regions

between 40N and 40S (Craig, 1957; Stuiver and Polach, 1977; Bard 1988). Fairbanks (1989) used a reservoir age of 400 years for Barbados radiocarbon ages based on an average of data for the western tropical Atlantic summarized in Bard (1988). In this paper, we compute the reservoir age for Barbados, Kiritimati, and Araki coral samples dated by  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  by subtracting the coral  $^{14}\text{C}$  ages from the tree ring radiocarbon calibration curve (Reimer et al., 2004). The results are plotted in Fig. 2. There is an advantage to computing an average reservoir age from data spread over the Holocene, rather than from only a few measurements of preindustrial ages. The application of a Holocene reservoir age to older time periods is only an assumption; however, by selecting sites in the western Atlantic and central and western Pacific, we have some assurance that surface waters at Barbados, Kiritimati, and Araki were not exposed to newly upwelled waters deficient in  $^{14}\text{C}$ . It is possible that large and rapid  $^{14}\text{C}$  concentration changes may have resulted in large transient increases in the difference between atmosphere and surface ocean waters that could last decades or even centuries. More importantly, the uncertainty in the reservoir age in samples older than the Holocene becomes less significant as the analytical age uncertainties in radiocarbon and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages increase with time. The computed reservoir ages are remarkably similar: Barbados =  $365 \pm 60$  years ( $n = 21$ ); Kiritimati =  $350 \pm 55$  years ( $n = 4$ ); and Araki =  $365 \pm 140$  years ( $n = 9$ ). Whereas additional measurements are needed to reduce the uncertainty of these reservoir ages, we believe that most of the variability is due to the high frequency fluctuations produced in the atmosphere that are attenuated in the surface ocean. In other words, the reported uncertainties in the reservoir ages do not reflect the natural variability in the local reservoir ages at these three sites (Appendix A).

### 2.7. Methodology of the radiocarbon calibration 0 to 50,000 yr BP

Our  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  radiocarbon calibration is intended as a stand-alone radiocarbon calibration that spans 0–50,000 yr BP and is based on our most stringent sample quality criteria. At this time, we see no benefit in amalgamating subsets of calibration points from other data sets based on the dramatic increase in scatter when we include data from other coral, varved-sediment, and speleothem calibration curves. Even the Cariaco (Hughen et al., 2000, 2004b) varved sequence seems to be offset between 13,300 and 14,000 yr BP compared to the floating tree ring chronology of Friedrich et al. (1999, 2001, 2004) and our coral data (Fig. 2). Most importantly, we believe that only calibration data points that have independent and quantifiable precision and accuracy error estimates for radiocarbon and calendar

ages are suitable for inclusion in any calibration curve. The pristine nature of our coral samples, data density, the fact that from 10,000 to 29,000 yr BP all of our samples have resided exclusively in the marine environment, our level of sample documentation, consistency of sample screening, handling, and analysis, and the precision of our measurements justify a stand-alone calibration curve that can be compared to many other independently determined curves. Sample selection criteria for inclusion in our calibration are more stringent than IntCal04 (Reimer et al., 2002, 2004) or Marine04 (Hughen et al., 2004) and are based on the sample quality Categories described above, and only samples that have been submerged in seawater are included unless subaerially exposed samples are the only available samples for a given time interval. Ultimately, we expect our calibration curve will include mostly samples submerged in seawater since growth, where coral aragonite is thermodynamically stable. Although we choose not to amalgamate our data with other calibration data in this paper, we are actively participating in combining our radiocarbon calibration data in international calibration efforts using a subset of our samples younger than 26,000 yr BP (Reimer et al., 2004; Hughen et al., 2004b) and in ice core age model development and  $\Delta^{14}\text{C}$  reconstructions combining our older samples with data from other groups (e.g., Shackleton et al., 2004).

One can make the argument that the calibration of a radiocarbon age is only as good as the precision, accuracy, and proximity of the pair(s) of coral calibration data points that bracket the radiocarbon date, because all errors are independent. The prime disadvantage of this simple approach is that errors in the calibration data occur in both calendar ( $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ) and radiocarbon measurements, and therefore, it is not a simple matter to rigorously estimate the error bars on the calibrated radiocarbon ages. The tree ring calibration routine (Stuiver et al., 1998b) and INTCAL98 (Stuiver et al., 1998a) assume that there is no error in tree ring calendar ages or coral  $^{230}\text{Th}/^{234}\text{U}$  ages, so they obviate this problem entirely, regardless of whether an 11,900 composite tree ring calibration or corals have calendar age uncertainties. More recently, IntCal04 (Reimer et al., 2004) and Marine04 (Hughen et al., 2004) calibration curves have adopted a more rigorous treatment of errors in radiocarbon and calendar years (Buck and Blackwell, 2004).

A statistically more rigorous treatment of error estimates in the calibration curve (in both calendar years and radiocarbon years) and the means to convert radiocarbon ages and errors to calendar years requires a statistical model of moderate complexity. In the following section, we present a statistical model that permits rigorous error treatment in radiocarbon ages calibrated using our coral data set. We provide a radiocarbon

calibration program on our web site <http://www.radiocarbon.LDEO.columbia.edu/> where our calibration curve can be accessed and where updates will be released. Our coral data sets and documentation are also archived at this web site.

## 2.8. Calibration procedure with error estimation based on a hierarchical bayesian statistical model

### 2.8.1. Calibration approach

Our main premise is that there exists a precise, deterministic functional relationship between the calendar age  $x$  and the radiocarbon age  $y$

$$y = f(x).$$

This relationship is not known exactly, but it is assumed to be applicable to the true (unaffected by measurement errors)  $x$  and  $y$  of samples. Were  $f$  known, the calendar age  $x$  of a sample with the measured radiocarbon age  $y$  could be found by the inversion  $x = f^{-1}(y)$  (possibly

with multiple values, because  $f$  is not necessarily monotonous). Error bars or a given error distribution for  $y$  could be converted easily to those for  $x$  as well.

Because the precise form of  $y = f(x)$  is not known, we attempt to develop its statistical description. The complete description would be a joint probability density of values  $f(x)$  for all  $x$ 's. However, here we only consider a problem of a single-sample calibration (as opposed to sets of samples with a priori information on their time sequence, e.g., Buck et al., 1996; Steier et al., 2001; Bronk Ramsey, 2001); hence, it will suffice to obtain marginal distributions for individual values of  $x$ . More precisely, we will only compute the function  $p_c(y, x) = p(y|x)$ , that for each given  $x$  expresses the density of probability with which  $f(x)$  may take value  $y$  (shown by colors in Fig. 4). Indeed, when this probability distribution is available, Bayes' formula provides an easy way to compute the distribution of the calendar age for an individual sample, given the measurement of its radiocarbon age  $y_m$  and the

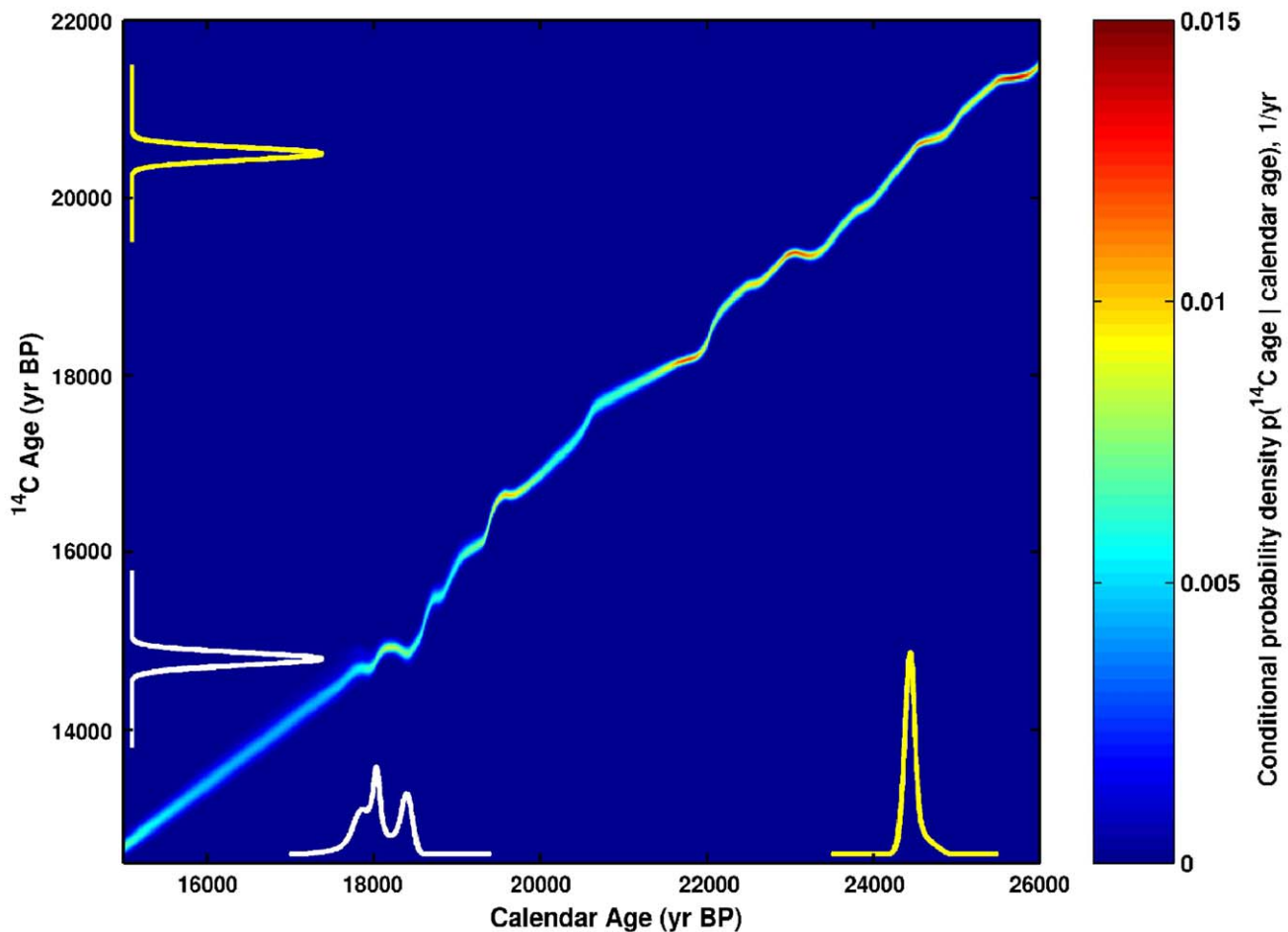


Fig. 4. Plot is an example of the conditional probability density function for <sup>14</sup>C age given the calendar age for the calendar interval between 15,000 and 26,000 yr BP. Two examples of radiocarbon age inputs and calendar year output estimates illustrate a simple unimodal conversion case (yellow line) and an example where the calibration curve has a fluctuation producing a broad uncertainty and bimodality in estimated calendar age (white line). White and yellow curves show probability density functions in 1/yr, so their values are not in the scale of the color plot axes. The areas under all probability density curves are equal to 1. (See Appendix Table 1 in the online version of this article for detailed statistics).

Table 1  
Typical examples of radiocarbon age conversion to calendar years using our calibration curve (Fig. 4)

	Mean	Median	Std
<b>Example 1</b>			
Radiocarbon age (raw) input:	14,800	14,800	70
Calendar age output:	18,114	18,090	257
	Mean	Median	Std interval
<b>Example 2</b>			
Radiocarbon age (raw) input:	20,500	20,500	70
Calendar age output:	24,533	24,510	116

distribution of the measurement error (Dehling and Van der Plicht, 1993):

$$p(x|y_m) = \frac{p(y_m|x)p_a(x)}{\int p(y_m|x)p_a(x) dx} \propto p(y_m|x)p_a(x), \quad (1)$$

where  $p_a$  is the assumed prior distribution of the sample's calendar age (before the radiocarbon age measurement became known), e.g., a uniform distribution on the entire calibration period. It follows that,

$$\begin{aligned} p(y_m|x) &= \int p(y_m|y)p(y|x) dy \\ &= \int q(y_m - y)p_c(y, x) dy, \end{aligned} \quad (2)$$

where  $q$  is the probability density function of the radiocarbon age measurement error. Inserting (2) into (1) obtain

$$p(x|y_m) \propto p_a(x) \int q(y_m - y)p_c(y, x) dy, \quad (3)$$

Fig. 4 shows examples of this conversion for the radiocarbon ages 14.8 K (white lines) and 20.5 K (yellow lines) when the radiocarbon age measurement error is assumed normally distributed with the standard deviation of 70 years (See Appendix Table 1 in the online version of this article for the statistics of the resulting distributions). Note the bimodal distribution of the calendar age produced by formula (3) in the former case, due to the non-monotonous behavior of the calibration curve.

### 2.8.2. General methodology

We use the hierarchical Bayesian modeling to estimate the conditional probability distribution function  $p_c(y, c) = p(y|x)$ . This uses two different stages to account for uncertainties in observations of  $x$  and  $y$ . The first stage computes the distribution  $p(y|x)$  for a given set of samples on the basis of a given uncertainty in their radiocarbon ages under assumption of no error in their calendar ages. This stage uses least-squares estimation approach with an additional weak constraint on the local slope of the calibration curve. The solution

at this stage is similar to the linear smoothing spline approximation (Wahba, 1990) or “random-walk” calibration approaches (Gómez Portugal Aguilar et al., 2002). The second stage of the hierarchical modeling uses the Monte Carlo approach for simulating the observational uncertainty in calendar ages of all samples: each member of this ensemble has its own realization of calendar ages for all samples, so the computation of the first stage is repeated for each ensemble member, and the corresponding marginal distribution  $p(y|x)$  for each member is produced. The final solution is obtained by averaging the marginal distributions  $p(y|x)$  over all members of the entire Monte Carlo ensemble.

### 2.8.3. Implementation details

In the practical implementation of this procedure, the grids of  $x$  and  $y$  were discretized for the 10 year resolution. The original multiple measurements of  $x$  and  $y$  were reduced to a single pair of  $x$  and  $y$  for each sample using an optimal averaging procedure. A  $\chi^2$ -based quality control procedure was used to prune out samples with inconsistent individual measurements, reducing the total number of samples from 154 to 152. Further consistency checks resulted in the uniform inflation of all measurement error estimates by the factors of 1.8 and 1.3 for the calendar and radiocarbon standardized errors respectively. An analysis of linear interpolation lines computed for a preliminary Monte Carlo ensemble (size 1000) of the entire set of 152 data points perturbed by simulated measurement errors was used to derive a priori estimates necessary for our procedure: expected slope changes from point to point, slope uncertainty (assumed normal with 0.8 yr/yr standardized deviation), and the age variability inside 10 year grids. The Monte Carlo ensemble of 4000 was used for obtaining the final solution (Figs. 3 and 4).

### 2.8.4. Description of the calibration curve

The offset between radiocarbon years and calendar years increases from the present to approximately 38,500 calendar years BP reaching more than 6000 years difference. From 38,500 calendar years BP to 50,000 calendar years BP the trend reverses and radiocarbon ages grow slightly closer to calendar ages (Fig. 3). By 50,000 calendar years BP, the corresponding radiocarbon age is younger by approximately 3700 years. The departure of the calibration curve from the one to one line ( $\Delta^{14}\text{C}$ ) contains fundamental information on solar output (Damon et al., 1978; Stuiver and Quay, 1980), the carbon cycle (Edwards et al., 1993; Hughen et al., 1998; Hughen et al., 2000), and the Earth's geomagnetic field (Bard et al., 1990; Beck et al., 2001). The overall shape of our calibration curve corresponds to the broad scale changes in the Earth's geomagnetic field intensity, but the magnitude of the

radiocarbon and calendar year offset is apparently too large to be explained by magnetic field intensity changes alone (Beck et al., 2001; Hughen et al., 2004a). Box model calculations of the radiocarbon production history computed as a function of estimated changes in the Earth's geomagnetic field intensity (Laj et al., 2000, 2004) show a sharp increase between 50,000 and 40,000 yr BP, followed by a gradual decrease between 35,000 yr BP and the present. The sharp decrease between 50,000 and 40,000 yr BP corresponds to the transition between Earth's field strength comparable to today's to the peak of the Laschamp geomagnetic excursion when Earth's geomagnetic field intensity nearly collapsed. Measurements of  $^{10}\text{Be}$  and  $^{36}\text{Cl}$  spikes in ice cores mark the Laschamp cosmogenic isotope production signal in the atmosphere (Beer et al., 1988). However, due to the brevity of the Laschamp excursion and the attenuation of the atmospheric  $^{14}\text{C}$  anomaly through ocean mixing, there is no dramatic radiocarbon age anomaly corresponding to the peak Laschamp event.

A possible additional explanation for the growing offset between radiocarbon years and calendar years is an inaccurate radiocarbon decay constant (Godwin, 1962). In general, higher precision and higher accuracy radioisotope data measured by mass spectrometry techniques have outgrown the lower precision and lower accuracy decay constants measured many decades ago by decay-counting methods (Renne et al., 1998; Cheng et al., 2000). A more accurate and precise measurement of the radiocarbon decay constant is required before we can quantify the role of the sun, carbon cycle, and the geomagnetic field in distorting the radiocarbon timescale. If the measured offset between radiocarbon years and calendar years were explained by Earth's geomagnetic field intensity alone, it requires a decrease in the radiocarbon decay constant by several percent below the adopted value (Godwin, 1962).

### 3. Conclusions

Paired radiocarbon and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age determinations on pristine corals provide a high precision, high accuracy radiocarbon calibration curve suitable for general use beyond the limits of the superior tree ring calibration curve (Stuiver et al., 1998a; Reimer et al., 2004). Results presented in this paper overlap with the existing tree ring calibration curve and extend the calibration to 50,000 yr BP. Our calibration curve can be used to convert radiocarbon ages to calendar ages with an online conversion program <http://www.radiocarbon.LDEO.columbia.edu/> that includes a rigorous error estimation.

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### Appendix A. Electronic Supplementary Material

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.quascirev.2005.04.007](https://doi.org/10.1016/j.quascirev.2005.04.007).

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