

# Extending the radiocarbon calibration beyond 26,000 years before present using fossil corals

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Received 10 January 2005; accepted 1 April 2005

## Abstract

Fossil coral is an excellent archive to extend the radiocarbon ( $^{14}\text{C}$ ) calibration beyond tree-ring records; however, published coral data older than 26,000 years before present are too disparate for practical calibration. We propose an explanation for these discrepancies: trace amounts of secondary calcite and organic matter in fossil corals shift the  $^{14}\text{C}$  ages toward younger ages. In a series of acid-leaching experiments to simulate the standard cleaning procedure prior to  $^{14}\text{C}$  analysis, we measure up to a 300% enrichment of diagenetic calcite in corals due to the solubility differences between calcite and aragonite. In model calculations, we show the  $^{14}\text{C}$  age offsets produced by acid leaching could be hundreds to thousands of years when typical amounts of calcite are present in samples. We demonstrate the necessity and our ability to detect  $<0.2\%$  calcite in aragonite by X-ray diffraction and apply “ $<0.2\%$  calcite” as our a priori criterion for our coral samples. The estimated age offsets of samples with  $<0.2\%$  calcite fall within the reported analytical uncertainty of  $^{14}\text{C}$  dating. In addition, we present  $^{14}\text{C}$  results from an extended hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) pretreatment for coral samples to remove organic matter. Our data show that treated samples yield consistent or older  $^{14}\text{C}$  dates compared to non-treated samples. These rigorous but necessary screening and cleaning techniques provide precise, reproducible and accurate radiocarbon calibration data.

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## 1. Introduction

The importance of the radiocarbon ( $^{14}\text{C}$ ) chronometer for age determinations in the fields of geology, paleoceanography, climate studies and archeology is well documented (Stuiver et al., 1986). The reported  $^{14}\text{C}$  ages, however, are not accurate because the initial activity of  $^{14}\text{C}$  in the atmosphere is not constant with time, and thus a basic principle of radioactive dating cannot be applied (de Vries, 1958; Suess, 1970; Damon et al., 1978). The atmospheric  $^{14}\text{C}$  concentration, and hence a sample's initial  $^{14}\text{C}$  activity, varies with solar activity (Stuiver, 1961; Stuiver and Quay, 1980), shielding effect from the Earth's geomagnetic field

(Elsasser et al., 1956; Lal, 1988; Bard et al., 1990a; Guyodo and Valet, 1999; Laj et al., 2000, 2002, 2004) and to a lesser degree carbon cycling (Edwards et al., 1993; Hughen et al., 2000).

Conversion of reported  $^{14}\text{C}$  ages to calendar ages requires a calibration data set and a statistical model to compute calendar age and uncertainty. Tree rings have been the most useful calibration archive up to  $\sim 11,500$  years before present (BP), but older samples are not easily obtained (Stuiver et al., 1998). Fossil corals are regarded as one of the best candidates for extending the radiocarbon calibration (Bard et al., 1990a) beyond the tree-ring records (Stuiver et al., 1998) because corals can be directly dated by both  $^{14}\text{C}$  and  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  methods with minimal assumptions and does not involve correlations to other climatic proxies (Bard et al., 1990a, 1993; Burr et al., 1998; Cutler et al., 2004;

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Paterne et al., 2004; Fairbanks et al., 2005). In addition, measured radiometric ages of corals have computed error estimates, which is not the case for most other archives used for extending radiocarbon calibration. Coral dates are completely independent to one another and so are their error estimates, unlike radiocarbon calibrations based on laminated sediments (Hughen et al., 1998; Goslar et al., 2000; Kitagawa and van der Plicht, 2000) and interpolated ages based on assumed sedimentation rates and correlations to other climatic proxy records measured in ice cores (Hughen et al., 2000, 2004; Voelker et al., 2000) in which correlation uncertainty and accumulated errors may be unavoidable. Additionally, it is critical to keep the ice core record of atmospheric changes, especially the atmospheric gas chemistry, independently dated from the radiocarbon calibration curve in order to be able to measure leads and lags between radiocarbon-dated records and ice core records. Although speleothems can also be independently dated by U-series and  $^{14}\text{C}$  methods with high precision, the assumed initial  $^{230}\text{Th}$  and dead carbon fraction (Beck et al., 2001) introduce some additional uncertainties and these two components may vary with time (Reimer et al., 2002). In order to compute the estimated calendar age error on a radiocarbon age conversion to calendar ages, it is necessary that the calendar and  $^{14}\text{C}$  age errors for the calibration curve are precisely measured (Fairbanks et al., 2005).

Published coral data display significant scatter beyond 26,000 years BP (Yokoyama et al., 2000) (Fig. 1). These corals were exposed to sub-aerial conditions due to island uplift and during the glacial lowstand, and are reported to contain between 0% and 3% diagenetic

calcite (Yokoyama et al., 2000). The IntCal04 workshop recommends using a limit of  $\leq 1\%$  calcite for inclusion in the radiocarbon calibration curve (Reimer et al., 2002) based on typical detection limits reported in the literature. Edwards et al. (1997) proposed  $^{231}\text{Pa}/^{235}\text{U}$  dating of coral samples as a rigorous test of the accuracy of the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age. This redundant dating technique has been applied to fossil coral and used for radiocarbon calibration in the age range of 12–50 kyr (Cutler et al., 2004; Mortlock et al., 2005). However, the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{231}\text{Pa}/^{235}\text{U}$  concordancy test confirms the accuracy of the calendar age but not the radiocarbon age. The observation that the majority of calibration data (Yokoyama et al., 2000) (Fig. 1) show considerable scatter and fall toward much younger radiocarbon ages suggests a source of contamination, possibly from inadequate screening criteria and/or cleaning prior to  $^{14}\text{C}$  dating. In this study, we provide paired  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  and  $^{14}\text{C}$  measurements and experimental evidence from chemically etched coral samples which suggest that the observed scatter in the published coral data in the period of 30–50 ka likely results from the presence of minor amounts of diagenetic calcite and potentially organic contamination in fossil corals. We further demonstrate that more stringent screening of diagenetic calcite (less than 0.2 wt%) can be achieved and is required.

Diagenetic calcite measured in corals is most likely precipitated from percolating rainwater during periods of lower sea level or due to island uplift, although the exact time history may not be well known. Although some authors have adopted acceptable concentrations of calcite in the range of 1–3% in fossil corals (Table 1), any calcite precipitated in coral is secondary and has the potential for producing coral  $^{14}\text{C}$  ages significantly younger than the “true radiocarbon age”. We suggest that relatively small amounts of diagenetic calcite become a more serious radiocarbon contaminant during the routine etching step just prior to graphite target preparation for accelerator mass spectrometry analysis for  $^{14}\text{C}$ . Standard practices in radiocarbon laboratories call for a 50–60% acid etch of coral samples just prior to dissolution of coral samples for the graphite target preparation (Bard et al., 1990b, 1993; Burr et al., 1992; Edwards et al., 1993; Yokoyama et al., 2000). The pretreatment is believed necessary for removing surface contamination and absorbed modern carbon. Burr et al.’s (1992) partial dissolution experiments were conducted on two samples older than 50 ka, both of which had detectable calcite in excess of 2 wt%. It was observed that a significant fraction of the radiocarbon was found in the initial 10% fraction dissolved and that background levels of radiocarbon could only be obtained when more than 50% of the original sample had been dissolved. Yokoyama et al. (2000) determined that coral samples reached a  $^{14}\text{C}$  age “plateau” after

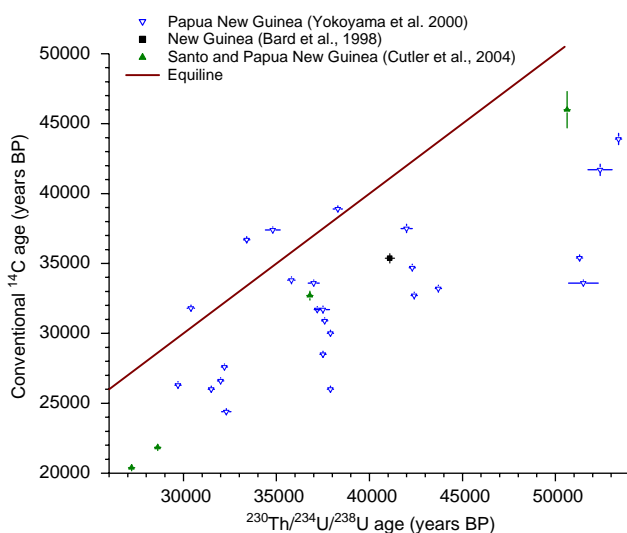


Fig. 1. Published radiocarbon and U-series ages for fossil corals older than 30,000 years BP (Bard et al., 1998; Yokoyama et al., 2000; Cutler et al., 2004). The equiline is presented only for reference. Samples in this figure are reported to contain diagenetic calcite concentrations in the range of 0–3%.

Table 1

Examples of the calcite contamination acceptance criteria in fossil corals selected for radiocarbon dating in the age range of 26,000–50,000 years BP (calendar year)

Sample locality	Reference source	Acceptance % calcite in corals
Papua New Guinea	Yokoyama et al. (2000)	<3
N/A	Reimer et al. (2002)	<1 suggested (IntCal04 workshop)
Barbados, Kiritimati, Santo and Araki Island	This study and Fairbanks et al. (2005)	<0.2
Vanuatu and Papua New Guinea	Cutler et al. (2004)	<1

50% leaching and concluded that most contamination had been eliminated.

Aragonite is more soluble than calcite (Chave et al., 1962; Milliman, 1974a), therefore chemical leaching could potentially have the adverse effect of enriching the mass fraction of calcite in coral, which would result in biasing radiocarbon results toward younger ages.

Organics are another source of contamination and are particularly common in corals from outcrop samples exposed to soils or from mold colonization during sample transit and storage. We observe that typical outcrop samples continue to whiten after several days of hydrogen peroxide ( $H_2O_2$ ) treatment in an ultrasonic bath that we attribute to continued oxidation of organic matter. The potential for using fossil coral to accurately extend radiocarbon calibration beyond 26,000 years BP ultimately relies on both selecting fossil corals of only the best preservation (i.e. no detectable calcite) and aggressive pretreatment methods that effectively remove resistant organic carbon.

We propose a two-step procedure before  $^{14}C$  dating a coral sample, a prior X-ray diffraction (XRD) screening and an extended hydrogen peroxide cleaning, to circumvent these problems. (1) We apply “<0.2% calcite” by XRD analysis as the screening criterion for fossil corals. (2) Sub-samples of fossil corals that pass “<0.2% calcite” criterion are subjected to an extended hydrogen peroxide pretreatment to remove any potential organic matter. Dry-down steps of samples after this pretreatment are eliminated to avoid any mineral precipitation. Additional leaching (50–60%) and a final hydrogen peroxide treatment are recommended immediately prior to preparation of graphite targets in  $^{14}C$  laboratories (Nadeau et al., 2001)

## 2. Methods

### 2.1. X-ray diffraction standards and samples

A pure aragonite end member was prepared from a modern coral specimen (*Acropora hyacinthus*) collected from Kiritimati Island in 1997. A pure calcite end member was prepared from NBS-19 marble. Aragonite and calcite end members were ground in an agate mortar separately, and then they were combined and

homogenized in an agate mortar to make a series of XRD standards. XRD slides were made by mounting the well-mixed standard powders on microscope glass covers (1 in diameter) using a mixture of one part of DucoCement diluted with 10 parts of acetone. Slides made with diluted DucoCement give comparable counts to conventional water-mounted slides but DucoCement slides can be stored indefinitely, allowing use of the same standard slides over time to establish instrument reproducibility. In order to obtain reproducible results, it is necessary to produce slides of relatively uniform thickness, grain size, and of sufficient mass to obtain optimal intensity. We determined that a standard or sample mass of  $\sim 8$  mg was required to yield a peak height value of  $\sim 2000$  counts/s which we determined to be the minimum intensity for the aragonite major peak. The standard powder is blended into the DucoCement/acetone mixture and evenly smeared onto a 1-in glass cover slide (Fisherbrand Microscope Cover Glass: 12-546-2 25CIR-2) to cover 90% of the central area. The slide dries rapidly and should take on an opaque appearance. Nine XRD standards with various calcite concentrations (weight percentage: 0%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 1.0%, 1.5% and 2.0%) were prepared and were routinely measured with each set of coral samples.

Corals were submerged in deionized water and sampled using a 5 mm ID diamond corer in order to avoid formation of calcite that is produced by dry drilling (Gill et al., 1995). The sub-sample was placed in deionized water and cleaned in a high power ultrasonic bath (Fisher Model 500 Sonic Probe) for 2 h. Samples were dried at  $T = 60^\circ C$ , and then were crushed and ground in an agate mortar to an ultra-fine powder. Sample slides were prepared from powdered samples in the same manner as the standards. Test shows that no calcite was produced from aragonite during the coring or grinding step in the method described here.

### 2.2. X-ray diffraction instrumentation

XRD analyses were performed using a Philips X'pert X-ray Diffractometer (PW3040-MPD) located at the Lamont-Doherty Earth Observatory (LDEO). This instrument is equipped with a  $\theta$ - $\theta$  goniometer and a computer-controlled,  $\theta$ -compensating, variable-beam,

slit system that allows a constant sample surface to be irradiated at all  $2-\theta$  angles during the diffraction scan. Aragonite and calcite were measured at the major peaks  $3.396\text{\AA}$ [111] and  $3.035\text{\AA}$ [104], respectively. Instrument “dwell times” and “ $2-\theta$  step size” were selected to optimize sensitivity and detection limits. Instrument settings permitting sufficient resolution of the calcite peak at  $<0.2\%$  calcite in aragonite require a dwell time of 1 s and a  $2-\theta$  step size of 0.02. These settings produce an analysis time of  $\sim 5$  min for each slide and permit analysis of  $\sim 7$  samples/h. In an attempt to improve detection limits, we explored other combinations of “dwell time” and “ $2-\theta$  step size”. We found that a combination of a dwell time of 2 s and a  $2-\theta$  step size of 0.01 ( $\sim 20$  min analysis time) produced aragonite peaks with greater definition but no better resolution of the calcite peak. We also investigated and rejected the combination of a dwell time of 1 s and a  $2-\theta$  step size of 0.01 (analysis time of  $\sim 10$  min) because standards displayed increased scatter with these settings.

The relative intensity of each component during XRD analysis is generally proportional to its amount in the powder mixture. Relative intensities were calculated by peak heights in this study although peak areas can also be used. We compared the relationship between weight percentage of calcite versus the peak height ratio of (calcite)/(calcite + aragonite) (Milliman, 1974b) for our XRD standards. The XRD standard data can best be described by a regression line: (calcite)/(calcite + aragonite) =  $0.0394 \times (\% \text{ calcite}) + 0.0033$  ( $R^2 = 0.9907$ ) (Fig. 2) based on the pooled mean of our nine XRD standards. We estimated our analytical limits of detection at 0.11% calcite by calculating the  $3\sigma$  uncertainty about our “0%” calcite standard. However, during the course of this study, the calcite peak of a 0.1% standard

slide may or may not be identified during the scan, and therefore “ $<0.2\%$  calcite” was conservatively selected as our detection limit.

### 2.3. Radiocarbon and uranium-series dating methods

Radiocarbon dates of coral samples in this study were measured either at the Center of Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory, University of California or at the Leibniz Laboratory for Dating and Isotope Analyses, Christian-Albrechts-Universität, Kiel, Germany. The target preparation methods, including sample pretreatment steps, are detailed elsewhere (Fairbanks et al., 2005). All uranium-series dates of coral samples in this study were obtained by using a multiple-collector ICPMS (PLASMA 54) at LDEO (Mortlock et al., 2005). Our entire coral data set and radiocarbon calibration (0–50,000 years BP) are presented in detail elsewhere (Fairbanks et al., 2005).

## 3. Results

### 3.1. Chemical leach

We test the hypothesis that standard chemical leaching procedures used by radiocarbon labs preferentially increase the fraction of diagenetic calcite in fossil corals. Leaching experiments were conducted on a calcite-bearing fossil coral sample ( $\sim 48,000$  years BP) determined to have a variable calcite content in the range of 0.5–2.7%. We replicated the leach pretreatment of coral samples used at CAMS at Lawrence Livermore National Lab by preparing an acid solution consisting of one part of 1 N HCl and three parts of 30%  $\text{H}_2\text{O}_2$  to yield a final normality of  $\sim 0.25$  N.

In one experiment, samples were divided in two parts with one-half subjected to a predetermined volume of the acid solution sufficient to dissolve approximately 20%, 40%, 60% and 80% of the original sample mass. Samples were weighed and then allowed to dissolve overnight after which they were rinsed with deionized water three times, dried at  $T = 60^\circ\text{C}$ , and re-weighed. All samples, treated and untreated were subsequently crushed in an agate mortar and prepared for XRD analysis (Table 2). In three out of four cases, the weight fraction of calcite increased in samples subjected to acid leaching (a factor of 1.3–3.4) when compared to the untreated sample half.

In the second experiment, the amount of acid necessary to dissolve 60% of the original sample mass was added. In four out of five cases, the weight fraction of calcite increased by a factor of 1.6–3.1 in the acid-treated samples (Table 2). Our experimental results suggest that pretreatment steps designed to remove

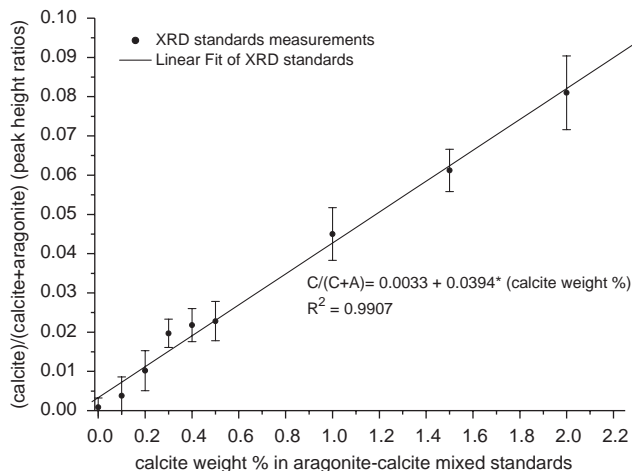


Fig. 2. Standards calibration curve of % calcite in aragonite by X-ray diffraction. (Calcite)/(calcite + aragonite) ratios were calculated by peak height. Error bars represent the  $1\sigma$  standard deviation about the mean value (minimum of eight replicates). Detection limit is smaller than 0.2% calcite (see text for details).

Table 2  
Enrichment of secondary calcite in Araki coral AK-D-2 during acid leaching

Sub-sample #	% Calcite (untreated)	% Weight loss	% Calcite (treated)	Calcite enrichment factor
AK-D-2 #1	0.9	19	2.4	2.7
AK-D-2 #2	1.3	38	1.7	1.3
AK-D-2 #3	0.5	54	1.6	3.4
AK-D-2 #4	1.4	70	0.5	0.3
AK-D-2 #5	2.0	54	3.2	1.6
AK-D-2 #6	0.5	56	1.0	2.0
AK-D-2 #7	0.6	56	1.3	2.3
AK-D-2 #8	0.7	56	2.3	3.1
AK-D-2 #9	2.7	56	1.4	0.5

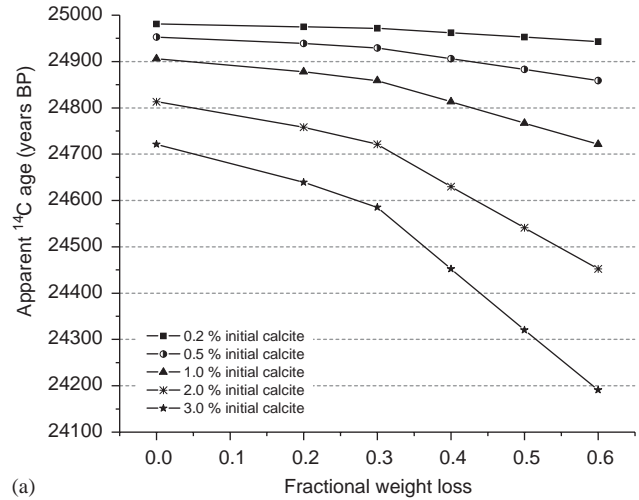
Note: Sub-samples (#1–#9) represent replicate drilled cores (5 mm ID diamond corer operated with the slab submerged in deionized water). Treated samples were leached with a mixed acid of ~0.25 N HCl/ ~22% H<sub>2</sub>O<sub>2</sub>.

contaminant radiocarbon are likely to enrich the mass fraction of secondary carbonate. We speculate that the cause of variable enrichments may be due to heterogeneous calcite contamination observed microscopically and variations in the skeletal microstructure.

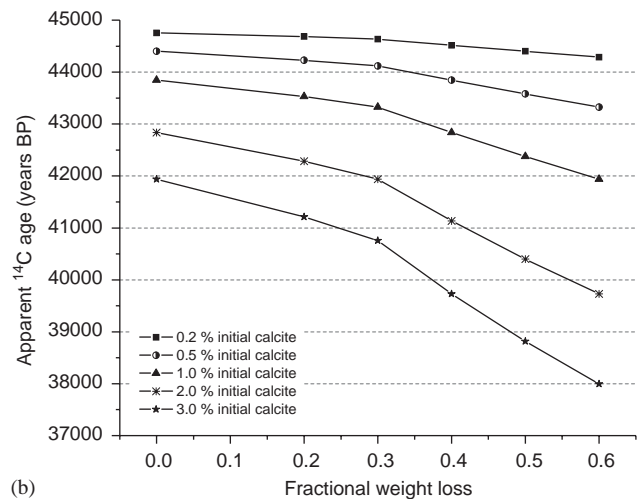
### 3.2. Modeling <sup>14</sup>C age offsets

In an attempt to quantify the effect of secondary calcite on the reported <sup>14</sup>C age of fossil corals and the sensitivity of calculated <sup>14</sup>C ages to a hypothetical chemical pretreatment, we applied a calcite addition model and calculated the apparent <sup>14</sup>C age for two scenarios. In the first scenario, we assumed a true <sup>14</sup>C age of 25,000 years BP and that calcite was added from 25,000 to 12,500 years BP (<sup>14</sup>C year) (Fig. 3a). The duration of calcite addition simulates the expected duration of sub-aerial exposure for samples of this age as determined from the Barbados sea level record (Fairbanks, 1989). We also assumed secondary calcite has been added continuously into the coral during exposure and that the average <sup>14</sup>C age of the calcite is 18,750 years BP. This assumption is based on the progressive alteration of fossil corals sampled from progressively older reef tracts (Mesoellea et al., 1969; Bloom et al., 1974). For the simplicity of the model, we assume the less soluble calcite (Chave et al., 1962) is resistant to acid and only primary aragonite dissolves during a hypothetical pretreatment step prior to <sup>14</sup>C dating. Finally, we assume the case that the calcite content is enriched by a factor of three (based on a worst case in Table 2) after leaching to 60% weight loss, and assign an enrichment factor to each fractional weight loss to simulate the effect of leaching.

The model output results in a series of calculated ages based on the initial amount of calcite (before leaching)



(a)



(b)

Fig. 3. (a) Apparent <sup>14</sup>C age as a function of fractional weight loss and initial calcite percentage in a hypothetical fossil coral. The “true” <sup>14</sup>C age in each example is assumed to be 25,000 years BP. We assume the calcite is added from 25,000 to 12,500 radiocarbon years BP and the mean age of the added calcite is 18,750 radiocarbon years BP. Calcite enrichment factor was assigned based on a worst case in our leaching experiment. In each hypothetical sample, the effect of 60% weight loss by chemical leaching is assumed to enrich the initial fraction of calcite by a factor of three. Only samples with <0.2% calcite have apparent <sup>14</sup>C ages that would be equal to the true ages (i.e. within 1σ analytical error) in a 50–60% weight loss scenario. (b) Apparent <sup>14</sup>C age as a function of fractional weight loss and initial calcite percentage in a hypothetical fossil coral. The “true” <sup>14</sup>C age in each example is assumed to be 45,000 years BP. In this scenario, we assume the reef was uplifted at 45,000 years BP and has been sub-aerially exposed to the present. Calcite has been added since the time of uplift and the mean age of the added calcite is 22,500 radiocarbon years BP. Calcite enrichment factor was assigned based on a worst case in our leaching experiment. In each hypothetical sample, the effect of 60% weight loss by chemical leaching is assumed to enrich the initial fraction of calcite by a factor of three. Note only samples with <0.2% calcite have <sup>14</sup>C apparent ages that would be equal to the true ages (i.e. within 1σ analytical error) in a 50–60% weight loss scenario.

in the coral and the weight fraction chemically leached. In the model case of a sample with a calcite concentration of 1% that is dissolved to 50% of the original mass

during the pretreatment, the measured age is >200 years younger than the true  $^{14}\text{C}$  age of the coral; for a sample having 3% initial calcite, the apparent  $^{14}\text{C}$  age can be ~700 years younger for the same 50% weight loss (Fig. 3a).

In a second calcite addition model, we adopt the same assumptions and enrichment factors above but consider a coral with a true  $^{14}\text{C}$  age of 45,000 years BP and which has had secondary calcite continuously added to the present time. The average  $^{14}\text{C}$  age of the added calcite is 22,500 years BP in this scenario (Fig. 3b). In the second model, a sample with a calcite concentration of 1% and dissolved to 50% of the original mass during pretreatment acquires a measured age ~2500 years younger than the true  $^{14}\text{C}$  age of the coral. Greater than 2500-year offsets in  $^{14}\text{C}$  ages are consistent with the outliers displayed in the range of 40,000–50,000 years BP of the published coral data (Fig. 1). A sample having 0.2% initial calcite acquires an apparent  $^{14}\text{C}$  age that is ~600 years younger after 50% weight loss in this particular scenario. Though a 600-year offset can reasonably be considered to fall within the analytical error of radiocarbon dating for an ~45,000 years BP sample, we conclude that only fossil corals determined to have less than “0.2% calcite” can be considered for accurate radiocarbon calibration (Fairbanks et al., 2005).

We did not obtain radiocarbon ages for the samples which were enriched in calcite during our etching experiments (Table 2), but we do have radiocarbon measurements on samples contaminated with varying amounts of secondary calcite. The results from previously cited dissolution experiments (Burr et al., 1992; Yokoyama et al., 2000), in fact, appear to contradict our model predictions. In both of those studies chemical etching of up to 50% in calcite-bearing fossil corals resulted in radiocarbon ages that were older than that of the bulk sample. In Yokoyama (2000), radiocarbon dating of progressively dissolved aliquots (following 50% etching) yielded  $^{14}\text{C}$  ages that agreed within analytical uncertainty. How and where secondary calcite precipitates within the coral aragonite matrix probably determines its susceptibility to selective dissolution. In the Yokoyama et al. (2000) study, secondary calcite was found to fill coralline voids and attempts were then made to mechanically remove the phase. That the 0–30% dissolved fraction yielded younger radiocarbon ages suggests other sources of  $^{14}\text{C}$  contamination. Younger or modern carbon may contaminate fossil coral as either an organic or inorganic phase. An acid leach (as phosphoric or HCl) would likely be very effective in removing any surface bound contaminants. However, depending on the specifics of the chemical etch, progressive leaching beyond 30% dissolution may or may not produce uniform dissolution of calcite and aragonite,

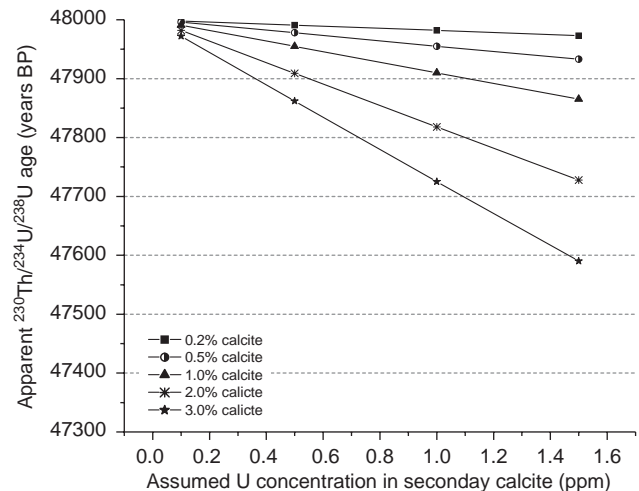


Fig. 4. Apparent  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  age as a function of the assumed U content of secondary calcite and the calcite percentage in a hypothetical fossil coral. The true age of the primary aragonite is assumed to be ~48,000 years BP (calendar age), and the average age of the calcite is assumed to be ~24,000 years BP (calendar age). The largest calculated age offset predicted by the 0.2% calcite scenario is about 30 years. Note we do not acid-leach fossil corals for  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  dated sub-samples and so there is no calcite enrichment issue.

Unlike  $^{14}\text{C}$  ages, the accuracies of corresponding U-series dates are presumably not sensitive to low levels of diagenetic calcite for several reasons. First, the tighter rhombohedral crystal structure of the calcite discriminates against the relatively large uranium atom (Milliman, 1974a) resulting in lower uranium concentrations in calcite cements compared to coral. Second, we do not acid-leach sub-samples for U-series dating because the insolubility of thorium might potentially lead to loss and re-absorption of  $^{232}\text{Th}$  and  $^{230}\text{Th}$ . Nevertheless, we can estimate age offsets for the  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages of coral samples by assuming a uranium content of 3 ppm for coral aragonite (Cross and Cross, 1983; Min et al., 1995) and 0.1–1.5 ppm for the secondary calcite. In an extreme hypothetical case, a 48,000 years BP (calendar age) coral sample, containing 3% calcite at 1.5 ppm U, acquires an apparent age ~400 years younger than the true age (Fig. 4). Therefore, the age offsets in  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages of coral samples (screened with <0.2% calcite criteria) due to secondary calcite are likely to be a small fraction of the reported calendar age uncertainty.

### 3.3. Organic carbon contamination

Corals from locations such as Papua New Guinea (Edwards et al., 1993; Yokoyama et al., 2000; Cutler et al., 2004), Barbados, Santo and Araki Islands (Fairbanks et al., 2005) may have been exposed to a freshwater environment during portions of their history due to uplift and/or lowering of sea level allowing soil,

plant roots or microbes the opportunity to penetrate and spread in fossil coral outcrops. Corals may be contaminated with mold during collection, storage and shipment under humid condition. Modern carbon may also be introduced during sample handling. Some fraction of the organic matter is fairly resistant to oxidation as evident by progressive whitening of fossil coral samples over several days of continuous soaking in 30% H<sub>2</sub>O<sub>2</sub>. Based on this qualitative visual assessment, we tested the efficacy of a 7-day H<sub>2</sub>O<sub>2</sub> treatment. Seven days were an arbitrary doubling of the 3 days we observed progressive whitening of corals soaked in 30% H<sub>2</sub>O<sub>2</sub> and is reaching practical time limitations.

We tested the extended (7-day) H<sub>2</sub>O<sub>2</sub> cleaning technique for corals older than 30,000 years BP for two reasons. First, these samples were exposed to sub-aerial conditions including exposure to soils and other organic contaminants. Second, radiocarbon ages of older samples are much more sensitive to modern <sup>14</sup>C contamination.

Coral samples were handled with gloves and were ultrasonically cleaned in 30% H<sub>2</sub>O<sub>2</sub> using a high power ultrasonic probe for 2 h. Samples were then transferred into 5 ml glass vials, filled with 30% H<sub>2</sub>O<sub>2</sub> and placed in a sonication bath (BRANSON 5210) for 1 h. The samples remained in the 30% H<sub>2</sub>O<sub>2</sub> for 24 h after which the H<sub>2</sub>O<sub>2</sub> was replaced and the samples were sonicated for 1 h. The process was repeated for a total of 7 days. Finally, the samples were placed in fresh 30% H<sub>2</sub>O<sub>2</sub> and sonicated with a high power probe for 2 h. Samples were immediately placed and stored (damp) in glass vials without drying in order to avoid any mineral precipitation. Sub-samples used for uranium-series dating were not subject to the H<sub>2</sub>O<sub>2</sub> treatment.

Paired radiocarbon dates were obtained from three coral samples (with and without the 7-day H<sub>2</sub>O<sub>2</sub> oxidation treatment) described above. Two samples showed no effect of the extended H<sub>2</sub>O<sub>2</sub> treatment based on <sup>14</sup>C ages that overlap at 1σ analytical uncertainty (Table 3). For the remaining sample, AK-BD-3, the H<sub>2</sub>O<sub>2</sub>-treated sample is several hundred years older than the untreated companion sample. The data suggest that some samples are free of oxidation-resistant organic matter while an occasional sample appears to be contaminated. Schleicher et al. (1998) demonstrated

similar effects of different pretreatments on the <sup>14</sup>C concentration detected in >100,000 years old foraminifera tests. In that study, ultrasonic and acid leaching (either using HCl or 30% H<sub>2</sub>O<sub>2</sub>) was applied. The lowest <sup>14</sup>C blank values were achieved by the combination of a H<sub>2</sub>O<sub>2</sub> leach and elimination of any dry-down step. Since we know of no a priori screening technique that is sensitive enough to quickly identify samples contaminated with trace amounts of resistant organic carbon, we adopted the conservative and somewhat time-consuming step of treating all samples older than 30,000 years BP with 7-day H<sub>2</sub>O<sub>2</sub> ultrasonic oxidation treatment. However, in an attempt to further eliminate the possibility of contamination from resistant organic carbon, we subsequently modified the H<sub>2</sub>O<sub>2</sub> treatment from that used in Table 3 so that the ultrasonic bath procedure consists of a continuous 1-h on/off cycle for 7 days. Based on Schleicher et al.'s (1998) results, we have avoided any dry-down step in the sample preparation of coral sub-samples for <sup>14</sup>C dating. Using these cleaning techniques, the background <sup>14</sup>C levels measured in Kiel on a 98,000-year-old Araki coral (AK-H-2) ranged from 0.12% to 0.15% modern carbon, equivalent to an average radiocarbon age of 53,000 years BP.

#### 3.4. 26,000–50,000 years BP calibration

In an effort to extend the radiocarbon calibration beyond 26,000 years BP, we applied our XRD screening to more than 100 fossil coral samples in this study. Based on terrace location, we selected only Araki samples that were expected to fall in the range of radiocarbon dating for screening. The majority of the samples were either collected from outcrops at Araki Island during a field expedition in 2004 or were sampled from the existing collection of A. Bloom, at Cornell University. The Barbados samples (RGF) were collected during offshore drilling of Barbados submerged reef terraces (Fairbanks, 1989). One-third of the samples passed the “<0.2% calcite” criteria by our XRD methods and were therefore subjected to the extended hydrogen peroxide cleaning prior to processing for <sup>14</sup>C dating. U-series ages were determined without any leaching pretreatment. The resulting coral radiocarbon

Table 3  
Comparison between <sup>14</sup>C ages of hydrogen peroxide treated versus untreated fossil corals

Sample	Non-treated <sup>14</sup> C age (uncorrected) (years BP)	H <sub>2</sub> O <sub>2</sub> -treated <sup>14</sup> C age (uncorrected) (years BP)	<sup>14</sup> C age offset (years)
AK-BD-3	29,090 ± 190	29,700 ± 220	610
AK-BD-2	30,690 ± 210	30,360 ± 240	–330
AK-BD-11	32,900 ± 300	33,390 ± 350	490

Note: All samples are from Araki Island and contain <0.2% calcite. Errors represent 1σ analytical uncertainties. All <sup>14</sup>C dates in this table were provided by the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. All <sup>14</sup>C dates in this table were not corrected for reservoir age, which is different from Table 4.

calibration data (U series and AMS  $^{14}\text{C}$ ) are listed in Table 4 and displayed in Fig. 5.

#### 4. Discussion

The significant scatter displayed by previously published coral radiocarbon calibration data older than 30,000 years BP (Yokoyama et al., 2000) suggests that the accuracy of the  $^{14}\text{C}$  ages of these samples may not be well constrained (Fig. 1) and that stepwise dissolution may not have been sufficient for identifying potential contamination from all forms of younger carbon. It is inevitable that the scarcity of unaltered samples in this age range contribute to selection of less than ideal quality samples and the identification of measurable amounts of calcite in many of these samples (Yokoyama et al., 2000) indicates the potential for diagenetic related artifacts. As we progressed in our first attempts to radiocarbon date fossil coral older than 30,000 years BP we clearly identified unacceptable scatter (Fig. 5) in the results, even though most of these samples passed the established criteria (Reimer et al., 2002) for selection ( $\delta^{234}\text{U}$ , negligible  $^{232}\text{Th}$  and  $<1\%$  calcite). We have argued in the previous sections that more stringent sample selection criteria and pretreatment steps are now required. We now present data to strongly suggest that our sample screening and pretreatment steps have eliminated the most common sources of radiocarbon contamination and provide more accurate data than previously published (Fig. 5). We base this conclusion on several factors. First, our data yield a relatively smooth, continuous curve with little “noise” from point to point, in contrasts sharply with the data of Yokoyama et al. (2000) that yield seemingly impossible rapid and large  $^{14}\text{C}$  production or carbon cycle mixing scenarios (Oeschger et al., 1975; Lal, 1988; Mikolajewicz, 1996). Second, our data are consistent with the general trend of reconstructed geomagnetic paleointensity stacks. These stacks demonstrate that the geomagnetic field intensity fell from the highest values to the lowest between 50,000 and 40,000 years BP (Guyodo and Valet, 1996; Guyodo and Valet, 1999; Laj et al., 2000, 2004). The decrease would have reduced the geomagnetic shielding effect and resulted in increased global  $^{14}\text{C}$  production (Elsasser et al., 1956; Lal, 1988). Excess  $^{14}\text{C}$  in the atmosphere contributes to larger offsets between  $^{14}\text{C}$  ages and calendar ages if recorded, and we observe such a trend during the time period 50,000–40,000 years BP in our coral data (Fig. 5). Our data also displays a trend more consistent with the modeled  $^{14}\text{C}$  concentrations based on geomagnetic field intensity (Laj et al., 2002; Beck et al., 2001; Hughen et al., 2004).

All of the paleointensity stacks show a distinctive excursion, Laschamp, around 38,000–42,000 years BP

(Guyodo and Valet, 1996; Guyodo and Valet, 1999; Laj et al., 2000, 2004), and recent published K–Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  dates ( $40,400 \pm 2,000$  years BP) for the type locality (Guillou et al., 2004) refines the timing of Laschamp event. The most distinct feature of our coral data is the general trend of increasing offset between  $^{14}\text{C}$  ages and calendar ages; however, there is no significant anomaly between 38,000 and 42,000 years BP (Fig. 5). Since our coral data in this study (26,000–50,000 years BP) were obtained mainly from outcrop samples, which are not stratigraphically continuous, it is possible that we simply did not sample corals that date to the Laschamp excursion. Alternatively, the “duration” of Laschamp excursion and  $^{14}\text{C}$  production spike may not be long enough to be recorded in surface ocean and fossil corals (Beck et al., 2001; Hughen et al., 2004). Similarly, although the “magnitude” of Laschamp excursion seems significant on the scale of paleointensity in most stacks, the resulting carbon cycle models of global  $^{14}\text{C}$  indicate that the Laschamp might not be large enough to be recorded in the fossil corals. The lack of a prominent Laschamp anomaly in our coral data might also be due to the non-linearity relationship between geomagnetic intensity and global  $^{14}\text{C}$  production if the intensity dropped more than 20% of its present value when decreasing intensity has little effect on global  $^{14}\text{C}$  production (Elsasser et al., 1956; Lal, 1988).

#### 5. Conclusions

The accuracy and precision of the radiocarbon calibration by fossil corals are ultimately limited by the availability and quality of samples. Published coral  $^{14}\text{C}$  dates for samples older than 30,000 calendar years BP (Bard et al., 1998; Yokoyama et al., 2000; Cutler et al., 2004) are, however, too disparate for practical calibration. A large portion of the published coral data in the age range of 30,000–50,000 years BP (Yokoyama et al., 2000) were generated from samples containing diagenetic calcite ( $>2\%$ ). We present a simple model which demonstrates that contamination of coral with the amounts of secondary calcite commonly reported in the literature (1–3%) may explain at least part of the observed offsets and scatter in published coral data. Model calculations demonstrate that significant dating artifacts can be generated in samples containing greater than 0.5% calcite. Contamination by calcite may be increased during  $^{14}\text{C}$  graphite target preparation when samples are subjected to an acid leach and subsequent weight loss (50–60%) prior to dating, during which the fractional mass of calcite may increase by a factor of two or three. We demonstrate our ability to detect less than 0.2% calcite in aragonite by XRD and we apply



Table 4  
 $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages and  $^{14}\text{C}$  ages of Barbados and Araki fossil corals in this study

Sample	sp.	U-series ID	[U] (ppm)	$1\sigma$	$^{232}\text{Th}$ (pg/g)	$[^{234}\text{U}/^{238}\text{U}]$	$1\sigma$	$\delta^{234}\text{U}_{\text{initial}}$	$1\sigma$	$[^{230}\text{Th}/^{234}\text{U}]$	$1\sigma$	Th/U age (years BP)	$1\sigma$	$^{14}\text{C}$ lab ID	$^{14}\text{C}$ age <sub>RC</sub> (years BP)	$1\sigma$
RGF 12-28-6	<i>Ap</i>	121801TC1	3.1239	0.0008	365	1.1298	0.0005	141.1	0.7	0.2388	0.0003	29,590	44	CAMS 73919	24,925	60
RGF 12-28-6														CAMS 73953	24,975	70
RGF 12-28-7	<i>Ap</i>	021301RM2	2.9820	0.0005	482	1.1274	0.0004	138.7	0.5	0.2432	0.0004	30,214	56	CAMS 73920	24,955	60
RGF 12-28-7		073101RM2	3.2159	0.0008	863	1.1284	0.0005	139.9	0.5	0.2423	0.0004	30,080	58	CAMS 73949	24,815	60
RGF 12-28-7														CAMS 75385	24,845	90
RGF 12-28-7														CAMS 77432	24,915	90
RGF 12-29-2	<i>Ap</i>													CAMS 73921	24,955	70
RGF 12-29-2		080201RM2	3.2406	0.0007	68	1.1269	0.0004	138.3	0.5	0.2433	0.0003	30,225	40	CAMS 73946	24,915	70
AK-BD-2	–	102803TC5	1.9947	0.0007	10	1.1263	0.0006	139.9	0.9	0.2829	0.0003	36,014	43	CAMS 99632	30,325	210
AK-BD-2														CAMS 104452	29,995	240
AK-BD-3	<i>P</i>	102903TC1	3.9029	0.0013	8	1.1268	0.0005	139.8	0.8	0.2725	0.0003	34,467	39	CAMS 99022	28,725	190
AK-BD-3														CAMS 104453	29,335	220
AK-BD-4	<i>P</i>	102903TC2	2.7232	0.0007	29	1.1274	0.0005	140.9	0.8	0.2796	0.0003	35,518	43	CAMS 99633	30,745	220
AK-BD-5	<i>P</i>	062603TC2	2.6362	0.0009	13	1.1264	0.0005	140.1	0.8	0.2844	0.0005	36,247	74	CAMS 99015	31,305	260
AK-BD-9	<i>Pl</i>	102903TC6	2.8262	0.0008	734	1.1249	0.0005	139.8	0.8	0.3074	0.0003	39,759	42	CAMS 99024	34,725	400
AK-BD-10	<i>Fs</i>	010803RM1	2.5785	0.0005	12	1.1263	0.0004	141.3	0.6	0.3069	0.0003	39,684	50	CAMS 93343	34,725	430
AK-BD-10														CAMS 99637	35,045	370
AK-BD-11	<i>Pl</i>	063003TC3	2.6913	0.0006	299	1.1256	0.0004	140.0	0.8	0.2986	0.0004	38,401	58	CAMS 99016	32,535	300
AK-BD-11														CAMS 104454	33,025	350
AK-L-1	<i>Fs</i>	010803RM2	2.1286	0.0004	16	1.1310	0.0004	144.1	1.1	0.2672	0.0003	33,677	39	CAMS 93342	29,365	230
AK-L-1														CAMS 99636	29,095	180
AK-K-1	<i>P</i>	112403TC1	3.8042	0.0011	27	1.1273	0.0007	141.0	1.1	0.2844	0.0003	36,240	46	CAMS 104459	31,775	300
AK-K-1														CAMS 106898	31,765	490
AK-K-2	<i>Plla</i>	042203TC2	2.4537	0.0005	24	1.1279	0.0005	141.7	1.5	0.2842	0.0003	36,216	49	KIA 24977	30,615	150
AK-F-1	<i>F</i>	082504TC1	2.8052	0.0008	13	1.1276	0.0007	141.3	1.0	0.2834	0.0004	36,091	67	CAMS 106896	31,885	500
AK-F-1														CAMS 106893	32,255	530
AK-F-2	<i>G</i>	082504TC3	2.5551	0.0006	9	1.1287	0.0006	142.5	0.9	0.2831	0.0006	36,047	96	CAMS 106897	31,245	460
AK-AA-1	<i>Fs</i>	082504TC4	2.2705	0.0005	15	1.1280	0.0004	142.5	0.7	0.2942	0.0004	37,724	68	CAMS 106890	33,725	630
AK-BE-1b	<i>Pl</i>	063003TC4	2.7054	0.0006	337	1.1228	0.0005	139.7	0.7	0.3446	0.0006	45,689	93	CAMS 99018	41,945	960
AK-BE-1b		082604TC3	2.6771	0.0007	300	1.1252	0.0006	142.5	0.9	0.3446	0.0006	45,681	98			
AK-AB-1	<i>Pl</i>	042303TC1	2.5163	0.0005	57	1.1231	0.0005	141.1	0.7	0.3602	0.0003	48,273	49	KIA 24976	44,045	530
AK-AB-1		111803TC4	2.7484	0.0007	70	1.1226	0.0005	140.5	0.8	0.3595	0.0003	48,164	45			
ARA04-2D	<i>G</i>	112304RM1	2.3337	0.0004	29	1.1299	0.0005	145.3	0.8	0.3077	0.0009	39,799	140	KIA 24978	34,685	230
ARA04-10D	<i>F</i>	112304TC2	2.4515	0.0004	9	1.1299	0.0005	145.4	0.7	0.3085	0.0004	39,930	58	KIA 24979	34,205	210
ARA04-11D	<i>G</i>	102604LC5	2.4407	0.0011	36	1.1280	0.0005	143.7	0.8	0.3149	0.0003	40,923	54	KIA 24980	35,275	200
ARA04-17D	—	011805TC1	3.1012	0.0007	6	1.1289	0.0005	142.9	0.8	0.2863	0.0003	36,521	44	KIA 24981	31,345	150
ARA04-19D	<i>P</i>	011805TC2	3.3744	0.0009	94	1.1307	0.0005	144.7	0.8	0.2830	0.0003	36,031	44	KIA 24982	31,705	150
ARA04-22D	<i>P</i>	112304RM4	2.9510	0.0005	44	1.1323	0.0005	146.5	0.7	0.2829	0.0004	36,008	64	KIA 24984	30,855	140
ARA04-40E	<i>Pl</i>	102604RM4	2.4933	0.0005	10	1.1236	0.0005	142.1	0.7	0.3658	0.0003	49,203	45	KIA 24987	44,795	570
ARA04-43E	<i>P</i>	092204LC2	2.8368	0.0007	17	1.1252	0.0005	143.5	0.7	0.3597	0.0006	48,183	102	KIA 24988	45,695	630
ARA04-44E	<i>P</i>	092204LC3	3.1435	0.0011	69	1.1262	0.0006	144.7	0.9	0.3609	0.0007	48,378	112	KIA 24989	44,385	550
ARA04-71E	<i>F</i>	092304LC1	2.2226	0.0008	27	1.1258	0.0005	142.2	0.8	0.3312	0.0005	43,519	82	KIA 24991	38,495	380
ARA04-73E	–	092304LC2	2.1453	0.0005	14	1.1270	0.0005	143.9	0.8	0.3348	0.0005	44,098	83	KIA 24992	39,345	310
ARA04-75E	<i>P</i>	092304LC3	2.9473	0.0005	27	1.1254	0.0005	142.3	0.7	0.3395	0.0006	44,850	90	KIA 24993	41,345	390
ARA04-77E	–	092304LC4	2.6076	0.0005	8	1.1280	0.0005	144.9	0.8	0.3333	0.0005	43,840	86	KIA 24994	39,335	320
ARA04-85E	<i>G</i>	092304LC5	2.5620	0.0005	4	1.1262	0.0004	142.8	0.7	0.3310	0.0004	43,474	72	KIA 24995	40,095	330

Note: Coral species: “*Ap*” is *Acropora palmata* and “*A*” is *Acropora* species. “*Pl*” is *Porites lutea* and “*P*” is *Porites* species. “*Fs*” is *Favia stelligera* and “*F*” is *Favia* species. “*G*” is *Goniastrea*. “*Plla*” is *Platygyra lamellina* and “*Pl*” is *Platygyra*. “–” Represents unidentified species. “[ ]” Represents activity ratio. All U-series analyses were made by an MC-MS-ICPMS (Plasma 54) at LDEO (Halliday et al., 1995; Mortlock et al., 2005).  $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$  ages are represented by “Th/U ages” in this table and were calculated using the following equation (Ivanovich et al., 1992):

$$[^{230}\text{Th}/^{234}\text{U}] = \frac{1 - e^{-\lambda_{230}t_1}}{[^{234}\text{U}/^{238}\text{U}]} + \left(1 - \frac{1}{[^{234}\text{U}/^{238}\text{U}]}\right) \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} (1 - e^{-(\lambda_{230} - \lambda_{234})t_1}).$$

In all calculations, we use decay constants of  $\lambda_{230} = 9.1577 \times 10^{-6} \text{ year}^{-1}$  and  $\lambda_{234} = 2.8263 \times 10^{-6} \text{ year}^{-1}$  (Cheng et al., 2000).  $^{14}\text{C}$  age<sub>RC</sub> reported in this table are based on the definition in Stuiver and Polach (1977) and have been corrected for reservoir age of 365 years, which was determined by differencing Holocene coral data from Santo, Araki and Barbados (Fairbanks et al., 2005), and other data from Vanuatu (Paterne et al., 2004) from the tree-ring calibration data set (Reimer et al., 2004). “CAMS” represents  $^{14}\text{C}$  dates performed at Lawrence Livermore National Laboratory, University of California. “KIA” represents  $^{14}\text{C}$  dates performed in the Leibniz Laboratory for Dating and Isotope Analyses, Christian-Albrechts-Universität, Kiel, Germany.

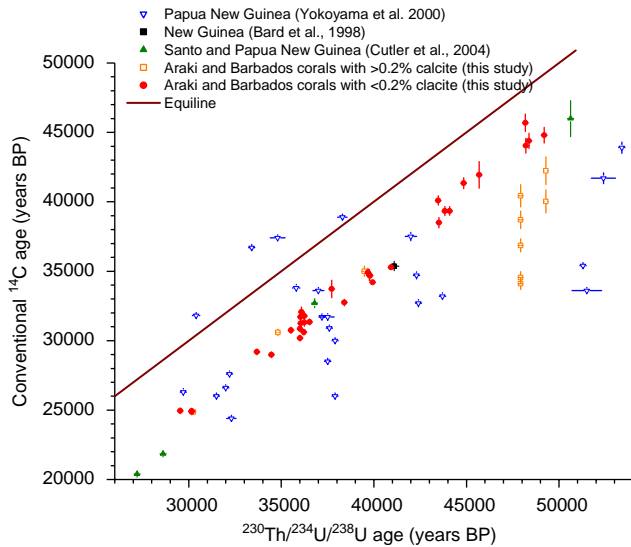


Fig. 5. Published radiocarbon and U-series ages for fossil corals between 26,000 and 50,000 years BP (Bard et al., 1998; Yokoyama et al., 2000; Cutler et al., 2004) compared to our data from Barbados and Araki Islands (Table 4). The equiline is presented only for reference. Yokoyama et al. (2000) reported calcite concentrations in the range of 0–3%, Bard et al. (1998) reported <1% and Cutler et al. (2004) reported <1%. Barbados and Araki coral samples were a priori screened by XRD method described in this study and were determined to have <0.2% calcite.

“<0.2% calcite” as our a priori criterion to select coral samples.

Organic matter is another source of radiocarbon contamination and is particularly common in outcrop coral samples exposed to soils or in corals having mold colonization in transit or during storage after sampling in humid environments. We observe visible “whitening” of typical outcrop samples following ultrasonic cleaning in 30% H<sub>2</sub>O<sub>2</sub> over a several day period that we attribute to continued oxidation of organic matter. An extended 7-day hydrogen peroxide pretreatment is used to remove any contaminating organic matter. We demonstrate that cleaning in hydrogen peroxide yields older or reproducible <sup>14</sup>C dates compared to non-treated samples. These are more rigorous screening and cleaning techniques than those adopted by IntCal04 (Reimer et al., 2002) for samples younger than 26,000 years BP. However, for samples older than 26,000 years BP these screening and cleaning techniques become essential and provide precise, reproducible and accurate radiocarbon calibration data.

### Acknowledgements

Radiocarbon measurements were performed at the Center of Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory, University of California by T. Guilderson and at the Leibniz Laboratory for

Dating and Isotope Analyses, Christian-Albrechts-Universität, Kiel, Germany under the supervision of P.M. Grootes. P. Biscaye provided technical support and advice on lowering the calcite detection limit at the XRD facility at LDEO. L. Britt assisted with developing the XRD methodology. L. Cao assisted with the <sup>14</sup>C sample preparation and U-series and XRD measurements. T. Fairbanks, M. Tamata, J. Tamata, J. Rongo and A. Somoli collected additional samples during a 2004 expedition to Araki Island. We thank two anonymous reviewers for their helpful comments. This work was supported by grants from the National Science Foundation (OCE99-11637, ATM03-27722) and the Climate Center at LDEO (6-80303). This is Lamont Contribution 6765.

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