



## RESEARCH ARTICLE

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A comparison of U/Th and rapid-screen  $^{14}\text{C}$  dates from Line Island fossil corals

Pamela R. Grothe<sup>1</sup>, Kim M. Cobb<sup>1</sup>, Shari L. Bush<sup>2</sup>, Hai Cheng<sup>3,4</sup>, Guaciara M. Santos<sup>2</sup>, John R. Southon<sup>2</sup>, R. Lawrence Edwards<sup>4</sup>, Daniel M. Deocampo<sup>5</sup>, and Hussein R. Sayani<sup>1</sup>

<sup>1</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA, <sup>2</sup>Department of Earth System Science, University of California, Irvine, California, USA, <sup>3</sup>Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China, <sup>4</sup>Department of Earth Sciences, University of Minnesota, Minneapolis, Minnesota, USA, <sup>5</sup>Department of Geosciences, Georgia State University, Atlanta, Georgia, USA

## Key Points:

- Rapid  $^{14}\text{C}$  dating is accurate for Holocene-aged fossil corals
- Both  $^{14}\text{C}$  and U/Th coral dates are sensitive to secondary calcite
- Concordant  $^{14}\text{C}$  and U/Th dates confirm closed system behavior

## Supporting Information:

- Supporting Information S1
- Table S1
- Table S2

## Correspondence to:

P. R. Grothe,  
Pamela.grothe@gatech.edu

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**Abstract** Time-consuming and expensive radiometric dating techniques limit the number of dates available to construct absolute chronologies for high-resolution paleoclimate reconstructions. A recently developed rapid-screen  $^{14}\text{C}$  dating technique reduces sample preparation time and per sample costs by 90%, but its accuracy has not yet been tested on shallow-water corals. In this study, we test the rapid-screen  $^{14}\text{C}$  dating technique on shallow-water corals by comparing 44 rapid-screen  $^{14}\text{C}$  dates to both high-precision  $^{14}\text{C}$  dates and U/Th dates from mid- to late-Holocene fossil corals collected from the central tropical Pacific (2–4°N, 157–160°W). Our results show that 42 rapid-screen  $^{14}\text{C}$  and U/Th dates agree within uncertainties, confirming closed-system behavior and ensuring chronological accuracy. However, two samples that grew ~6500 years ago have calibrated  $^{14}\text{C}$  ages ~1000 years younger than the corresponding U/Th ages, consistent with diagenetic alteration as indicated by the presence of 15–23% calcite. Mass balance calculations confirm that the observed dating discrepancies are consistent with  $^{14}\text{C}$  addition and U removal, both of which occur during diagenetic calcite recrystallization. Under the assumption that aragonite-to-calcite replacement is linear through time, we estimate the samples' true ages using the measured  $^{14}\text{C}$  and U/Th dates and percent calcite values. Results illustrate that the rapid-screen  $^{14}\text{C}$  dates of Holocene-aged fossil corals are accurate for samples with less than 2% calcite. Application of this rapid-screen  $^{14}\text{C}$  method to the fossil coral rubble fields from Kiritimati Island reveal significant chronological clustering of fossil coral across the landscape, with older ages farther from the water's edge.

## 1. Introduction

Absolutely dated, high-resolution paleoclimate records provide a detailed account of past climate variability. Precise radiometric dating of Holocene-aged carbonate proxies, such as speleothems [e.g., Wang *et al.*, 2005], bivalves [e.g., Mangerud, 1972], foraminifera [e.g., Broecker *et al.*, 1984], and corals [e.g., Edwards *et al.*, 1987], is necessary for accurate chronological control of paleoclimate records. Most carbonate proxies are dated using high-precision  $^{14}\text{C}$ -accelerator mass spectrometry (AMS) and U/Th methods, whose expensive and time-consuming analyses limit the number of samples used to constrain the chronologies of paleoclimate records. In most cases, limits on the time and/or funding that can be dedicated to radiometric dating dictate the number of paleoclimate reconstructions and potentially the resolution thereof that can be pursued.

High-precision U/Th disequilibrium dating is the most precise method for dating late Pleistocene- and Holocene-aged corals [e.g., Edwards *et al.*, 1987; Cobb *et al.*, 2003a; Potter *et al.*, 2005; Zhao *et al.*, 2009]. High-precision measurements of  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  using multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) provide low uncertainties on the order of 0.1% ( $2\sigma$ ) for material less than 10,000 years [Cheng *et al.*, 2013]. However, high-precision U/Th disequilibrium dating is time-consuming and expensive, requiring the chemical separation of U and Th fractions in a clean room followed by ICPMS analyses. Recently, Douville *et al.* [2010] simplified tedious chemical separations and simultaneously measured U and Th atoms on an inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS), achieving 50 dates per day with precision levels of less than 2%. Additional rapid U/Th dating methods have been developed using laser ablation (LA) MC-ICPMS [Eggins *et al.*, 2005; Potter *et al.*, 2005; McGregor *et al.*, 2011] and

are capable of analyzing 50 dates per day with only 1 day of sample preparation [Spooner *et al.*, 2016], but uncertainties of  $\pm 33\%$  ( $2\sigma$ ) [McGregor *et al.*, 2011] or more [Potter *et al.*, 2005] on late-Holocene corals are too large for many paleoclimate applications.

A variety of recent studies investigate techniques for expediting the  $^{14}\text{C}$  dating process. For example, gas ion source AMS removes graphitization steps [Ramsey *et al.*, 2004] and can now measure up to 30 samples per day with precisions of  $<0.7\%$  [Wacker *et al.*, 2013]. However, those setups have been both mostly dedicated to compound specific work, source apportionment and biomedical analysis, and so far do not provide any additional discount in sample processing and spectrometer measurement costs for reconnaissance work. Recently, Bush *et al.* [2013] developed a rapid-screen  $^{14}\text{C}$  dating method using a standard source AMS for application to Holocene-aged marine carbonates. The rapid-screen  $^{14}\text{C}$  method bypasses the time-consuming leaching, hydrolysis and graphitization steps required for the preparation of carbonate samples for high-precision  $^{14}\text{C}$ -AMS dating [Santos *et al.*, 2004]. Rather, the new technique involves direct AMS analysis of powdered calcium carbonate samples mixed with powdered iron catalyst. Analytical precisions of  $\pm 1.8\%$  ( $1\sigma$ ) can be achieved on carbonate samples younger than 10 kyr BP [Bush *et al.*, 2013]. This work improves upon more complex but fast  $^{14}\text{C}$  dating methods by Burke *et al.* [2010] and McIntyre *et al.* [2011], which requires  $>10$  mg of  $\text{CaCO}_3$  powder for measurement, and is similar to the method developed by Longworth *et al.* [2013] who use titanium instead of iron as a catalyst. The rapid-screen  $^{14}\text{C}$  method has been applied to date dozens of deep-sea corals [Bush *et al.*, 2013], but has never been tested on shallow-water corals.

A major caveat of any dating method for shallow-water corals is the fact that diagenesis can cause the gain or loss of radiogenic parents or daughters through open system behavior [e.g. Lazar *et al.*, 2004; Scholz *et al.*, 2004]. Diagenesis in corals typically manifests itself in two forms: (1) as secondary aragonite needles precipitated in a submarine environment [e.g., Enmar *et al.*, 2000; Hendy *et al.*, 2007; Nothdurft and Webb, 2009; Sayani *et al.*, 2011], or (2) as secondary calcites derived from dissolution of the primary aragonite skeleton and subsequent recrystallization in subaerial environments [e.g., Rabier *et al.*, 2008; McGregor and Gagan, 2003; Sayani *et al.*, 2011]. For the latter,  $^{14}\text{C}$  is incorporated into the newly formed crystals, resulting in a measured  $^{14}\text{C}$  age that is younger than the true age [Burr *et al.*, 1992]. The recrystallization process results in U loss to the coral sample [e.g., Henderson *et al.*, 1993; Shen and Dunbar, 1995; Scholz *et al.*, 2004; Scholz and Mangini, 2007], given that U is soluble in natural water [James, 1974; Bathurst, 1974; Pingitore, 1976; Maliva and Dickson, 1992; Rabier *et al.*, 2008] and has lower concentrations in the more compact calcite lattice [Reeder *et al.*, 2001].

Many studies documenting the effects of diagenesis on coral U/Th dates focus on fossil corals from the late Pleistocene [e.g., Broecker *et al.*, 1968; Edwards *et al.*, 1988; Gallup *et al.*, 1994; Cutler *et al.*, 2003]. Open system behavior is characterized by elevated initial  $^{234}\text{U}/^{238}\text{U}$  activity ratios caused by the post-depositional formation of secondary carbonates with seawater  $^{234}\text{U}/^{238}\text{U}$  ratios [e.g., Bender *et al.*, 1979; Gallup *et al.*, 1994; Henderson, 2002; Thompson *et al.*, 2003; Scholz *et al.*, 2004; Robinson *et al.*, 2006]. Marine carbonates incorporate the  $^{234}\text{U}/^{238}\text{U}$  activity ratio from seawater [e.g., Chen *et al.*, 1986; Cheng *et al.*, 2000; Robinson *et al.*, 2004], which is thought to be constant to within 1% over the last glacial interglacial cycle [Henderson, 2002; Esat and Yokoyama, 2006]. If decay occurs in a closed system then age-corrected  $^{234}\text{U}/^{238}\text{U}$  ratios (reported as  $\delta^{234}\text{U}_{\text{initial}}$  values) should be the same as modern day [Edwards *et al.*, 1987]. However, corals with  $(^{234}\text{U}/^{238}\text{U})_{\text{initial}}$  activity ratios within the range of modern seawater may still have experienced open system behavior during diagenesis [Gallup *et al.*, 2002; Cutler *et al.*, 2003]. Additional screening criteria for corals (i.e., U concentrations should be in the range of modern analogues and calcite percentages should be  $<2\%$  [Scholz and Mangini, 2007]) help guide sample selection and ensure closed-system U/Th dates. Given the importance of obtaining accurate age constraints from fossil corals used for sea level reconstruction, recent efforts have established models for correcting U/Th dates from corals characterized by open system behavior [Thompson *et al.*, 2003; Villemant and Feuillet, 2003; Scholz *et al.*, 2004], which are fully explored in Scholz and Mangini [2007].

Very young corals ( $<1000$  years) with intact  $^{234}\text{U}/^{238}\text{U}$  initial values can exhibit elevated  $\Delta^{14}\text{C}$  values associated with secondary carbonate precipitation [Zaunbrecher *et al.*, 2010], illustrating the limitations of  $^{234}\text{U}/^{238}\text{U}$  as a screening tool in young corals. Given that atmospheric exchange during the precipitation process adds appreciable  $^{14}\text{C}$  to the sample,  $^{14}\text{C}$  ages are much more sensitive to diagenesis than U/Th ages [Burr *et al.*, 1992; Yokoyama and Esat, 2004]. Techniques such as X-ray diffraction (XRD) and scanning

electron microscope (SEM) imaging that enable the identification of diagenetic phases have become common screening tools prior to dating samples for paleoclimate reconstruction. However, the diagenetic condition of a given sample is heterogeneous on the mm scale, as evidenced by poor replication of duplicate U-series measurements from the same sample [Scholz and Mangini, 2007], which makes it challenging to establish whether the specific sample used for radiometric dating is pristine or not.

In this study, we assess the rapid-screen  $^{14}\text{C}$  dating method from Bush *et al.* [2013] as a tool for dating Holocene-aged fossil corals by comparing rapid-screen  $^{14}\text{C}$  dates with high-precision U/Th dates from a large collection of fossil corals from the Line Islands. We investigate the effects of calcite recrystallization observed in two older samples on both  $^{14}\text{C}$  and U/Th dates by modeling a continuous replacement of aragonite to calcite. Lastly, we apply the rapid-screen  $^{14}\text{C}$  dating method to a large number of fossil coral samples collected around Kiritimati Island and provide a preliminary map of fossil coral age distributions at this site.

## 2. Methods

### 2.1. Sample Selection

We selected 44 samples for paired  $^{14}\text{C}$  and U/Th dating, including 3 samples from Cobb *et al.* [2003b] and 13 samples from Cobb *et al.* [2013]. The bulk of the remaining 28 samples represent newly collected fossil *Porites* coral samples collected from Kiritimati Island in May 2012. These samples, averaging 10 cm in length, were collected from fossil coral deposits lining ocean-facing beaches. Using the new and previously published dates, we achieved an approximately even temporal distribution of samples across the last 7000 years.

We subsampled each fossil coral sample for dating by cutting a roughly 1 cm<sup>3</sup>-sized piece from the sample using a Dremel<sup>®</sup> Rotary tool. This subsample size equates to less than 1 year of skeletal accretion for the fast growing *Porites* corals. In most cases, dating subsamples were >10 cm away from the exposed surface. However, some subsamples were taken within ~2 cm of the exposed surface using a hammer and chisel in the field. To test whether this difference affected the dating, we compared dating results for subsamples taken from the exterior as well as the interior of select fossil coral cores.

### 2.2. Screening by X-Ray Diffraction

Select samples were screened for calcite using a Panalytical XPERT PRO X-ray diffractometer (XRD) at Georgia State University (GSU) using CuK<sub>α</sub> radiation, 1° fixed incident and diffracted beam slits, 0.04 rad incident and diffracted beam Soller slits, a 2° incident beam anti-scatter slit, a Ni diffracted beam filter, and a Panalytical PIXcel-1D fast detector. Finely powdered samples (~300 mg) were analyzed on low background mounts in the XRD operating at 45 kV and 40 mA. All samples were initially analyzed in the range 25.5–30.0°2θ, and examined for the presence of the [111] and [102] aragonite peaks (3.40Å and 3.27Å, respectively), and the [104] calcite peak (3.04Å). Based on analysis of synthetic standards, the limit of detection of calcite by this method is below 0.5 weight % calcite. This limit of detection was selected to provide a high rate of sample throughput to rapidly screen samples. Those samples with detectable calcite were subsequently analyzed by slow scans in the range 5–70°2θ to obtain high quality diffraction data to allow Rietveld refinements for precise quantification [Bish and Post, 1993] using Panalytical HighScore+ vers. 3.0 with reference to the PDF-2-2011 and ICSD-2011 crystal structure databases.

### 2.3 Rapid-Screen $^{14}\text{C}$ Dating

Radiocarbon measurements were performed at the W.M. Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory (KCCAMS) at the University of California Irvine, following methods outlined in Bush *et al.* [2013]. Small chunks of ~1 g were chipped from the larger coral samples and ultrasonically cleaned in deionized water three times for 5 min, or until water was clear after sonication. Using a mortar and pestle, the cleaned coral chunks were ground to a fine powder, and 0.3 mg of the powder was mixed with ~5.0 mg of Fe powder (Sigma-Aldrich-400 mesh, 99.9% pure) and pressed directly into a target for AMS analysis.

Three primary standards of oxalic acid (OX-I) >0.7 mg C graphite were used per wheel to tune the AMS and to normalize the  $^{14}\text{C}/^{12}\text{C}$  ratios [Santos *et al.*, 2007a; Bush *et al.*, 2013]. For background corrections from modern contamination and quality control, two calcite blanks and one secondary standard (IAEA-C2 - chalk, Fm = 0.411; ~7135 years BP) were also measured in each wheel. Both the calcite blanks and the IAEA-C2

standard were powdered and processed using the same methodology as the coral samples. As a coral-based  $^{14}\text{C}$  blank sample was unavailable, we used a calcite  $^{14}\text{C}$  blank derived from a  $\sim 250$  kyr old stalagmite from Borneo (K. M. Cobb, personal communication, 2015). We recognize that calcite blanks are cleaner than biogenic carbonates [Eltgroth *et al.*, 2006], however, since our coral samples are less than 7000 years old, underestimating the blank correction by a few micrograms is not significant enough to skew the ages [Wood, 2015]. For the  $^{14}\text{C}$  rapid-screen method, the AMS measurement time for each sample is limited to  $\sim 4$  runs of 150 s each, as opposed to  $\sim 10$ – $15$  runs each required for a high-precision  $^{14}\text{C}$  date. Under these conditions, the analytical precision on a  $^{14}\text{C}$  date for a young ( $< 10,000$  years old) carbonate is approximately  $\pm 1.8\%$  ( $1\sigma$ ), versus the high-precision  $^{14}\text{C}$ -AMS analytical precision of  $\pm 0.2$  to  $0.3\%$  ( $1\sigma$ ) [Beverly *et al.*, 2010]. We performed replicate analyses on several samples to test the reproducibility of the rapid-screen  $^{14}\text{C}$  method in our fossil coral material. Five samples were replicated six times and 15 samples were run in duplicate. Replicate values all fell within the  $1\sigma$  analytical precision limits.

Measured  $^{14}\text{C}/^{12}\text{C}$  ratios were fractionation-corrected using the AMS  $\delta^{13}\text{C}$  values and normalized to a  $\delta^{13}\text{C}$  value of  $-25\text{‰}$ . A mass balance background correction was also applied following Santos *et al.* [2013]. Radiocarbon ages (years BP = years before 1950 AD) were converted to calibrated calendar ages (years AD for  $< 1000$  years old and cal years BP for samples  $> 1000$  years old) using the Calib 7.1 software [Stuiver and Reimer, 1993] and MARINE13 calibration data sets [Reimer *et al.*, 2013]. Additionally, we used a local radiocarbon marine reservoir correction ( $\Delta R$ ) of  $39 \pm 56$  years ( $1\sigma$ ) [McGregor *et al.*, 2011]. Final calibrated ages are reported as the  $2\sigma$  age ranges about the median probability. It is important to note that significant analytical uncertainties associated with the rapid-screen  $^{14}\text{C}$  analysis protocol translate to relatively large age uncertainties once propagated through the  $^{14}\text{C}$  calibration curve, especially for younger samples dating to the last millennium [Taylor and Bar-Yosef, 2014].

For high-precision  $^{14}\text{C}$ -AMS dates ( $N=3$ ), coral samples were prepared and analyzed following protocols outlined in Santos *et al.* [2004]. Coral powder was initially leached to remove surface adsorptions ( $\sim 10\%$  by mass), acidified to  $\text{CO}_2$  and converted to graphite using an Fe catalyst and the hydrogen reduction method. Analytical uncertainties for high-precision  $^{14}\text{C}$  dates range from 0.2 to 0.3%.

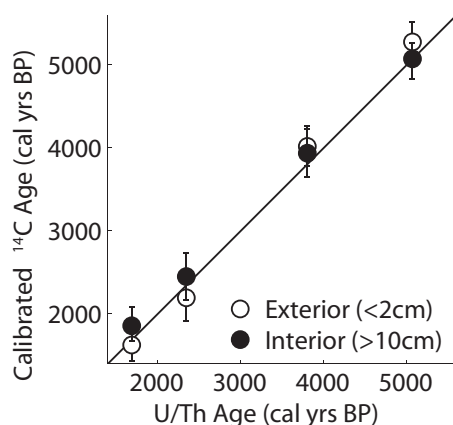
#### 2.4. U/Th Dating

The fossil coral U/Th chemistry and isotopic analyses were performed at the Minnesota Isotope Lab at the University of Minnesota using a ThermoFinnigan Neptune multicollector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS). Of the 56 U/Th dates discussed in this paper, 18 dates were published in Cobb *et al.* [2003b] and Cobb *et al.* [2013]. P. Grothe measured the remaining 38 fossil coral U/Th ages in June 2013.

U/Th dating was performed following procedures outlined in Cheng *et al.* [2013] following general protocols first outlined in Edwards *et al.* [1987] and subsequently revised by Shen *et al.* [2002]. Following fossil coral sampling procedures outlined in Cobb *et al.* [2003a], small pieces of  $\sim 0.05$  g were broken from the coral using a stainless steel chisel and hammer. The samples were visually inspected under a microscope and any discoloring and/or debris were removed using an exacto knife. The pieces were then ultrasonically cleaned in deionized water three times and dried overnight at  $30^\circ\text{C}$ . Then a  $\sim 0.05$  g sample was dissolved in concentrated  $\text{HNO}_3$  and spiked with solution containing known concentrations of  $^{233}\text{U}$ ,  $^{235}\text{U}$ , and  $^{229}\text{Th}$ . The U and Th atoms were separated from the bulk sample by Fe precipitation, and subsequently dissolved in a dilute  $\text{HNO}_3$  and HF solution for MC-ICPMS analyses. For each batch, a blank that was run through the same chemistry was analyzed to correct for procedural contamination. In addition, one duplicate per run was analyzed to ensure reproducibility. The age was solved iteratively using the standard age equation presented in Edwards *et al.* [1987], using decay constants of  $1.55125 \times 10^{-10}$  for  $\lambda_{238}$  [Jaffey *et al.*, 1971],  $2.82206 \times 10^{-6}$  for  $\lambda_{234}$  [Cheng *et al.*, 2013], and  $9.1705 \times 10^{-6}$  for  $\lambda_{230}$  [Cheng *et al.*, 2013]. Samples were corrected for initial nonradiogenic Th using a  $^{230}\text{Th}/^{232}\text{Th}$  atomic ratio of  $4.4 \pm 2.2 \times 10^{-6}$ .

### 3. Results

Sample P11, whose original U/Th age was reported as  $2218 \pm 10$  cal years Before Present (BP) [Cobb *et al.*, 2013], yielded U/Th ages of  $5075 \pm 16$  and  $5061 \pm 14$  cal years BP during replicate reanalysis over the course of this study. Four different P11 samples dated via the rapid-screen  $^{14}\text{C}$  method fall within analytical error of the revised U/Th ages, ranging from 4898 to 5437 cal years BP. In the absence of any evidence of diagenetic



**Figure 1.** U/Th and calibrated <sup>14</sup>C dates of four fossil corals sampled near the exterior (<2 cm from the weathered surface; open circles) and interior (>10 cm from the weathered surface; black circles). The median probability of the calibrated rapid-screen <sup>14</sup>C date is plotted with error bars representing the 2σ age range. The 2σ error bars for U/Th dates are smaller than the symbol size.

alteration, and given that P. Grothe resampled the archived core clearly labeled “P11” for this study, we use the new U/Th ages for the paired rapid-screen <sup>14</sup>C-U/Th ages.

Calibrated rapid-screen <sup>14</sup>C ages for coral samples derived from the interior (>10 cm from the weathered coral surface) versus exterior (<2 cm from the weathered surface) are statistically indistinguishable from one another, and from the corresponding U/Th dates (Figure 1 and Table 1).

The rapid-screen <sup>14</sup>C calibrated age ranges (±2σ) correspond well with the high-precision <sup>14</sup>C calibrated ages for the three fossil coral samples tested (Table 2), with an average difference of 2.4%. These differences are well within the ±2% (1σ) analytical uncertainty of the rapid-screen <sup>14</sup>C dating method, as outlined by Bush *et al.* [2013].

### 3.1. High-Precision <sup>14</sup>C-U/Th Comparisons

High-precision <sup>14</sup>C and U/Th ages from two unaltered samples, SB7 and V30, agree within error (2σ) (Table 2).

We calculate the ΔR value for SB7 (U/Th date 1342 ±5

AD) and find agreement with ΔR=39 ±56 years (1σ) used in our <sup>14</sup>C age calibrations [McGregor *et al.*, 2011]. For V30 (U/Th age 5979 ±13 cal years BP), we calculate a ΔR value of -77 ±33years. However, since the high-precision <sup>14</sup>C and U/Th ages for V30 are concordant when using ΔR= 39 ±56 years and we do not have any additional constraints on ΔR during this time period, we continue to use ΔR= 39 ±56 years for all of our <sup>14</sup>C age calibrations.

### 3.2. Rapid-Screen <sup>14</sup>C-U/Th Comparisons

Fossil coral rapid-screen <sup>14</sup>C ages match U/Th ages within combined errors (2σ) in 42 of the 44 paired analyses (Figure 2 and Table 2). Concordant samples differ on average by 3.4% between the <sup>14</sup>C calibrated median probability age and U/Th age, with no systematic offsets. Such differences are well within the combined uncertainties of the analytical precision for the rapid-screen <sup>14</sup>C dating and subsequent calibration. Additionally, samples that dated post-bomb with the rapid-screen <sup>14</sup>C dating method were confirmed with U/Th dates to be younger than 1950 AD. All age-concordant samples contain no detectable calcite (<0.5%), as determined using XRD.

Rapid-screen <sup>14</sup>C ages from two mid-Holocene samples, V28 and V33, are 17% and 25% younger, respectively, than the corresponding U/Th ages. Published U/Th ages for V28 and V33 are 6350 ±13 and 6593

**Table 1.** Rapid-Screen <sup>14</sup>C and U/Th Dates for Exterior and Interior Samples

Sample	U/Th Age (cal years BP) <sup>a,b</sup>		Edge or Interior <sup>c</sup>	<sup>14</sup> C Age (years BP)		Rapid-Screen Calibrated Age (cal years BP) <sup>d</sup>	
	Age	±		Age	±	Age	±
P2	1685	±5	Exterior	2090	±60	1625	±203
			Interior	2290	±80	1858	±246
P37	2342	±7	Exterior	2570	±60	2195	±205
			Interior	2760	±60	2450	±220
P43	3802	±17	Exterior	4040	±80	4015	±283
			Interior	3980	±90	3934	±294
P11	5068	±15	Exterior	4990	±100	5275	±298
			Interior	4830	±80	5071	±237

<sup>a</sup>Errors quoted are 2σ.  
<sup>b</sup>U/Th dates are published in Cobb *et al.* [2013].  
<sup>c</sup>Exterior is defined as <2 cm from the weathered surface whereas interior refers to samples taken >10 cm from the weathered surface.  
<sup>d</sup><sup>14</sup>C ages were calibrated to calendar years using Calib7.1 software [Stuiver and Reimer, 1993] and Marine13 calibration data sets [Reimer *et al.*, 2013] and corrected for a local reservoir age using ΔR of 39 ±56 [McGregor *et al.*, 2011]. The <sup>14</sup>C calibrated age is reported as the median probability. Calibrated <sup>14</sup>C errors are 2σ.

**Table 2.** Paired <sup>14</sup>C and U/Th Dates

Sample <sup>a</sup>	U/Th Age <sup>b</sup>		Rapid-Screen <sup>14</sup> C Age (years BP)		Rapid-Screen Calibrated Age <sup>c</sup>		High-Precision <sup>14</sup> C-AMS Age (years BP)		High-Precision <sup>14</sup> C-AMS Calibrated Age <sup>c</sup>	
<i>Last Millennium (Years in AD)</i>										
X12-3-2	2003	±4	-540	±60	post-1950					
X12-9-10	1993	±3	-725	±40	post-1950					
X12-D6-1	1986	±3	-790	±40	post-1950					
X12-4-111	1969	±3	-190	±80	post-1950					
X12-1-19	1930	±3	630	±60	1734	±199				
X12-9-6	1919	±3	590	±50	1775	±156				
X12-1-11	1910	±3	610	±60	1756	±183				
X12-1-8	1887	±4	630	±70	1733	+200				
X12-13-19	1873	±3	570	±50	1792	±193				
X12-13-8	1742	±5	590	±50	1775	±156				
X12-6-75	1733	±4	670	±60	1679	±226				
X12-D2-3	1723	±4	640	±60	1720	±208				
SB3b <sup>d</sup>	1674	±5	710	±60	1628	±181				
X12-16-1	1622	±5	760	±60	1586	±180				
X12-16-6	1599	±5	710	±70	1633	±195				
X12-13-5	1566	±4	700	±50	1640	±173				
X12-3-23	1428	±5	950	±60	1427	±140				
SB7 <sup>d</sup>	1342	±5	1020	±70	1376	±137	1040	±15	1365	±82
X12-3-26	1229	±4	1350	±60	1099	±170				
NB12 <sup>d</sup>	945	±10	1490	±60	944	±189				
<i>1000–7000 Years (cal Years BP)</i>										
X12-3-47	1133	±6	1720	±60	1234	±175				
X12-3-106	1258	±6	1830	±60	1346	±169				
X12-3-107	1307	±6	1880	±50	1393	±149				
X12-16-9	1623	±7	2110	±60	1647	±204				
P2 <sup>d</sup>	1685	±5	2190	±70	1739	±212				
X12-D3-1	1979	±9	2480	±70	2088	±214				
P37 <sup>d</sup>	2342	±7	2670	±60	2321	±248				
V10 <sup>d</sup>	3066	±12	3310	±100	3097	±281				
X12-D1-6	3234	±11	3340	±70	3136	±234				
X12-D1-4	3295	±12	3380	±70	3192	±232				
P26 <sup>d</sup>	3531	±11	3690	±80	3561	±238				
X12-D2-1	3742	±13	3810	±60	3710	±218				
P43 <sup>d</sup>	3802	±17	4010	±90	3975	±299				
P38 <sup>d</sup>	4978	±14	4880	±70	5129	±261				
P11 <sup>d</sup>	5068	±15	4920	±80	5175	±270				
V39 <sup>d</sup>	5951	±13	5360	±90	5694	±222				
V24 <sup>d</sup>	5955	±13	5480	±80	5810	±221				
V30 <sup>d</sup>	5979	±13	5460	±90	5792	±232	5525	±20	5861	±147
V13 <sup>d</sup>	6020	±12	5710	±100	6073	±252				
V2 <sup>d</sup>	6051	±14	5710	±90	6074	±223				
V8 <sup>d</sup>	6073	±18	5780	±80	6145	±211				
V28 <sup>d</sup>	6350	±13	5060	±90	5369	±264				
V33 <sup>d</sup>	6593	±13	4900	±90	5151	±280	5120	±20	5439	±131
V11 <sup>d</sup>	6878	±15	6360	±90	6788	±273				

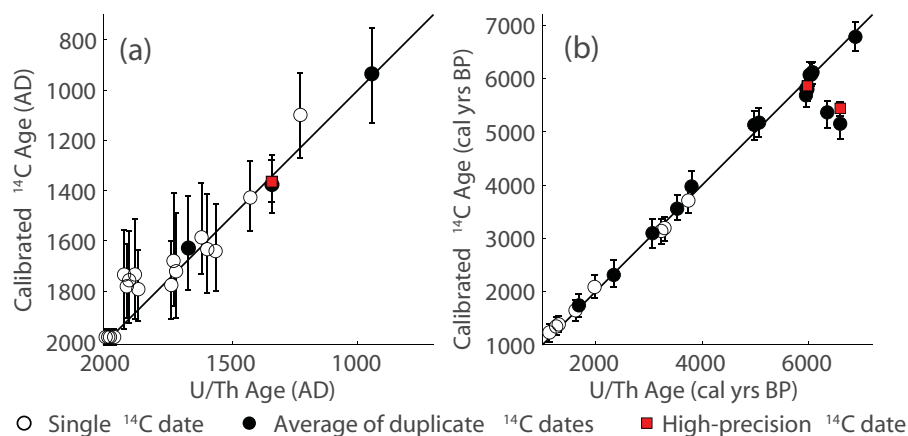
<sup>a</sup>Samples italicized were originally published in Cobb et al. [2003b] and Cobb et al. [2013].

<sup>b</sup>Errors quoted are 2σ.

<sup>c</sup><sup>14</sup>C ages were calibrated to calendar years using Calib7.1 software [Stuiver and Reimer, 1993] and Marine13 calibration data sets [Reimer et al., 2013] and corrected for a local reservoir age using ΔR of 39 ± 56 [McGregor et al., 2011]. The <sup>14</sup>C calibrated age is reported as the median probability. Calibrated <sup>14</sup>C errors are 2σ.

<sup>d</sup><sup>14</sup>C age shown are averages, rounded to the nearest decade.

± 13 cal years BP, respectively [Cobb et al., 2013], whereas the calibrated rapid-screen <sup>14</sup>C ages fall between 5057 and 5585 cal years BP for V28 and 4867 and 5427 cal years BP for V33. Duplicate analyses of the rapid-screen <sup>14</sup>C ages from these samples agree with our initial <sup>14</sup>C ages within error (see supporting information Table S1). One high-precision <sup>14</sup>C-AMS age from sample V33 also falls within error of the rapid-screen <sup>14</sup>C ages. However, duplicate U/Th ages from V28 and V33 differ by 3% and 5%, respectively, from the published results (see supporting information Table S2), indicative of small-scale heterogeneity in U/Th chemistries in these samples. Subsequent XRD analysis confirms that V28 and V33 contain 15% and 23% calcite, respectively, indicating substantial post-depositional alteration of the primary aragonitic skeleton and signaling open system geochemical behavior. The δ<sup>234</sup>U<sub>initial</sub> values for both V28 and V33 reflect seawater



**Figure 2.** U/Th and calibrated <sup>14</sup>C fossil coral dates plotted for (a) the last millennium (in years AD) and (b) 1000–7000 cal years BP. Open circles represent samples with only one rapid-screen <sup>14</sup>C date; black circles represent the average of multiple rapid-screen <sup>14</sup>C dates using replicate samples from the same coral. The median probability of the calibrated rapid-screen <sup>14</sup>C date is plotted with error bars representing the 2σ age range. The 2σ error bars for U/Th dates are smaller than the symbol size. Calibrated high-precision <sup>14</sup>C-AMS dates are plotted as red squares.

δ<sup>234</sup>U values within error, illustrating the limitations of <sup>234</sup>U initial as a screening tool for open system behavior in young corals [Chen et al., 1991; Gallup et al., 2002; Cutler et al., 2003; Henderson, 2002; Zaunbrecher et al., 2010].

### 3.3. Effect of Secondary Calcite on <sup>14</sup>C and U/Th Ages

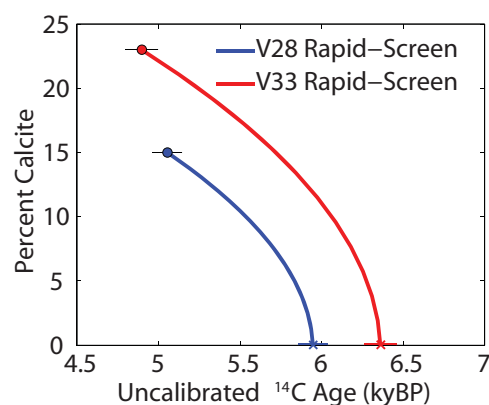
In an effort to reconcile the discrepancies between the measured <sup>14</sup>C and U/Th ages for fossil corals V28 and V33, we use a mass balance model to estimate the effect that continuous replacement of aragonite to calcite has on <sup>14</sup>C and U/Th ages (Figure 3). The model is calculated using the following mass balance equation:

$$A_m = A_T * (1 - C) + (T * C)$$

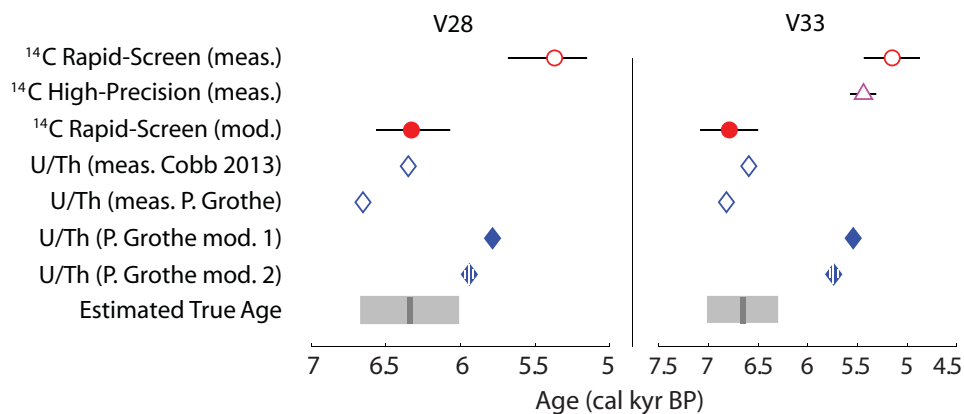
where  $A_m$  is the measured age,  $A_T$  is the true age,  $C$  is the percent calcite and  $T$  is the time at which alteration occurs. The equation is solved iteratively for true age for both <sup>14</sup>C and U/Th systems, beginning with 100% aragonite at the time of formation (true age) and ending with 15% and 23% calcite, respectively, at 1950 AD (prebomb). While we acknowledge that a continuous replacement of aragonite to calcite oversimplifies the diagenetic history of these samples, our approach provides a means of roughly quantifying

potential diagenetic effects on the radiometric dating systematics for these two samples. For <sup>14</sup>C ages, we use the uncalibrated, rapid-screen <sup>14</sup>C ages as inputs into the model and calibrate the resulting estimates of modeled <sup>14</sup>C ages for comparison with the corals' estimates of true U/Th ages (Figure 4). While V33 has a high-precision <sup>14</sup>C age that would ideally provide a better input to our model, the chemical leaching performed as part of sample preparation for graphitization likely removed some of the secondary phases of interest [Santos et al., 2004]. For U/Th, we only model the ages measured by P. Grothe since that is the sample for which we have XRD analyses.

The continuous replacement of aragonite to calcite has the effect of adding <sup>14</sup>C to the coral skeleton through time, making our measured <sup>14</sup>C ages 900–1500 years younger than the estimated modeled age. Fossil coral V28's uncalibrated modeled <sup>14</sup>C age is 5950 ± 90 years BP, or 893 years older than the measured rapid-screen <sup>14</sup>C age, while V33's corrected



**Figure 3.** Mass balance model of coral <sup>14</sup>C ages assuming continuous replacement of aragonite to calcite, for V28 (rapid-screen <sup>14</sup>C date—blue solid line) and V33 (rapid-screen <sup>14</sup>C date—red solid line), assuming 15 and 23% calcite, respectively. Dates plotted are for uncalibrated <sup>14</sup>C dates. Note 2σ error bars on the high-precision date are smaller than the symbol size.



**Figure 4.** Measured and modeled ages for all coral U/Th dates and calibrated  $^{14}\text{C}$  dates. Error bars ( $2\sigma$ ) are shown for all calibrated  $^{14}\text{C}$  dates but are smaller than the symbol for the U/Th dates. Measured dates are plotted as open symbols and modeled dates are plotted as closed symbols, with circles for rapid-screen  $^{14}\text{C}$  dates, triangles for high-precision  $^{14}\text{C}$  dates, and diamonds for U/Th dates. The modeled 1 (mod. 1) U/Th date (solid blue diamond) represents no U incorporation into the calcite whereas the modeled 2 (mod. 2) U/Th date (blue diamond with white stripes) represents 19% of the U loss being incorporated into the calcite. The dark gray vertical line represents our estimate true age with gray boxes denoting error bars that are 50% of the original difference between the measured  $^{14}\text{C}$  and U/Th dates.

modeled  $^{14}\text{C}$  age is  $6360 \pm 100$  years BP, or 1493 years older than the measured rapid-screen  $^{14}\text{C}$  age. Our model does not account for changes in atmospheric  $\Delta^{14}\text{C}$  through time because incorporating such variations results in age differences that are smaller than the stated uncertainties on our modeled ages. When we calibrate the modeled  $^{14}\text{C}$  ages, the dates range from 6096 to 6588 cal years BP (median probability 6329 cal years BP) for V28 and 6503 to 7087 cal years BP (median probability 6789 cal years BP) for V33. The calibrated modeled  $^{14}\text{C}$  ages agree with one of the two measured U/Th dates for V28 and both of the measured U/Th dates for V33. One of the measured U/Th dates for V28 is older than the calibrated modeled  $^{14}\text{C}$  age, implying that U loss may have occurred heterogeneously in the sample.

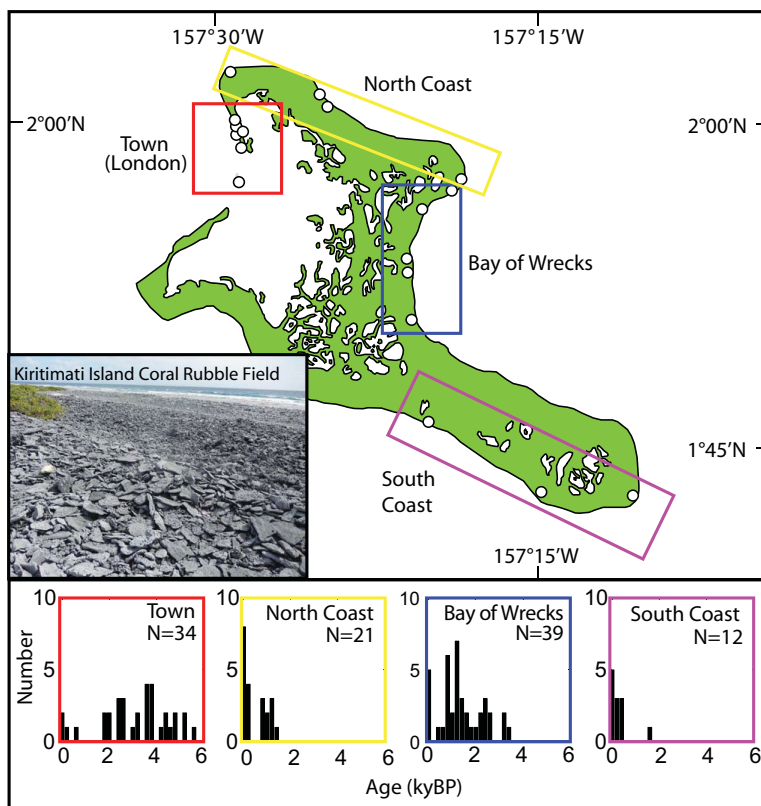
We apply the same continuous calcite replacement model to investigate potential impacts on the samples' U/Th ages, assuming that the modeled U/Th ages will be younger owing to U loss during recrystallization [e.g., Henderson *et al.*, 1993; Shen and Dunbar, 1995; Scholz *et al.*, 2004; Scholz and Mangini, 2007]. Here we assume that 15% and 23% of V28's and V33's aragonite has dissolved and reprecipitated as calcite, respectively, mobilizing the soluble U but not the immobile Th [Chen *et al.*, 1991]. Experimental estimates for U distribution coefficients (D) in calcite range from  $\sim 8 \times 10^{-3}$  for biotic processes [Russell *et al.*, 1994] to 0.19 for abiotic processes [Kitano and Oomori, 1971; Meece and Benninger, 1993; Reeder *et al.*, 2001; Heberling *et al.*, 2008]. If we assume that no U is incorporated into the calcite after aragonite dissolution (i.e., equivalent to 15 and 23% U loss), then V28's modeled age estimate is 5785 cal years BP and V33 is 5543 cal years BP (Figure 4)—roughly 900 and 1300 years younger than the measured ages, respectively. Assuming that up to  $\sim 19\%$  of the aragonite-derived U may be reincorporated into the calcite (i.e., equivalent to  $D=0.19$ ), then the samples would have experienced 12% and 19% U loss (modeled as 12% and 19% calcite), with modeled U/Th age estimates of 5941 cal years BP and 5739 cal years BP, respectively (Figure 4). Both modeled U/Th age estimates for V28 and V33 are older than the measured  $^{14}\text{C}$  ages but younger than the corrected  $^{14}\text{C}$  ages using the same model.

To obtain a best estimate of the true ages of our diagenetically altered samples, we take the median of the modeled  $^{14}\text{C}$  ages, the modeled U/Th ages assuming 19% of the aragonite-derived U is reincorporated into the calcite, and both measured U/Th dates. This choice reflects the fact that there is mixed evidence for U loss during diagenesis in these samples—three of the four measured U/Th dates agree with the modeled rapid-screen  $^{14}\text{C}$  dates. By assigning  $1\sigma$  error bars that are at least 50% of the original difference between the measured  $^{14}\text{C}$  and U/Th dates, we estimate true ages to be  $6340 \pm 325$  ( $1\sigma$ ) cal years BP for V28 and  $6690 \pm 345$  ( $1\sigma$ ) cal years BP for V33 (Figure 4 and see supporting information Table S3).

### 3.4. Age Distribution of Fossil Coral Rubble on Kiritimati Island

The rapid-screen  $^{14}\text{C}$  and U/Th dating analyses of 106 undated fossil coral samples yielded a first-order chrono-map of the coral rubble fields across Kiritimati Island. Forty-four of these samples were randomly screened for XRD analysis to detect the presence of diagenetic calcite. Of these, only one sample had a





**Figure 5.** Age distributions of fossil coral samples collected on ocean-facing beaches at Kiritimati Island. Sites are grouped into four regions—the town, the north coast, the Bay of Wrecks and the south coast. Histograms were computed using bins of 200 years. For samples that have both rapid-screen  $^{14}\text{C}$  and U/Th dates, only the U/Th date is represented as it has the lowest uncertainty. Inset is a fossil coral rubble field seen on Kiritimati Island. The ridgelines of fossil coral rubble are characteristic of the rubble fields along the windward side of the island.

detectable amount of calcite ( $>0.5\%$ ), with a Rietveld refinement estimate of  $\sim 15$  weight %. We thus conclude that the vast majority of fossil coral samples we collected on the rubble beaches at Kiritimati Island are well preserved with respect to calcite recrystallization.

Our results show that the fossil coral dates cluster by site whereby older samples (2000–6000 cal years BP) originate from sites in and around the town of London and younger samples ( $<3000$  cal years BP) occur along the windward sites including the Bay of Wrecks (Figure 5). Coral ages progressively get older farther back from the waterline (as documented at FS-1, FS-3, FS-13, FS-24, and FS-25, see supporting information Table S4), indicative of storm-derived deposits [Richmond and Morton, 2007]. At fossil coral collection site FS-1, samples collected just behind the intertidal zone date within a narrow range of 20–63 cal years BP ( $N=3$ ). Along a well-defined ridgeline roughly 17 m from the waterline at site FS-24, fossil corals date in a relatively narrow range between 808 and 940 cal years BP ( $N=3$ ). Moving even farther inland at the same site to a ridge  $\sim 80$  m from the waterline, samples date across a wide range of 1870 and 3163 cal years BP ( $N=3$ ).

#### 4. Discussion

Concordant rapid-screen  $^{14}\text{C}$  and U/Th dates from 42 of the 44 corals analyzed suggest the rapid-screen  $^{14}\text{C}$  dating method, when combined with XRD, is an accurate method for dating fossil corals from the last 7000 years. However, most of our rapid-screen  $^{14}\text{C}$  dates are associated with uncertainties on the order of several hundred years ( $2\sigma$ ). The magnitude of this uncertainty is largely independent on the sample's age, as it derives from uncertainties in the  $^{14}\text{C}$  blank subtraction, which is arbitrarily set at  $\pm 50\%$  [Bush *et al.*, 2013]. These large uncertainties are prohibitive for some applications, particularly reconstructions of climate during the last millennium [e.g., Kuhnert *et al.*, 2002; Cobb *et al.*, 2003b; Holland *et al.*, 2014], but are relatively modest for samples from the early to mid-Holocene.

Variations in  $\Delta R$  on centennial to millennial timescale in the Line Islands may explain some differences in concordant  $^{14}\text{C}$  and U/Th ages, particularly where the  $^{14}\text{C}$  points cluster above and below the one-to-one line at 5000 and 5900 cal years BP. Some studies using paired  $^{14}\text{C}$  and U/Th dates for  $\Delta R$  calculations do find significant variations in  $\Delta R$  during the mid-Holocene in the tropical Pacific [Yu *et al.*, 2010; McGregor *et al.*, 2008; Hua *et al.*, 2015], most likely due to changes in the  $^{14}\text{C}$  content of upwelled water and/or variations in ocean circulation [Hua *et al.*, 2015]. However, without additional paired high-precision  $^{14}\text{C}$  and U/Th ages and sample replication to assure against diagenetic influences on our derived  $\Delta R$  estimates, we cannot provide robust new constraints on  $\Delta R$  from our study. It is important to note that variations on  $\Delta R$  cannot explain the large age discrepancies in V28 and V33.

Rapid-screen  $^{14}\text{C}$  ages from five samples that grew between 1950 and  $\sim 1800$  AD are consistently older than the corresponding U/Th ages, though still within  $2\sigma$  errors. This consistent offset likely derives from a prolonged plateau in the  $^{14}\text{C}$  calibration curve from  $\sim 1800$  to 1950 AD that causes calibrated  $^{14}\text{C}$  dates of samples that formed during this time to be slightly biased toward older ages [Stuiver *et al.*, 1998; Taylor and Bar-Yosef, 2014].

Two discordant  $^{14}\text{C}$  and U/Th ages from samples with moderate calcite recrystallization (15–30%) illustrate the profound effect that diagenesis can have on the accuracy of coral radiometric ages. The measured  $^{14}\text{C}$  ages from the altered samples have diagenetically derived age offsets that are 3–4 times larger than analytical error. Assuming a continuous replacement of aragonite to calcite for a sample 7000 years old, as little as 2% of recrystallized calcite can change a coral's  $^{14}\text{C}$  age by  $\sim 1.7\%$ , with effects increasing with greater calcite contents. Obviously, if any recrystallization occurred in the post-bomb era, then the effect on the measured  $^{14}\text{C}$  age would be much larger.

Age biases due to diagenetic alteration can be identified a priori and independently through the application of both XRD and SEM, as we have demonstrated. SEM images of V28 and V33 reveal evidence for some trace carbonate dissolution and precipitation [Cobb *et al.*, 2013], but SEM cannot be used to quantitatively screen fossil corals for radiometric dating. XRD, however, provides a quantitative measurement of the amount of calcite in a sample, allowing us to correct for such age biases, but cannot detect secondary aragonite. Evidence of secondary aragonite crystals on Line Island corals has been observed to varying degrees on modern [Nurhati *et al.*, 2011], last millennium [Zaunbrecher *et al.*, 2010; Sayani *et al.*, 2011], and mid-Holocene corals [Cobb *et al.*, 2013] via SEM, with most containing less than  $\sim 1\%$  by weight. We find insignificant age affects with samples containing trace amounts of secondary aragonite, in agreement with Lazar *et al.* [2004]. As a best timesaving practice for radiometric dating, we recommend a priori screening by XRD followed by SEM imaging on samples subsequently chosen for paleoclimate studies.

The convergence of modeled  $^{14}\text{C}$  and measured U/Th ages for altered fossil corals using the continuous alteration mass balance model strongly implies that this approach yields reasonable constraints on these two samples' true ages. We assume that calcite is continuously replaced to aragonite, which oversimplifies the true diagenetic history as recrystallization may have occurred episodically [Cheng *et al.*, 1998; Scholz *et al.*, 2004]. The model also assumes an open system behavior when previous other studies suggest the dissolution and recrystallization could occur in a closed or semiclosed system [Bathurst, 1974; Pingitore, 1976; Maliva and Dickson, 1992], or through simultaneous open and closed-system calcite precipitation [Rabier *et al.*, 2008]. Our assumption that diagenesis is a continuous process echoes similar assumptions made in a suite of other studies that model open-system U/Th systematics in corals [Bender *et al.*, 1979; Gallup *et al.*, 1994; Thompson *et al.*, 2003; Villemant and Feuillet, 2003; Scholz *et al.*, 2004]. When our mass balance model is applied to the two altered samples' measured dates, the convergence of corrected rapid-screen  $^{14}\text{C}$  and uncorrected U/Th dates implies that only as little as 6–8% U may have been lost from the samples in the course of diagenesis, based on our estimated true ages. Nonetheless, we assign conservative error bars for our estimate of true ages for altered fossil corals, reflecting 50% of the difference between measured  $^{14}\text{C}$  and U/Th dates, amounting to errors of roughly  $\pm 5\%$  ( $1\sigma$ ) for these  $\sim 6.4$  cal kyr BP corals.

## 5. Conclusion

The rapid-screen  $^{14}\text{C}$  dating method provides a quick, inexpensive, and accurate dating method for relatively young ( $< 10,000$  year old) carbonate samples with mild alteration ( $< 2\%$ ) compared to high-precision  $^{14}\text{C}$  and U/Th dating methods. Rapid-screen  $^{14}\text{C}$  dating uncertainties amount to  $\pm 100$ – $200$  years ( $2\sigma$ ) for last millennium-aged samples and  $\pm 200$ – $300$  years ( $2\sigma$ ) for mid-Holocene-aged samples. However,

screening for diagenesis via XRD is necessary as both U/Th and  $^{14}\text{C}$  ages are sensitive to calcite recrystallization levels of  $>2\%$ .  $^{14}\text{C}$  ages of altered corals are more sensitive to open system behavior owing to the incorporation of atmospheric  $^{14}\text{C}$  during the recrystallization process, and its shorter half-life. We demonstrate that fossil coral U/Th ages are more robust for Holocene-aged samples exhibiting moderate alteration (10–20%), owing to the relatively long half-lives of U and Th isotopes. Our results show that significant diagenesis-related age discrepancies between rapid-screen  $^{14}\text{C}$  and U/Th dates can be reconciled by modeling a continuous aragonite-to-calcite replacement, given XRD estimates of percent calcite in the sample as inputs. Lastly, application of this rapid-screen  $^{14}\text{C}$  method to the fossil coral rubble fields from Kiritimati Island reveal significant chronological clustering of fossil corals along pronounced ridgelines, where older ages are found farther from the coastline, consistent with storm-derived origin of the fossil coral deposits.

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