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# Redundant $^{230}Th/^{234}U/^{238}U$, $^{231}Pa/^{235}U$ and $^{14}C$ dating of fossil corals for accurate radiocarbon age calibration

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## Abstract

$^{230}Th/^{234}U/^{238}U$ dating of fossil corals by mass spectrometry is remarkably precise, but some samples exposed to freshwater over thousands of years may gain and/or lose uranium and/or thorium and consequently yield inaccurate ages. Although a $\delta^{234}U_{initial}$ value equivalent to modern seawater and modern corals has been an effective quality control criterion, for samples exposed to freshwater but having $\delta^{234}U_{initial}$ values indistinguishable from modern seawater and modern corals, there remains a need for additional age validation in the most demanding applications such as the $^{14}C$ calibration (Fairbanks et al., 2005. Radiocarbon calibration curve spanning 0 to 50,000 years BP based on paired $^{230}Th/^{234}U/^{238}U$ and $^{14}C$ dates on pristine corals. Quaternary Science Reviews 24(16–17), 1781–1796). In this paper we enhance screening criteria for fossil corals older than 30,000 years BP in the Fairbanks0805 radiocarbon calibration data set (Fairbanks et al., 2005) by measuring redundant $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dates via multi-collector magnetic sector inductively coupled plasma mass spectrometry (MC-MS-ICPMS) using techniques described in Mortlock et al. (2005. $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ ages from a single fossil coral fragment by multi-collector magnetic-sector inductively coupled plasma mass spectrometry. Geochimica et Cosmochimica Acta 69(3), 649–657.). In our present study, we regard paired $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ ages concordant when the $^{231}Pa/^{235}U$ age ($\pm 2\sigma$) overlaps with the associated $^{230}Th/^{234}U/^{238}U$ age ($\pm 2\sigma$). Out of a representative set of 11 Fairbanks0805 (Fairbanks et al., 2005) radiocarbon calibration coral samples re-measured in this study, nine passed this rigorous check on the accuracy of their $^{230}Th/^{234}U/^{238}U$ ages. The concordancy observed between $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dates provides convincing evidence to support closed system behavior of these fossil corals and validation of their $^{230}Th/^{234}U/^{238}U$ dates for radiocarbon calibration and $\Delta^{14}C$ reconstruction.

## 1. Introduction

The records of atmospheric $^{14}C$ concentrations contain important information about the Earth's history (Libby, 1955; Stuiver and Quay, 1980; Damon, 1988; Bard et al., 1990a; Edwards et al., 1993). Fluctuations in atmospheric $^{14}C$ are controlled by changes in the solar magnetic field (de Vries, 1959; Stuiver and Quay, 1980), in the geomagnetic field intensity (Sternberg and Damon, 1992; Bard et al., 1990a; Guyodo and Valet, 1999; Laj et al., 2000; Laj et al., 2002), and in the carbon cycling (Siegenthaler et al., 1980; Edwards et al., 1993; Hughen et al., 2000), and these factors operate on different time scales. As a result of these geophysical and geochemical processes, the radiocarbon age of an ancient sample is not equivalent to the calendar age and the radiocarbon chronometer must be calibrated. The most precise and accurate calibration can be achieved when both $^{14}C$ ages and calendar ages are obtained from the same archived sample (Stuiver and Pearson, 1986; Fairbanks et al., 2005).

Tremendous efforts have been made to extend the history of atmospheric or surface ocean $^{14}C$ content beyond tree-ring records (Stuiver and Reimer, 1993;

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Stuiver et al., 1998) using various archives such as speleothems, lake sediments, marine carbonates, and deep-sea sediments (Vogel, 1980, 1983; Vogel and Kronfeld, 1997; Kitagawa and van der Plicht, 2000; Schramm et al., 2000; Voelker et al., 2000; Beck et al., 2001; Haase-Schramm et al., 2004; Hughen et al., 2004; van der Plicht et al., 2004), and corals (Bard et al., 1990a, b; Burr et al., 1998; Yokoyama et al., 2000; Cutler et al., 2004; Fairbanks et al., 2005). Although some of these radiocarbon calibration or radiocarbon comparison data sets have been incorporated in radiocarbon calibration programs (Stuiver et al., 1998; Jöris and Weninger, 2000; Weninger and Jöris, 2004; Reimer et al., 2004; Hughen et al., 2004; Fairbanks et al., 2005), others were utilized for the reconstruction of atmospheric or surface ocean $^{14}$C content. The various archives of atmospheric $^{14}$C content depart from one another beyond 13,000 years BP and depart dramatically beyond 24,000 years BP (Fig. 1), suggesting significant dating inaccuracies or weak assumptions in more than one of these studies (van der Plicht et al., 2004). Despite the quantity and quality of the radiometric measurements, most of these prior radiocarbon calibration or radiocarbon comparison attempts have not been widely adopted for radiocarbon calibration purposes (Reimer et al., 2004; van der Plicht et al., 2004) mainly because of uncertainties in the sample quality and geochemical history. The IntCal04 group formally concluded (Reimer et al., 2004; van der Plicht et al., 2004) that the discrepancies between competing radiocarbon calibration data sets older than 26,000 years BP were too large and the sources of these differences too uncertain that they were unsuitable for inclusion in the IntCal04 radiocarbon calibration curve. Instead, IntCal04 published an updated data "comparison curve" entitled NOTCal04 (van der Plicht et al., 2004).

Fossil corals may be regarded as one of the best archives for providing absolute chronology and extending $^{14}$C calibration beyond that obtained with tree rings (i.e. beyond 12,400 years BP) (Bard et al., 1990a; Cutler et al., 2004; Reimer et al., 2004; Hughen et al., 2004; Fairbanks et al., 2005). One of the greatest advantages to using fossil corals for radiocarbon calibration is that both $^{14}$C and $^{230}$Th/$^{234}$U/$^{238}$U ages can be measured accurately and precisely, and the corresponding errors are independent and have known uncertainties. Another advantage to corals is the fact that large samples may be collected from many tropical and subtropical locations worldwide and can be analyzed by independent laboratories using a range of processing procedures and instrumentation types for radiocarbon calibration validation.

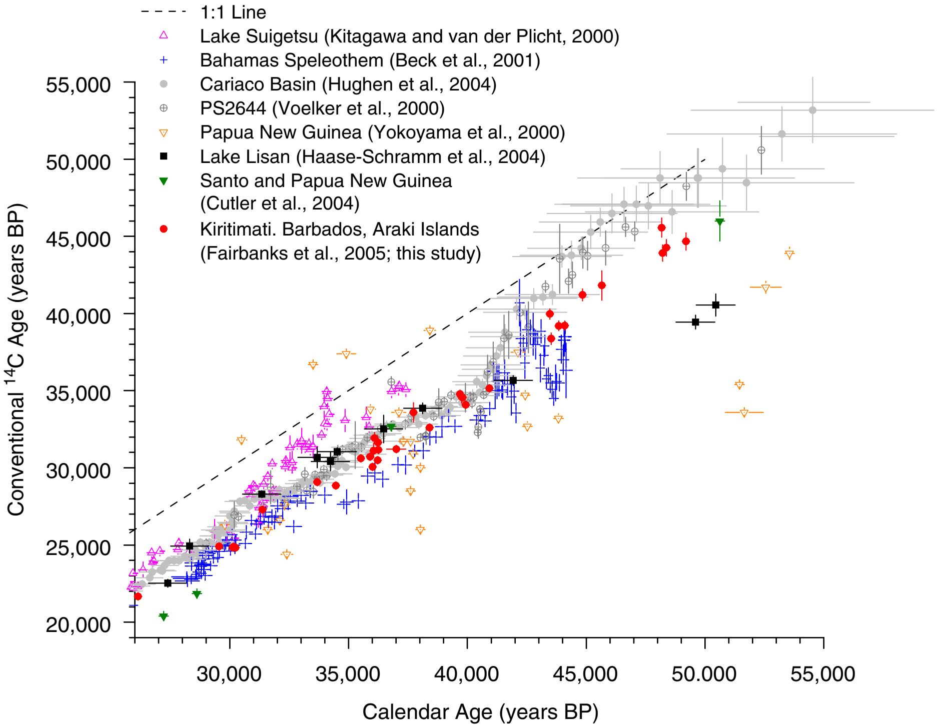

Fig. 1. Various attempts for radiocarbon calibration between 20,000 and 50,000 years BP. The 1:1 line is presented merely for reference. Pink triangles represent varve records from Lake Suigetsu in Japan (Kitagawa and van der Plicht, 2000). Blue crosses represent a stalagmite record from a submerged cave in the Bahamas (Beck et al., 2001). Solid and open gray circles represent deep-sea sediment records from Cariaco Basin (Hughen et al., 2004) and the Iceland Sea (Voelker et al., 2000), respectively. $^{14}$C ages in Core PS2644 in the Iceland Sea have been corrected for 600-year reservoir age for comparison. Orange open reversed triangles represent fossil corals from Papua New Guinea (Yokoyama et al., 2000). Green solid reversed triangles represent coral records from Santo and Papua New Guinea in Cutler et al. (2004). Black squares represents the records obtained from carbonates in Lake Lisan, Dead Sea (Haase-Schramm et al., 2004). Solid red circles represent fossil corals from Kiritimati, Barbados and Araki Island (Fairbanks et al, 2005; this study). All U-series dated coral archives were corrected using the most recent estimates of the $^{230}$Th and $^{234}$U half-lives (Cheng et al., 2000) in this figure.

While age dating of fossil corals by mass spectrometry is remarkably precise, a potential shortcoming of $^{230}Th/^{234}U/^{238}U$ dating in samples older than 30,000 years BP is that corals may have been exposed to fresh water during sea level low stands. Only coral samples that grew at paleo-water depths deeper than 120 m remained in seawater during the subsequent glacial sea level lowstand (Fairbanks 1989; Peltier and Fairbanks, 2005). Exposure to the vados (rainwater percolating zone) and phreatic lens (fresh water table) may lead to gain and/or loss of U and/or Th, changing the [$^{230}Th/^{234}U$] activity ratio in the samples and thus compromising the accuracy of age determinations (Bender et al., 1979; Edwards et al., 1987; Hamelin et al., 1991; Gallup et al., 1994). Such open system behavior of samples cannot be easily identified but is typically recognized by the departure from the initial [$^{234}U/^{238}U$] activity ratio (denoted as $\delta^{234}U_{initial}$) of a coral from the modern seawater value (Bender et al., 1979; Edwards, 1988; Hamelin et al., 1991; Henderson et al., 1993; Thompson et al., 2003; Scholz et al., 2004; Mey et al., 2005). For samples that have been exposed to the vados or phreatic lens but have $\delta^{234}U_{initial}$ values consistent with modern seawater and modern corals, there remains a need for age validation (Gallup et al., 2002; Cutler et al., 2003, 2004; Mortlock et al., 2005) in the most demanding applications such as the $^{14}C$ calibration (Fairbanks et al., 2005).

In this study, we present redundant $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dates on fossil coral samples older than 29,000 years BP used in the Fairbanks0805 calibration curve (Fairbanks et al., 2005). On the basis of the redundant and concordant $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ coral ages in our radiocarbon calibration data set and the prescreening criteria for our radiocarbon measurements outlined in Chiu et al. (2005), we contend that the concordant data are accurate, reproducible and validate their use for calibration purposes.

## 2. Methods

### 2.1. Sampling

A minimum of 200–500 fg of $^{231}Pa$ is required for accurate $^{231}Pa/^{235}U$ dating of fossil coral by MC-MS-ICPMS, and so the required sample size is dependent upon the age and U content of the coral. For a coral with a U content of 2.5–3.5 ppm and in the age range of 30,000–55,000 years BP, about 500–800 mg of sample is needed. Fragments are mechanically cleaned for a two-hour duration in Mili-Q (18 MΩ) water with a high-powered ultrasonic probe and dried at $T = 60\,^{\circ}C$. The U-series samples in this study were ultrasonically cleaned but not chemically etched prior to dissolution in order to avoid potential Th adsorption problems. Nevertheless, the reliability of U-series dates determined from samples found to contain significant $^{232}Th$ (greater than 1 ppb) should be questioned. Samples are screened for calcite by XRD at <0.2% detection level (Chiu et al., 2005). This is a particularly important screening step for outcrop coral samples which have been exposed to freshwater and have the potential of being contaminated with diagenetic calcite, thereby compromising the accuracy of the $^{14}C$ age.

### 2.2. Chemical procedures

The chemical procedure used to separate U, Th, and Pa in fossil coral is briefly described in this section although a more detailed description and documentation can be found in Mortlock et al. (2005). A mixed $^{233}U$–$^{229}Th$ spike was added to the sample to approximate a target ratio of $^{229}Th/^{230}Th$ equal to 10 and $^{233}Pa$ spike was added to approximate a target ratio of $^{233}Pa/^{231}Pa$ equal to 2. For corals in the age range of 30,000–55,000 years BP, about 1.5 ng $^{233}U$ and about 0.5–1 pg of $^{233}Pa$ is added as spike. Since the spiking of samples with $^{233}Pa$ may take place hours to days following its purification, some additional quantity of its daughter product, $^{233}U$, may be added. Although the additional contribution to the $^{233}U$ spike from $^{233}Pa$ decay represents at most about 0.1% of the total, a correction is made to the isotope dilution calculation for total uranium.

Following sample dissolution in concentrated nitric acid and spike equilibration, iron-hydroxide precipitation, and sample re-dissolution, separation of U, Th, and Pa was achieved through anion exchange column chemistry (Mortlock et al., 2005). In the case where only U and Th measurements are required, separation of U from Th can be accomplished by the chemistry slightly modified from previous studies (Edwards, 1988; Bard et al., 1990b) (Table 1).

Table 1
Column chemistry to separate Th and U from the same dissolved solution slightly modified from previous studies (Edwards, 1988; Bard et al., 1990b). One drop approximately equals 33 micro-liters

| Column | 500 µl, AG1-X8 200–400 m | |
|---|---|---|
| Step | Description | Comments |
| 1. Cleaning | 7 N $HNO_3$ (2 ml) | |
| | 0.1 N HCl (1 ml) | |
| | 6 N HCl (1 ml) | |
| | Mili-Q $H_2O$ (1 ml) | |
| 2. Cleaning | Repeat step 1. | |
| 3. Cleaning | Repeat step 1. | |
| 4. Condition | 7 N $HNO_3$ (20 drops) | |
| | 7 N $HNO_3$ (20 drops) | |
| 5. Load sample | 7 N $HNO_3$ (0.5 ml) | |
| 6. Wash beaker | 7 N $HNO_3$ (16 drops) | |
| 7. Wash column | 7 N $HNO_3$ (30 drops) | Major waste cations eluted |
| | 7 N $HNO_3$ (30 drops) | |
| 8. Collect Th | 6 N HCl (15 drops) | |
| | 6 N HCl (30 drops) | |
| | 6 N HCl (15 drops) | Th eluted, adsorption of U |
| 9. Collect U | 1 N HBr (15 drops) | |
| | 1 N HBr (30 drops) | |
| | 1 N HBr (30 drops) | U eluted |

Table 2
Results of the Yemen speleothem, Y99-7Ra, selected to be a secular-equilibrium standard in terms of $^{231}$Pa/$^{235}$U system and processed via our Pa–Th–U methods (see text for details). Numbers in quotes represent the analytical error (2σ). We use decay constants $\lambda_{230} = 9.1577 \times 10^{-6}$ year$^{-1}$ and $\lambda_{234} = 2.8263 \times 10^{-6}$ year$^{-1}$ (Cheng et al., 2000) in all calculations

| Sample ID | [$^{230}$Th/$^{234}$U] measured activity | [$^{234}$U/$^{238}$U] measured activity | $^{232}$Th (pg/g) | [U] (ppm) |
|---|---|---|---|---|
| Y99-7Ra #1 | 1.0057 (0.0019) | 1.0040 (0.0009) | 56 | 3.15 |
| Y99-7Ra #2 | 1.0047 (0.0016) | 1.0082 (0.0010) | 59 | 3.05 |
| Y99-7Ra #3 | 1.0026 (0.0021) | 1.0099 (0.0008) | 75 | 3.45 |
| Y99-7Ra #4 | 1.0027 (0.0015) | 1.0106 (0.0009) | 79 | 3.38 |

In order to estimate the Pa "yield" for our column chemistry procedure, a "yield-check" test was conducted. 0.8 pg of $^{233}$Pa was added to a 7 ml PFA (Savillex) beaker and diluted with 5 ml of 1% HF in 2% $HNO_3$. The radioactive activity of this solution was determined by a well-type Na(I) detector connected to a multiple channel analyzer and measured the 311 keV $^{233}$Pa emission. The date and time were recorded. The solution was then dried down to a small volume (equivalent to a drop). We added 7 N $HNO_3$ and dried the solution to completeness. This procedure was repeated for several times to convert the original matrix (1% HF in 2% $HNO_3$) to 7 N $HNO_3$. After final dry-down, 16 drops of 7 N $HNO_3$ was added in the beaker and the entire solution was loaded on a column. The Pa in the solution was then separated from U and Th by the methods already described (Mortlock et al., 2005). The purified Pa fraction was diluted with 4 ml of 1% HF in 2% $HNO_3$ to a total volume of 5 ml and was again measured by the same well-type Na(I) detector for its activity. After correcting for radioactive decay of $^{233}$Pa (half-life = 26.967 ± 0.004 days) (Jones et al., 1986) and comparing gamma counts before and after column chemistry, we conclude that the recovery for Pa in this test was 98%.

### 2.3. Mass spectrometry

U, Th, and Pa isotopic measurements are made using a multi-collector magnetic sector inductively coupled plasma mass spectrometer (MC-MS-ICPMS), FISONS Plasma 54, at Lamont–Doherty Earth Observatory (LDEO) by the methods described in Mortlock et al. (2005). Measurement precision of the U and Th isotope ratios are generally better than ±0.09% and ±0.3% (2 RSD), respectively. Precision of the $^{233}$Pa/$^{231}$Pa ratio measurement in the speleothem standard and most coral samples averaged about ±1% (2 RSD).

Discussions of some of the analytical challenges associated with the determination of Pa concentrations and $^{231}$Pa/$^{235}$U dating by Thermal Ionization Mass Spectrometry (TIMS) can be found in earlier studies (Pickett et al., 1994; Edwards et al., 1997). Pa concentration measurements by standard isotope dilution methods are complicated because no certified Pa standard exists and so a suitable $^{231}$Pa standard must be selected in order to calibrate the $^{233}$Pa spike.

We selected a speleothem specimen from Yemen (sample ID: Y99-7Ra) to serve as our reference standard. During the course of this study, Y99-7Ra was routinely processed in duplicate with each batch of coral samples. The reported uranium content (3.05–3.45 ppm) and low $^{232}$Th content (56–79 pg/g) makes it an ideal standard for this study (Table 2). The measured activity ratio of [$^{230}$Th/$^{234}$U] averaged 1.0039 ± 0.0031 (2SD; $n = 4$) (Table 2) and so the speleothem can be assumed to be in secular equilibrium in terms of the $^{231}$Pa/$^{235}$U decay system (i.e. $[^{231}\mathrm{Pa}/^{235}\mathrm{U}]_{\mathrm{activity}} = 1$).

We measured the 233/231 mass ratio in a mixed $^{233}$Pa/$^{231}$Pa solution and found the ratio to be constant with time regardless of the decay of $^{233}$Pa to $^{233}$U. During the past 4 years, the measured 233/231 ratio in an unprocessed mixed Pa solution averaged 3.415 ± 0.045 (2SD; $n = 14$). Therefore, we conclude that no fractionation of Pa from U occurs during sample storage and that Pa and U behave similarly during sample nebulization, sample ionization in the plasma, and during transport and ion detection using our MC-MS-ICPMS system, PLASMA 54 (Mortlock et al., 2005). Since fractionation of $^{233}$Pa and $^{233}$U is not observed during ratio measurements, it is unnecessary to minimize the accumulation of $^{233}$U from decay of $^{233}$Pa, and isotopic measurements of samples are not required to be made immediately after the column separation of Pa from U. In addition, the accuracy of $^{233}$Pa/$^{231}$Pa ratio measurements using an ICP source is not dependent on the efficiency of uranium "burn-off" from filaments, as is the case with TIMS (Pickett et al., 1994).

Our results appear to be in contrast to those reported using another MC-MS-ICPMS system (Finnigan Neptune), where it was observed that the measured 231/233 ratio in a Pa solution was found to decrease with time as $^{233}$Pa decayed to $^{233}$U (Regelous et al., 2004). The authors suspected the decrease in the ratio was due to more efficient ionization of U compared to Pa in the plasma source. The effect precluded the possibility of long-term storage of Pa fractions after the final chemical separation (Regelous et al., 2004).

## 3. Results

$^{230}$Th/$^{234}$U/$^{238}$U and $^{231}$Pa/$^{235}$U ages were obtained on selected fossil corals collected at two locations: Barbados and Araki Island. U-series dates from these samples were previously reported in Fairbanks et al. (2005) as part of the radiocarbon calibration data set. The Barbados sea level record (Fairbanks, 1989, 1990; Peltier and Fairbanks, 2005) indicates that the Barbados corals re-measured in this study were subaerially exposed to freshwater for about 15,000 years while the Araki samples were subaerially exposed nearly continuously due to the high uplift rate of Araki Island. The results presented in this section demonstrate that the MC-MS-ICPMS methodology (Mortlock et al., 2005) can be used to obtain $^{231}Pa/^{235}U$ ages to the precision necessary to confirm the reliability of closed system $^{230}Th/^{234}U/^{238}U$ ages.

Araki Island (166.93 °E, 15.63 °S) is located off the south coast of Santo, Vanuatu in the South Pacific and is mantled by ten uplifted coral reefs ranging in age from the Holocene to the Last Interglacial (Gilpin, 1982; Urmos, 1985). Some of the Araki corals chosen for this study were obtained from the collections of A. Bloom at Cornell University. Other Araki coral samples were collected during a field trip to Araki Island conducted by R. Fairbanks in 2004. XRD analysis and U-series ages determined by α-counting in earlier studies of Araki fossil corals (Gilpin, 1982; Urmos, 1985) suggested excellent preservation and the potential for using Araki fossil corals to extend $^{14}C$ calibration (Fairbanks et al., 2005) and for reconstructing sea level (Urmos, 1985) and atmospheric radiocarbon changes during marine isotope stage 3 (Chiu et al., 2006). Since our primary justification for redundant $^{231}Pa/^{235}U$ ages is for validation of the $^{230}Th/^{234}U/^{238}U$ ages in samples which can also be radiocarbon dated, we limited our selection of Araki fossil corals to only specimens found to contain $<0.2\%$ calcite and which were expected to fall within the age range of radiocarbon dating. Sample ARA04-58E was chosen as a test of the $^{231}Pa/^{235}U$ methodology. Visual inspection of fossil coral specimens in the field can generally screen those samples with more than 1% calcite. For general reference, 61 out of 145 fossil Araki corals analyzed by XRD methods (Chiu et al., 2005) were found to contain $<0.2\%$ calcite.

Prior to applying the $^{231}Pa/^{235}U$ dating methodology, $^{230}Th/^{234}U/^{238}U$ dating of all Barbados and Araki samples by the conventional method confirmed the following: (1) the $\delta^{234}U_{initial}$ falls within the range of values (138–150) determined for recent and modern corals (Delanghe et al., 2002; Cutler et al., 2004; Fairbanks et al., 2005), (2) U concentration falls within the range expected for corals after taking into consideration the coral species, and (3) $^{232}Th$ concentrations were determined to be less than 1 ppb. The complete data set of triple-dated Barbados and Araki Island samples measured in this study, including the ages obtained by the conventional $^{230}Th/^{234}U/^{238}U$ method is summarized in Table 3.

The uncertainty of a sample $[^{231}Pa/^{235}U]$ activity ratio inherits the uncertainty from both the measured $^{233}Pa/^{231}Pa$ and $^{233}U/^{238}U$ ratios and from the uncertainty in the concentration of the $^{233}Pa$ spike. Therefore, we estimated the overall external precision of the measured sample $[^{231}Pa/^{235}U]$ activity ratio to be equal to the combined uncertainty in both the sample and standard $[^{231}Pa/^{235}U]$ measured activity ratios. The averaged combined uncertainty in the $[^{231}Pa/^{235}U]$ activity ratio in these 12 samples is about 1.5% (2 RSD) and corresponds to a relative age uncertainty of about $\pm 2\%$. We shall regard a paired $^{231}Pa/^{235}U$ age and $^{230}Th/^{234}U/^{238}U$ age to be concordant when the analytical error in $[^{231}Pa/^{235}U]$ is $\leqslant 2\%$ (2 RSD) and the $^{231}Pa/^{235}U$ age ($\pm 2\sigma$) overlaps the associated $^{230}Th/^{234}U/^{238}U$ age ($\pm 2\sigma$). One replicate $^{231}Pa/^{235}U$ age (RGF12-28-6 [a]) clearly fails the concordancy test and is regarded as an outlier and is excluded from later discussion. Three samples have ages that fall only slightly outside of the corresponding $^{230}Th/^{234}U/^{238}U$ age at 2σ (Fig. 2 and 3) but must be designated discordant, even though the $\delta^{234}U_{initial}$ values measured in these samples do not suggest open system behavior. The remaining nine samples have $^{231}Pa/^{235}U$ ages that are concordant with the $^{230}Th/^{234}U/^{238}U$ ages.

## 4. Discussion

The $\delta^{234}U_{initial}$ values obtained from the Pa–Th–U method in the twelve samples reported here ranged from 140 to 144 (Table 3) and fall within the range of $\delta^{234}U_{initial}$ reported for other concordant $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dated samples in this age range (Cutler et al., 2004; Fairbanks et al., 2005) and within the range of $\delta^{234}U_{initial}$ reported for modern corals (Delanghe et al., 2002). In contrast, open system corals are typically characterized by elevated $\delta^{234}U_{initial}$, and open system corals of approximately the same age generally plot as positive trends on $[^{230}Th/^{238}U]$ activity versus $\delta^{234}U_{measured}$ (or $[^{234}U/^{238}U]$ activity) diagrams (Hamelin et al., 1991; Gallup et al., 1994; Thompson et al., 2003; Scholz et al., 2004; Mey et al., 2005). Alpha recoil addition of $^{234}U$ (Villemant and Feuillet, 2003; Thompson et al., 2003) has been proposed to explain the anomalous ages and elevated $\delta^{234}U_{initial}$, but evidence from Holocene and last interglacial corals from the Gulf of Aqaba (Scholz et al., 2004) and marine isotope stage 3 Barbados corals (Mey et al., 2005) indicate that adsorption and not alpha recoil is probably responsible for the elevated $\delta^{234}U_{initial}$ values generally characteristic of open system samples. Using Red Sea coral data, Scholz et al. (2004) tested the diagenetic model age correction routines using the model program code provided by Villemant and Feuillet (2003) and Thompson et al. (2003) and concluded that the “corrected ages” were inconsistent among pieces of the same coral sample. Mey et al. (2005) present data that indicate diagenetically elevated $[^{234}U/^{238}U]$ and $[^{230}Th/^{238}U]$ activity ratios among samples from the same reef or within samples is set early during initial fresh water diagenesis when uranium isotopes are released from dissolving aragonite-rich reef sands and coral rubble (Mey et al., 2005) surrounding the coral specimens. While various open system models can make predictions as to the processes

Table 3

Results of Barbados and Araki corals in this study. $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ ages were determined from the same dissolved fragments by methods described in Mortlock et al. (2005). [A] versus [B] and [a] versus [b] designate pairs of replicates from different fragments. $^{230}Th/^{234}U/^{238}U$ ages* were previously determined by methods without Pa spiking and with chemical separation of U and Th only. Numbers in quotes represent the estimated error (2σ). "□" represents the outlier sample and it is excluded from discussion. Ages were calculated using the following equations (Ivanovich et al., 1992): $\left[^{230}Th/^{234}U\right] = \frac{1-e^{-\lambda_{230}*t_1}}{\left[^{234}U/^{238}U\right]} + \left(1 - \frac{1}{\left[^{234}U/^{238}U\right]}\right) * \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}} * \left(1 - e^{-(\lambda_{230}-\lambda_{234})*t_1}\right)$, $\left[\frac{^{231}Pa}{^{235}U}\right] = 1 - e^{-\lambda_{231}*t_2}$. We use decay constants $\lambda_{230} = 9.1577 \times 10^{-6}$ year$^{-1}$, $\lambda_{231} = 2.1158 \times 10^{-5}$ year$^{-1}$, and $\lambda_{234} = 2.8263 \times 10^{-6}$ year$^{-1}$ (Robert et al., 1969; Cheng et al., 2000) in all calculations. "$t_1$" is $^{230}Th/^{234}U/^{238}U$ age and "$t_2$" is $^{231}Pa/^{235}U$ age. Note: $^{231}Pa/^{235}U$ ages reported in Mortlock et al. (2005) for samples RGF 12-28-7 [a] & [b], RGF 12-29-2 [a] & [b], and RGF 12-30-3 [a] & [b] were calculated using $\lambda_{231} = 2.1197 \times 10^{-5}$ year$^{-1}$

| Sample name | U-series ID | [$^{231}Pa/^{235}U$] measured activity | $^{231}Pa/^{235}U$ age (years) | [$^{230}Th/^{234}U$] measured activity | $^{230}Th/^{234}U/^{238}U$ age (years) | $\delta^{234}$Ui | $^{232}$Th (pg/g) | [U] (ppm) | [$^{230}Th/^{234}U$] measured activity* | $^{230}Th/^{234}U/^{238}U$ age* (years) | $\delta^{234}$Ui* | [U]* (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I. Pilot study | | | | | | | | | | | | |
| RGF 12-28-6* | 021301RM1 | | | | | | | | 0.2385 (0.0006) | 29590 (82) | 137 (1) | 3.19 |
| RGF 12-28-6 [a] | 112901RMTC2 | 0.4360 (0.0075) | 27068 (632)□ | 0.2403 (0.0005) | 29844 (76) | 142 (2) | 988 | 3.15 | | | | |
| RGF 12-28-6 [b] | 121801TC1 | 0.4686 (0.0059) | 29877 (528) | 0.2388 (0.0006) | 29641 (88) | 141 (1) | 365 | 3.12 | | | | |
| RGF 12-28-7 [A]* | 021301RM2 | | | | | | | | 0.2432 (0.0008) | 30264 (1 1 1) | 139 (1) | 2.98 |
| RGF 12-28-7 [B]* | 073101RM2 | | | | | | | | 0.2423 (0.0008) | 30130 (116) | 140 (1) | 3.22 |
| RGF 12-28-7 [a] | 113001RMTC1 | 0.4690 (0.0063) | 29915 (565) | 0.2416 (0.0004) | 30028 (60) | 145 (2) | 173 | 3.15 | | | | |
| RGF 12-28-7 [b] | 121801TC2 | 0.4668 (0.0062) | 29724 (551) | 0.2393 (0.0005) | 29708 (68) | 143 (1) | 267 | 3.05 | | | | |
| RGF 12-29-2 [A]* | 021401RM2 | | | | | | | | 0.2410 (0.0010) | 29948 (149) | 137 (1) | 3.25 |
| RGF 12-29-2 [B]* | 080201RM2 | | | | | | | | 0.2433 (0.0006) | 30275 (80) | 138 (1) | 3.24 |
| RGF 12-29-2 [a] | 113001RMTC2 | 0.4709 (0.0063) | 30090 (566) | 0.2434 (0.0005) | 30290 (73) | 142 (1) | 55 | 3.10 | | | | |
| RGF 12-29-2 [b] | 121801TC3 | 0.4777 (0.0051) | 30701 (464) | 0.2414 (0.0005) | 30011 (68) | 140 (2) | 63 | 3.19 | | | | |
| RGF 12-30-3* | 021401RM1 | | | | | | | | 0.2434 (0.0007) | 30292 (95) | 140 (2) | 3.04 |
| RGF 12-30-3 [a] | 112901RMTC1 | 0.4730 (0.0072) | 30276 (647) | 0.2462 (0.0004) | 30679 (54) | 144 (1) | 106 | 3.16 | | | | |
| RGF 12-30-3 [b] | 121901TC1 | 0.4830 (0.0058) | 31180 (530) | 0.2450 (0.0005) | 30515 (75) | 145 (2) | 105 | 3.08 | | | | |
| II. Araki corals | | | | | | | | | | | | |
| AK-BD-4* | 102903TC2 | | | | | | | | 0.2796 (0.0006) | 35571 (86) | 141 (2) | 2.72 |
| AK-BD-4 | 012505TC2 | 0.5219 (0.0058) | 34877 (577) | 0.2804 (0.0007) | 35691 (1 0 0) | 144 (1) | 31 | 2.66 | | | | |
| AK-BD-9* | 102903TC6 | | | | | | | | 0.3074 (0.0005) | 39812 (84) | 140 (2) | 2.83 |
| AK-BD-9 | 012505TC3 | 0.5695 (0.0057) | 39831 (631) | 0.3065 (0.0010) | 39675 (161) | 142 (2) | 509 | 2.75 | | | | |
| AK-BD-11* | 063003TC3 | | | | | | | | 0.2986 (0.0008) | 38454 (116) | 140 (2) | 2.69 |
| AK-BD-11 | 012605TC3 | 0.5611 (0.0047) | 38918 (508) | 0.2966 (0.0006) | 38144 (98) | 142 (1) | 377 | 3.21 | | | | |
| AK-BE-1B* | 051205RM4 | | | | | | | | 0.3493 (0.0014) | 46510 (237) | 143 (2) | 2.95 |
| AK-BE-1B | 012505TC4 | 0.6329 (0.0076) | 47362 (987) | 0.3494 (0.0008) | 46521 (139) | 142 (1) | 337 | 2.76 | | | | |
| ARA04-40E* | 102604RM4 | | | | | | | | 0.3658 (0.0005) | 49257 (90) | 142 (1) | 2.49 |
| ARA04-40E | 012505TC5 | 0.6499 (0.0042) | 49603 (665) | 0.3675 (0.0008) | 49545 (129) | 143 (1) | 5 | 2.55 | | | | |
| ARA04-58E* | 092204LC4 | | | | | | | | 0.4003 (0.0013) | 55231 (237) | 144 (2) | 2.76 |
| ARA04-58E | 012605TC4 | 0.6808 (0.0072) | 53969 (1071) | 0.4016 (0.0008) | 55484 (141) | 143 (1) | 39 | 2.91 | | | | |
| ARA04-73E* | 092304LC2 | | | | | | | | 0.3348 (0.0010) | 44152 (166) | 144 (2) | 2.15 |
| ARA04-73E | 012605TC2 | 0.6084 (0.0052) | 44307 (632) | 0.3331 (0.0011) | 43866 (174) | 142 (1) | 13 | 2.17 | | | | |
| ARA04-75E* | 092304LC3 | | | | | | | | 0.3395 (0.0011) | 44904 (181) | 142 (1) | 2.95 |
| ARA04-75E | 012605TC1 | 0.6151 (0.0057) | 45123 (709) | 0.3398 (0.0012) | 44954 (193) | 143 (1) | 23 | 2.92 | | | | |

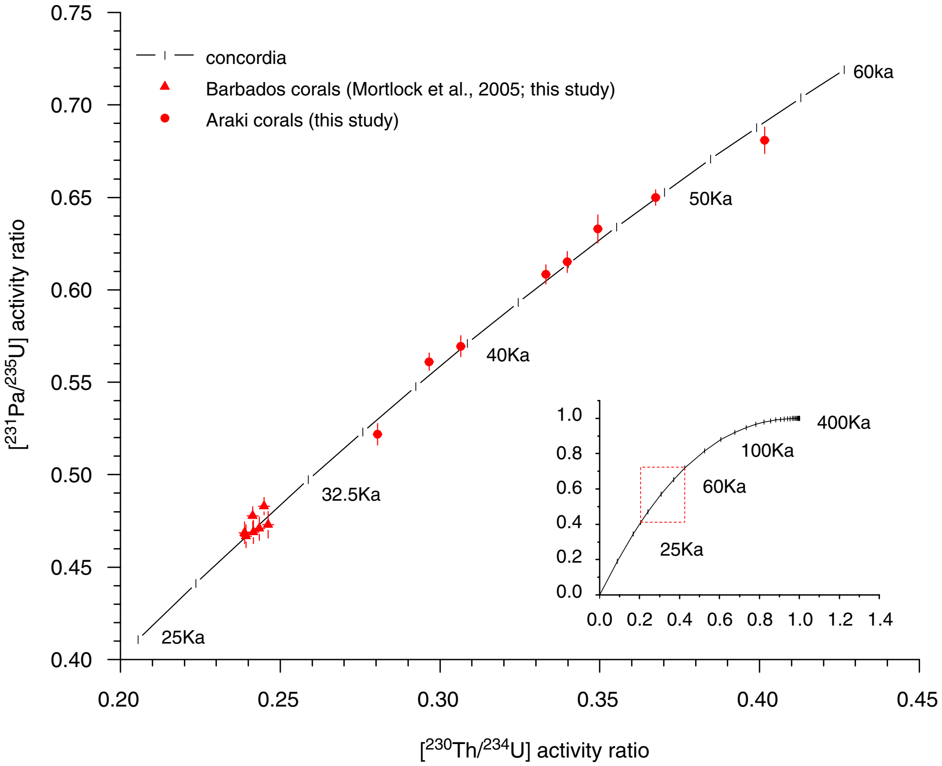

Fig. 2. Plots of [$^{231}$Pa/$^{235}$U] activity ratio versus measured [$^{230}$Th/$^{234}$U] activity ratio in Araki and Barbados fossil corals. The specific Pa–Th concordia in this figure was calculated assuming a $\delta^{234}U_{initial}$ value equal to 145. Different $\delta^{234}U_{initial}$ generates different concordias (Edwards et al., 1997; Cheng et al., 1998), but their positions on [$^{231}$Pa/$^{235}$U]–[$^{230}$Th/$^{234}$U] diagram are not significantly different in the age range displayed here. The solid line represents the case in which the $^{231}$Pa/$^{235}$U age is equal to the $^{230}$Th/$^{234}$U/$^{238}$U age. Solid circles represent fossil corals from Araki Island; solid triangles represent those from offshore Barbados. Error bars represent the analytical uncertainty ($2\sigma$). The insert diagram is the full-range decay evolution, and the dotted rectangle represents the age range in this study. Numbers next to tick label ("|") represent the ages. Note that beyond 200 ka, the [$^{231}$Pa/$^{235}$U] activity ratio approaches one and it becomes very difficult to precisely determine the $^{231}$Pa/$^{235}$U age of a sample.

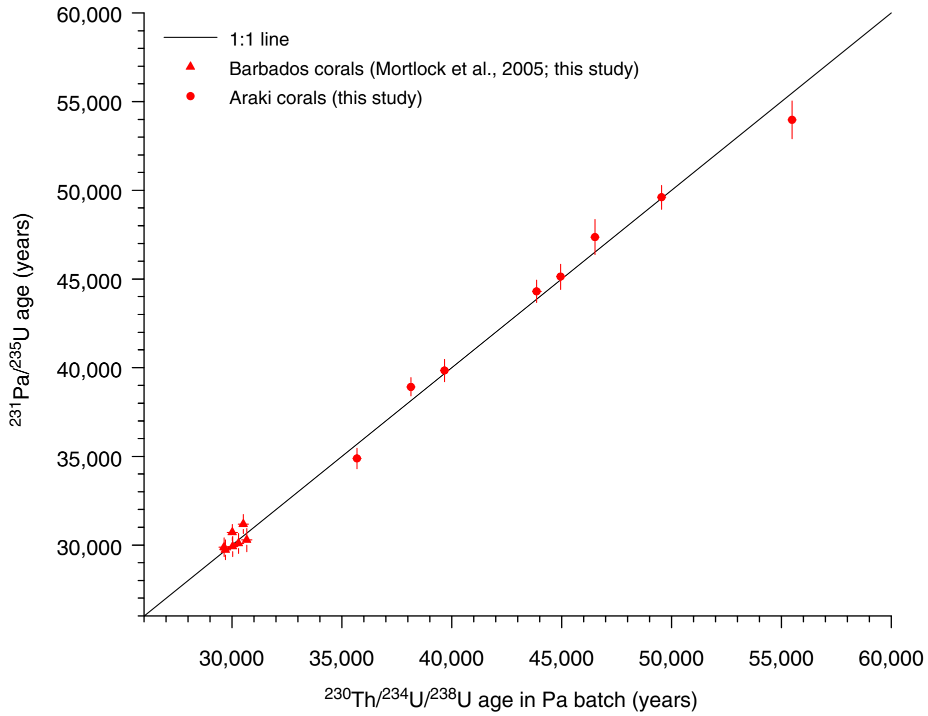

Fig. 3. $^{231}$Pa/$^{235}$U ages and $^{230}$Th/$^{234}$U/$^{238}$U ages of Barbados and Araki fossil corals. Solids circles represent fossil corals from Araki Island; solid triangles represent those from Barbados. Error bars represent the analytical uncertainties ($2\sigma$). The 1:1 line is presented merely for reference.

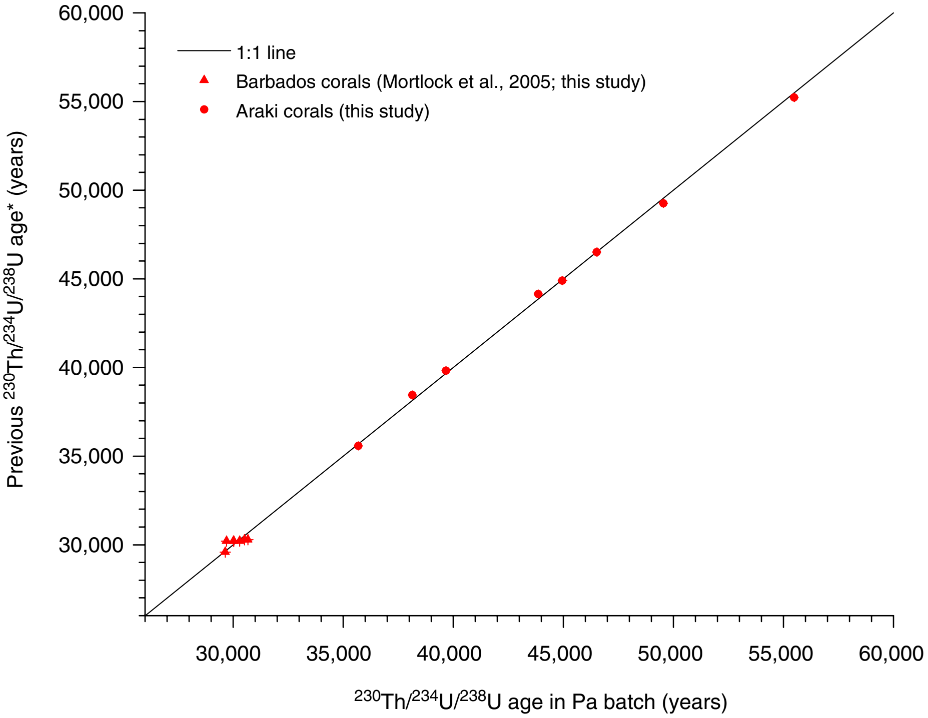

Fig. 4. $^{230}$Th/$^{234}$U/$^{238}$U ages determined from Pa–Th–U chemistry plotted against the $^{230}$Th/$^{234}$U/$^{238}$U ages* from conventional Th–U chemistry (Table 1). Solids circles represent fossil corals from Araki Island; solid triangles represent those from Barbados. Error bars represent $2\sigma$ analytical uncertainties and are smaller than the size of the symbols. The 1:1 line is presented merely for reference. This comparison demonstrates there is no compromise of accuracy and precision of $^{230}$Th/$^{234}$U/$^{238}$U ages from Pa–Th–U chemistry.

creating discordant U–Th–Pa isotopic systems (Cheng et al., 1998), it appears unlikely, although not impossible, that diagenetic processes would consistently maintain concordancy and still yield inaccurate ages.

The $^{232}$Th concentration in the Barbados and Araki samples ranged from several parts per trillion to approximately one part per billion. Given an estimate of about $10^5$ for the $^{232}$Th/$^{230}$Th detrital ratio (atom/atom) (Robinson et al., 2004), any age correction for initial $^{230}$Th would be much smaller than the analytical uncertainty and so we have made no age correction to the data in Table 3 for initial $^{230}$Th.

Lastly, Fig. 4 demonstrates the consistency between $^{230}$Th/$^{234}$U/$^{238}$U ages obtained from Pa–Th–U methods presented here and in Mortlock et al. (2005) and $^{230}$Th/$^{234}$U/$^{238}$U ages obtained using conventional Th–U MC-MS-ICPMS methods (Table 1). The consistency clearly demonstrates that there is no compromise of accuracy and precision of $^{230}$Th/$^{234}$U/$^{238}$U ages obtained from Pa–Th–U methods nor do we observe any systematic differences in the U isotopic compositions or U content (Table 3) between the two processing methods. Therefore, these new Araki coral results reaffirm our earlier finding that the methods presented here can be used to obtain $^{231}$Pa/$^{235}$U ages to the precision necessary to confirm the validity of closed system $^{230}$Th/$^{234}$U/$^{238}$U ages. The methods also provide the advantage of obtaining the $^{230}$Th/$^{234}$U/$^{238}$U age of a sample and at the same time confirming its accuracy by $^{231}$Pa/$^{235}$U ages in the same chemical procedure. The redating of 11 representative samples in our radiocarbon calibration curve for the time interval spanning 30,000 years BP to 50,000 years BP using the Pa–Th–U method confirms the accuracy of the coral calibration curve (http://www.radiocarbon.LDEO.columbia.edu) over this time interval where other archives yield disparate results (Fig. 1). By virtue of the redundant dating, nine calibration samples have been elevated from Categories IV to III (Fairbanks et al., 2005) and two samples are excluded from future versions of our radiocarbon calibration (e.g. Fairbanks0406).

## 5. Conclusions

We have applied our procedure for obtaining redundant $^{231}$Pa/$^{235}$U and $^{230}$Th/$^{234}$U/$^{238}$U ages from a single coral fragment by multi-collector magnetic sector inductively coupled plasma mass spectrometry (Mortlock et al., 2005) to fossil corals from Barbados and Araki Island. Assuming that fossil coral samples have been thoroughly screened to meet the criterion of $<0.2\%$ calcite (Chiu et al., 2005), a $\delta^{234}U_{\text{initial}}$ in the range of modern or recent corals, a U content in the expected range for corals, and less than 1 ppb of $^{232}$Th, the $^{231}$Pa/$^{235}$U age of fossil corals can be determined with sufficient precision to confirm the accuracy of $^{230}$Th/$^{234}$U/$^{238}$U ages. A very high percentage of screened fossil corals from Barbados and Araki Island in the age range of 30,000–50,000 years BP give concordant $^{231}$Pa/$^{235}$U and $^{230}$Th/$^{234}$U/$^{238}$U ages. High-precision, high-accuracy $^{230}$Th/$^{234}$U/$^{238}$U dating of pristine fossil corals may be the ultimate solution to establishing an absolute chronology, and $^{231}Pa/^{235}U$ dating of fossil corals provides a redundant means for confirming the assumption of closed system behavior in samples that may have been exposed to fresh water either in the vados (percolating zone) or in the phreatic lens (ground water table) over prolonged periods of time. For corals that have been submerged in seawater (no freshwater alteration) for their entire history (e.g. Barbados offshore samples younger than 30,000 years BP), redundant $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ dating may not be necessary.

Paired $^{230}Th/^{234}U/^{238}U$ and $^{14}C$ age determinations of pristine fossil corals provide the most direct means for reconstructing past atmospheric $^{14}C$ content beyond the superior tree ring data set (Stuiver et al., 1998). Having demonstrated closed system behavior of these samples, the Barbados and Araki fossil corals can be used with even greater confidence to extend both the radiocarbon calibration and atmospheric $^{14}C$ content from 26,000 to 50,000 years BP (Chiu et al., 2006; Fairbanks et al., 2005).

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