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$^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages from a Single Fossil Coral Fragment by Multi-collector Magnetic-sector Inductively Coupled Plasma Mass Spectrometry

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Abstract—The $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ age dating of corals via alpha counting or mass spectrometry has significantly contributed to our understanding of sea level, radiocarbon calibration, rates of ocean and climate change, and timing of El Nino, among many applications. Age dating of corals by mass spectrometry is remarkably precise, but many samples exposed to freshwater yield inaccurate ages. The first indication of open-system $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages is elevated $^{234}\text{U}/^{238}\text{U}_{\text{initial}}$ values, very common in samples older than 100,000 yr. For samples younger than 100,000 yr that have $^{234}\text{U}/^{238}\text{U}_{\text{initial}}$ values close to seawater, there is a need for age validation. Redundant $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages in a single fossil coral fragment are possible by Multi-Collector Magnetic Sector Inductively Coupled Plasma Mass Spectrometry (MC-MS-ICPMS) and standard anion exchange column chemistry, modified to permit the separation of uranium, thorium, and protactinium isotopes from a single solution. A high-efficiency nebulizer employed for sample introduction permits the determination of both $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages in fragments as small as 500 mg. We have obtained excellent agreement between $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages in Barbados corals (30 ka) and suggest that the methods described in this paper can be used to test the $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ age accuracy.

Separate fractions of U, Th, and Pa are measured by employing a multi-dynamic procedure, whereby ^{238}U is measured on a Faraday cup simultaneously with all minor isotopes measured with a Daly ion counting detector. The multi-dynamic procedure also permits correcting for both the Daly to Faraday gain and for mass discrimination during sample analyses. The analytical precision of $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ dates is generally better than $\pm 0.3\%$ and $\pm 1.5\%$, respectively (2 Relative Standard deviation [RSD]). Additional errors resulting from uncertainties in the decay constant for ^{231}Pa and from undetermined sources currently limit the $^{231}\text{Pa}/^{235}\text{U}$ age uncertainty to about $\pm 2.5\%$. U isotope data and $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages agree with National Institute of Standards and Technology (NIST) reference materials and with measurements made by Thermal Ionization Mass Spectrometry (TIMS) in our laboratory. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Uranium series age dating of corals, by high-precision and high-accuracy mass spectrometric techniques, has advanced our understanding of the timing and magnitude of sea level change (Edwards et al., 1987; Bard et al., 1990; Fairbanks, 1990; Stirling et al., 1995; Chappell et al., 1996; Yokoyama et al., 2001; Gallup et al., 2002; Cutler et al., 2003), has greatly extended the calibration of ^{14}C years to calendar years (Bard et al., 1990; Burr et al., 1998; Chiu et al., 2003), and has made possible reconstructions of past atmospheric radiocarbon variations (Bard et al., 1990; Edwards et al., 1993; Beck et al., 2001; Cao et al., 2003). A potential shortcoming of uranium series dating is that open system behavior is not uncommon in coral exposed to freshwater over prolonged periods, particularly alteration in a phreatic lens. This may lead to either gain or loss of U and Th, modifying the sample $^{230}\text{Th}/^{234}\text{U}$ activity ratio and thus compromising the accuracy of age determinations in fossil corals (Edwards et al., 1987; Hamelin et al., 1991; Gallup et al., 1994; Thompson et al., 2003). In many instances, the suitability of samples for $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ dating

cannot be confirmed by available screening criteria, so the data must be scrutinized by other means, such as the degree of departure of the $^{234}\text{U}/^{238}\text{U}$ initial activity ratio of a coral (or $\delta^{234}\text{U}_i$) from modern day seawater (Edwards et al., 1988; Hamelin et al., 1991; Henderson et al., 1993). ^{231}Pa ($t_{1/2} = 32,760$ yr; Robert et al., 1969; Schmorak, 1977) is produced directly by α -decay of ^{235}U and provides a redundant means for confirming $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages in the range of 10 ka to 150 ka. Only a few studies have reported high-precision mass spectrometric Pa measurements in fossil corals (Edwards et al., 1997; Gallup et al., 2002; Cutler et al., 2003) using thermal ionization mass spectrometry (TIMS). In this work, we describe a new procedure for determining both the $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages from a single coral fragment by MC-MS-ICPMS and discuss some clear advantages.

2. ANALYTICAL METHODS

2.1. Sampling

U-series and a companion archive sample are taken from 2 concentric cores (13 mm and 5 mm) drilled into 4 mm thick coral slabs while submerged in water. The coring tubes are thin-walled stainless steel tubes impregnated on one end with fine diamonds. The concentric coring assures consistent sampling procedures and the proximal location of the multiple age determinations. Systematic and proximate sampling is of particular importance if U-series dates of fossil material are to be paired with radiocarbon ages and other sample analyses such

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Table 1. Chemical separation of U, Th, and Pa from coral samples.

First Column	500 μ l, AG1-X8 200–400m		
	Step	description	comments
1. Cleaning	2 ml 7N HNO ₃ 1 ml 0.1N HCl 1 ml 12N HCl 1 ml 0.13N HF in 12N HCl 1 ml Mili-Q H ₂ O		
2. Cleaning	repeat of step 1		
3. Condition	20 drops 7N HNO ₃		
4. Load sample	16 drops 7N HNO ₃		
5. Wash beaker	16 drops 7N HNO ₃		
6. Wash column	16 drops 7N HNO ₃		major waste cations eluted
7. Collect Th	15 drops 12N HCl 30 drops 12N HCl 15 drops 12N HCl		Th eluted, absorption of U and Pa
8. Collect Pa	15 drops 0.13N HF in 12N HCl 30 drops 0.13N HF in 12N HCl 30 drops 0.13N HF in 12N HCl		Pa eluted, absorption of U
9. Collect U	15 drops 1N HBr 30 drops 1N HBr 30 drops 1N HBr		U eluted
Second Column	100 μl, AG1-X8 200–400m		
10. Cleaning	20 drops 7N HNO ₃ 20 drops 0.1N HCl 20 drops 12N HCl 20 drops 0.13N HF in 12N HCl 20 drops Mili-Q H ₂ O		
11. Cleaning	Repeat of step 10.		
12. Condition	10 drops 0.13N HF in 12N HCl 10 drops 0.13N HF in 12N HCl		
13. Load & collect Pa	10 drops 0.13N HF in 12N HCl		Pa eluted
14. Wash beaker	7 drops 0.13N HF in 12N HCl		
15. Final collection Pa	16 drops 0.13N HF in 12N HCl 5 drops 0.13N HF in 12N HCl		

as X-ray diffraction (XRD), thin sections, and other isotopic analyses. The larger (500 mg) of the cored samples is used for the U-series, and the small piece (50 mg) is archived. Fragments are cleaned multiple times in Mili-Q (18 M Ω) water with an ultrasonic probe cleaner immediately before analysis. Although fossil corals are microscopically screened for any extraneous material, the U-series samples in this study were not chemically cleaned before dissolution due to potential Th adsorption problems. Samples are routinely screened for calcite by XRD at 0.2% detection limits and for detrital material by examination of thin sections. Nevertheless, the reliability of U-series dates determined from samples found to contain significant ²³²Th (greater than 1 ppb) should be questioned.

2.2. Chemical Procedures

A previously calibrated mixed ²³³U-²²⁹Th spike is added to the sample in sufficient quantity, based on the estimated age of the sample, to approximate a ²²⁹Th/²³⁰Th target ratio equal to 10. ²³³Pa spike is added to approximate a ²³³Pa/²³¹Pa target ratio equal to 2. The levels of activity in the ²³³Pa spike introduced to the ICP-MS source are very small (<10⁴ dpm) and we have not found it necessary to take special precautions during sample preparation and introduction. The handling of ²³⁷Np during the initial preparation of spike must be performed in a laboratory suited for such purposes.

The use of a mixed ²³⁶U-²²⁹Th spike would avoid the potential for contaminating the Pa fraction with ²³³U and is a suggested improvement over our ²³³U spike. In the discussion to follow, we present evidence to suggest that contamination of the Pa fraction with U is not encountered with our methods. Coral samples are dissolved in 1 mL

concentrated nitric acid. Following overnight sample dissolution and spike equilibration, 9 mg Fe (as FeCl₃) is added. NH₄OH is added to pH 7 to 8 to precipitate iron hydroxide. The precipitated solution is centrifuged, the supernatant is discarded, and the precipitate is washed in Mili-Q water and centrifuged again. The precipitate is dissolved in 0.5 mL 16N HNO₃ sealed and refluxed at 110°C until the solution is clear. The samples are heated to near dryness in a filtered atmosphere.

Separation of U, Th, and Pa in solution is achieved through anion exchange column chemistry. In the case where only U and Th measurements are required, separation of U from Th can be accomplished by the chemistry presented in Edwards (1988) as modified by Bard et al. (1990). With TIMS, a second column cleaning of the Th fraction (to remove U) is necessary since the presence of U interferes with the ionization of Th. The time consuming additional cleaning step is not required with MC-MS-ICPMS. The complete column chemistry used to separate U, Th, and Pa is described in Table 1. Since both ²³⁵U and ²³³Pa are used as a spike, any U eluted with the Pa fraction presents an isobaric interference and compromises the accurate determination of ²³³Pa. Therefore, the collected Pa fraction requires an additional cleaning step, and a second column exchange of the Pa fraction successfully separates residual U from Pa. The analyses of procedural blanks (spiked) confirmed the absence of any U in the Pa fraction and complete separation among the elements used in this procedure. The final collected U fraction is dried, redissolved in 0.5 mL 7N HNO₃, dried and diluted with 2% HNO₃ to produce a solution of ~30 to 50 ppb U. The Th fraction is dried, redissolved in 0.5 mL 7N HNO₃, dried and diluted to volume of 3 mL with 2% HNO₃ in 1% HF. The Pa fraction is dried, redissolved, and diluted to a volume of 2 mL with 2% HNO₃ in 1% HF. During drying steps, care must be taken to prevent the Pa

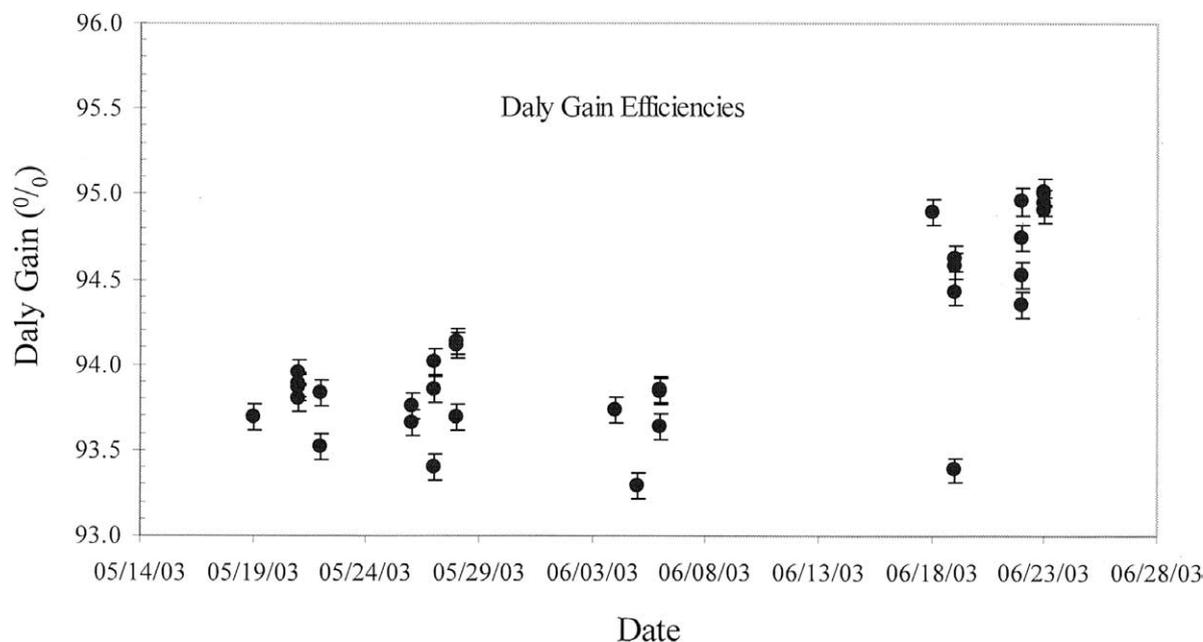


Fig. 1. Plot of Daly/Faraday gain efficiency (from $^{235}\text{U}/^{238}\text{U}$) vs. time where the percent gain is calculated as the ratio of the Daly to Faraday measurement to a Faraday-to-Faraday measurement. Error bars denote the typical 2-sigma standard deviation for the gain measurement ($\pm 0.08\%$).

fraction from drying to hardness to avoid formation of insoluble fluorides.

2.3. Mass Spectrometry

U, Th, and Pa isotopic measurements are made using a multi-collector magnetic sector double-focusing Inductively Coupled Mass Spectrometer (FISONS PLASMA 54). U-series ages of fossil corals have been previously obtained by MC-MS-ICPMS using a similar instrument (Stirling et al., 2001), and a detailed description of the PLASMA 54 instrument design can be found elsewhere (Walder et al., 1993) along with initial results (Halliday et al., 1995, Halliday et al., 1998). In general, the instrument combines a double focusing magnetic sector mass spectrometer with an ICP source. Our instrument is equipped with a nine-collector Faraday cup array. Behind the Faraday array is an additional 30-cm radius electrostatic analyzer (ESA) filter and an ion-counting Daly detector. The secondary ESA reduces abundance sensitivity to better than 0.3 ppm (measured as the contribution to mass 237 from mass 238). Our instrument is equipped with an additional single stage rotary pump (S-option) that improves the vac-

uum in the expansion region by a factor of 10 (to 0.1 e^{-4} mbar) vs. the standard interface-pumping configuration. The improved vacuum translates directly to a 50% increase in sensitivity.

Sample solutions are introduced using a desolvating nebulizer (CETAC MCN6000). In practice, sample introduction is considerably simpler than TIMS. We initially used an MCN 100 micro-nebulizer (CETAC) with the MCN6000 but found superior washout, particularly for Th, using the MNC6000 fitted with PFA spray chamber and PFA 50 nebulizer (Elemental Scientific Inc.). Sample volume uptake is $60 \mu\text{L}/\text{min}$. Typical sensitivity for our instrument coupled with the MCN6000 nebulizer is $\sim 0.4 \text{ pA ppb}^{-1}$ for ^{238}U . Maximum ^{235}U intensities as measured on the Daly detector are limited to a range of 0.5 to 1×10^6 ions s^{-1} . ^{230}Th and ^{231}Pa intensities, depending on the age of the sample, are in the range of 10^3 to 10^4 ions s^{-1} and 200 to 500 ions s^{-1} , respectively. Ionization efficiencies (the ratio of atoms detected to atoms introduced) for U, Th, and Pa are $\sim 0.1\%$, which are about a factor of 5 to 10 lower than those reported by TIMS (Edwards et al., 1987; Pickett et al., 1994; Stirling et al., 1995). For the U, Th, and Pa data collection, a minimum of 75, 50, and 40 ratio measurements are made, respectively. Each U or Th analysis takes about one h and

Table 2. Collector configurations for multi-dynamic isotopic analysis of U, Th, and Pa by MC-MS-ICPMS.

Collector	Axial (Daly)	High 1	High 2	High 3	High 4	comments
Uranium	^{235}U		^{238}U			gain meas.
	^{234}U	^{235}U		^{238}U		bias meas.
	^{233}U				^{238}U	
Thorium	^{229}Th				^{238}U	
	^{230}Th			^{238}U		
	^{232}Th	^{235}U	^{238}U			bias meas.
	^{235}U	^{238}U				gain meas.
Protactinium	^{231}Pa				^{238}U	
	^{233}Pa	^{235}U		^{238}U		bias meas.
	^{235}U		^{238}U			gain meas.

The normalization of Th and Pa isotopes to ^{238}U within a sequence eliminates the need to gain correct the $^{229}\text{Th}/^{230}\text{Th}$, $^{229}\text{Th}/^{232}\text{Th}$, and $^{231}\text{Pa}/^{233}\text{Pa}$ ratios, and so the ^{235}U sequence in the Th and Pa routines is not necessary. Nevertheless, we routinely measure the Daly gain at higher precision by measurement of the $^{235}\text{U}/^{238}\text{U}$ ratio in order to identify detector drift or noise that might otherwise go undetected.

consumes $\sim 0.3 \mu\text{g U}$ and 1 to 10 pg ^{230}Th . Each Pa analysis takes ~ 30 min and consumes 300 to 500 fg ^{231}Pa . The total amounts of Pa and Th consumed are comparable to filament loadings performed with TIMS. Rinsing of the nebulizer (with ultra pure 2% HNO_3 for U and 2% HNO_3 in 1% HF for Th and Pa) is continued until count rates less than 2 cps are observed for ^{234}U , ^{230}Th , and ^{233}Pa . Procedural blanks are less than 10 to 40 fg and 1 to 5 pg for ^{230}Th and ^{232}Th respectively, and less than 5 pg for ^{238}U .

The precise determination of isotopic ratios of U, Th, and Pa requires that mass fractionation (bias) and gain efficiency (calibration of the Daly detector) be known. Plasma sources produce mass fractionation that is time independent. Therefore, it is possible to correct for biasing in samples by comparison with the results obtained from standards by MC-ICP-MS, assuming that tuning parameters affecting the temperature of the sampled plasma, particularly torch position and gas flows, remained unchanged. There are, however, distinct advantages to making simultaneous fractionation and gain corrections. The Daly detector can display excellent internal precision ($<0.08\%$ 2RSD) during a one h analysis, but differences in gain efficiencies of as much as 1% may be observed during the course of a day (Fig. 1). Simultaneous corrections for mass bias and Faraday/Daly gain also eliminate the need for separate calibration measurements. Consequently, we employ separate multi-dynamic routines for U, Th, and Pa (Table 2). This approach is similar to that described in Luo et al. (1997), where it was demonstrated that multi-static routines yielded superior analytical precision for both U and Th isotopic analyses. In the case of uranium, ^{235}U is measured sequentially using both the Daly and Faraday collectors. The measured Daly to Faraday gain is then used to correct the $^{234}\text{U}/^{238}\text{U}$ and $^{233}\text{U}/^{238}\text{U}$ ratios. Mass bias is calculated by comparison of the measured $^{235}\text{U}/^{238}\text{U}$ ratio with the accepted value (0.0072527). Under typical plasma conditions (cool gas = 16 L min^{-1} , auxiliary gas = 2 L min^{-1} , nebulizer gas = 0.45 L min^{-1} , sweep gas = 2.7 L min^{-1} , and $\text{N}_2 = 0.010 \text{ L min}^{-1}$) our mass fractionation is $\sim 0.7\%$ amu $^{-1}$.

Before Th and Pa measurement, $\sim 100 \text{ ng}$ of natural U (NIST CRM 129) is added to each solution. Isotopic measurements of Th (^{229}Th , ^{230}Th , ^{232}Th) and Pa (^{231}Pa , ^{233}Pa) are made with the Daly detector and are accompanied by simultaneous measurement of ^{238}U using one of the high-mass Faraday cups (Table 2). The "normalization" of intensities to ^{238}U eliminates the need for gain correction of the $^{229}\text{Th}/^{230}\text{Th}$, $^{229}\text{Th}/^{232}\text{Th}$, and $^{231}\text{Pa}/^{233}\text{Pa}$ ratios. In the case of Th and Pa, mass fractionation is determined during sample analysis by comparison of the measured $^{235}\text{U}/^{238}\text{U}$ ratio with the accepted value. Since natural uranium may contain a small quantity of ^{230}Th and ^{231}Pa (decay products of U) an aliquot of CRM 129 is cleaned before analysis, to separate U from Th and Pa (steps 1 thru 9 in Table 1). The cleaned U

shows no detectable ^{230}Th and ^{231}Pa . Measurement precision of the U and Th isotope ratios are generally better than $\pm 0.08\%$ and $\pm 0.3\%$ (2 RSD), respectively. Precision of the $^{233}\text{Pa}/^{231}\text{Pa}$ ratio measurement in the speleothem standard averaged less than 0.8% (2 RSD).

2.4. Calculations

Standard isotope dilution equations are used to calculate the concentrations of ^{230}Th , ^{234}U , and U in samples. $^{234}\text{U}/^{238}\text{U}$ isotope ratios are corrected for contributions from the spike. Contributions to the $^{235}\text{U}/^{238}\text{U}$ ratios from the spike are negligible and can be ignored. The $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ age and $^{231}\text{Pa}/^{235}\text{U}$ ages are calculated using the age equations reported in Ivanovich et al. (1992).

The determination of Pa concentrations and ^{231}Pa dating by Thermal Ionization Mass Spectrometry (TIMS) is described in detail elsewhere (Pickett et al., 1994; Edwards et al., 1997); however, some of the associated analytical difficulties will be discussed here. Unlike U and Th, there is no long-lived isotope to serve as a spike for measurement of Pa. The short-lived ^{233}Pa isotope ($t_{1/2} = 26.967$ days; Jones et al., 1986) is the only spike option. A standard isotope dilution approach must be modified because no certified reference standard for Pa exists and the ^{233}Pa spike concentration cannot be accurately determined before spiking and analysis. This is due to the rapid decay of ^{233}Pa to ^{233}U ; and therefore, the ^{233}Pa concentration must be calculated by reverse isotope dilution methods. In this study, we chose a 500 ka speleothem as our ^{231}Pa standard. We assume secular equilibrium ($^{231}\text{Pa}/^{235}\text{U}$ ratio equal to unity) for the speleothem, and calculate the concentration of the ^{233}Pa spike from the U concentration of the speleothem and the measured $^{233}\text{Pa}/^{231}\text{Pa}$ activity. Standard isotope dilution equations permit the calculation of the ^{231}Pa concentration and age of samples.

3. RESULTS

Before developing procedures for determining both $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages from a single fragment, we verified the accuracy of the $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ method via MC-MS-ICPMS. The mean value of 34 measurements of the $^{234}\text{U}/^{238}\text{U}$ ratio of NIST U-010 made during the course of a three-yr study was 5.42 ± 0.02 (2 SD) $\times 10^{-5}$, within the uncertainty of the certified value of $5.47 (\pm 0.06) \times 10^{-5}$. The average value of $\delta^{234}\text{U}$ in seawater and modern corals (*Acropora hyacinthus* sp.) collected at Kiritimati Island is 146.3 ± 1.2 (1 SD; $n = 5$)

Table 3. Comparison of TIMS and MC-MS-ICPMS ages.

Sample	TIMS age	$\delta^{234}\text{U}$	MC-MS-ICPMS age	$\delta^{234}\text{U}$
RGF12-5-2 [^]	11,623(60)	142	11,440(27)	146
RGF12-9-3*	11,919(118)	145	12,052(49)	141
CHR5-2-5*	11,951(154)	142	11,966(30)	144
RGF12-9-5 [^]	12,301(86)	147	12,253(75)	143
RGF12-12-2*	12,809(73)	145	12,848(50)	143
RGF12-15-4*	13,175(87)	142	13,042(34)	145
RGF12-17-2*	13,206(49)	144	13,229(32)	143
RGF12-21-2*	13,389(117)	143	13,605(37)	143
RGF12-21-6 [^]	13,745(174)	146	13,624(51)	143
RGF12-21-10 [^]	13,697(138)	141	13,682(31)	144
RGF9-8-2 [^]	14,278(100)	139	14,133(40)	145
RGF9-11-2*	14,365(59)	145	14,301(23)	145
RGF9-12-7*	14,505(30)	144	14,446(25)	145
RGF9-20-2*	18,078(64)	147	18,224(65)	144
RGF9-21-11*	18,297(142)	143	18,019(298)	143
RGF9-27-5 [^]	19,068(92)	144	19,125(110)	142
RGF9-32-4 [^]	20,670(120)	141	20,389(158)	143
RGF9-34-8 [^]	22,198(258)	140	21,852(82)	145

Data are from Fairbanks (1990) and Hamelin et al. (1991) although those ages have been recalculated using the half-lives reported in Cheng et al. (2000). TIMS data was acquired using either the Lamont Doherty VG Micromass 30 instrument ([^]) or the Lamont Doherty VG Micromass Sector instrument (*). Numbers in brackets represent analytical error (2 SD) only.

and 145.9 ± 0.8 (1 SD; $n = 8$), respectively, and is consistent with the range of values for modern corals and seawater published elsewhere (Chen et al., 1986; Delanghe et al., 2002). $\delta^{234}\text{U}$ initial in 75 fossil corals (6 ka to 15 ka) averages 145 ± 2 (1 SD) and is consistent with $\delta^{234}\text{U}$ of the modern corals and seawater, all by the same MC-MS-ICPMS method.

As a more thorough accuracy test of our methods, we compare coral ages previously determined by TIMS with those determined by MC-MS-ICPMS. All TIMS data were generated on either the Lamont-Doherty VG Micromass 30 mass spectrometer or VG Micromass Sector 54 mass spectrometer. Ten of the TIMS $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages have been published elsewhere (Bard et al., 1990; Fairbanks, 1990). We observe fine agreement between the two analytical methods (Table 3), with 70% of the paired ages overlapping within the measured error. Agreement between TIMS and MC-MS-ICPMS $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages have been reported elsewhere in fossil corals in the age range of 125 ka to 600 ka (Stirling et al., 2001), and confirms the reliability of MC-MS-ICPMS in U-series dating. The markedly improved precision of the MC-MS-ICPMS results vs. the earlier Lamont-Doherty TIMS data are also clearly demonstrated (Fig. 2). Fractional errors associated with our PLASMA 54 measurements are typically one half to one third

the errors associated with measurements made on Lamont TIMS instruments, and our PLASMA 54 errors are comparable to the most precisely measured TIMS results published elsewhere (Stirling et al., 1995; Edwards et al., 1997; Burr et al., 1998; Gallup et al., 2002). High-precision $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ dating of speleothems has been reported using a single collector magnetic sector ICP-MS (Shen et al., 2002). However, the improved abundance sensitivity of the PLASMA 54 eliminates the application of tailing corrections, and the multi-collector capability of the PLASMA 54 eliminates the need for external mass bias and intensity bias corrections, both of which must be performed sequentially when using the single collector instrument.

3.1. $^{231}\text{Pa}/^{235}\text{U}$ Age Dating

The precision and accuracy of the $^{231}\text{Pa}/^{235}\text{U}$ dating method is largely limited by the measurement precision of the $^{233}\text{Pa}/^{231}\text{Pa}$ ratio and our external reproducibility, which is limited by our ability to accurately calculate the concentration of our ^{233}Pa spike and the efficiency by which we are able to chemically separate ^{233}U and ^{233}Pa . Any estimate in the $^{231}\text{Pa}/^{235}\text{U}$ age uncertainty must also include the uncertainty in the ^{231}Pa decay

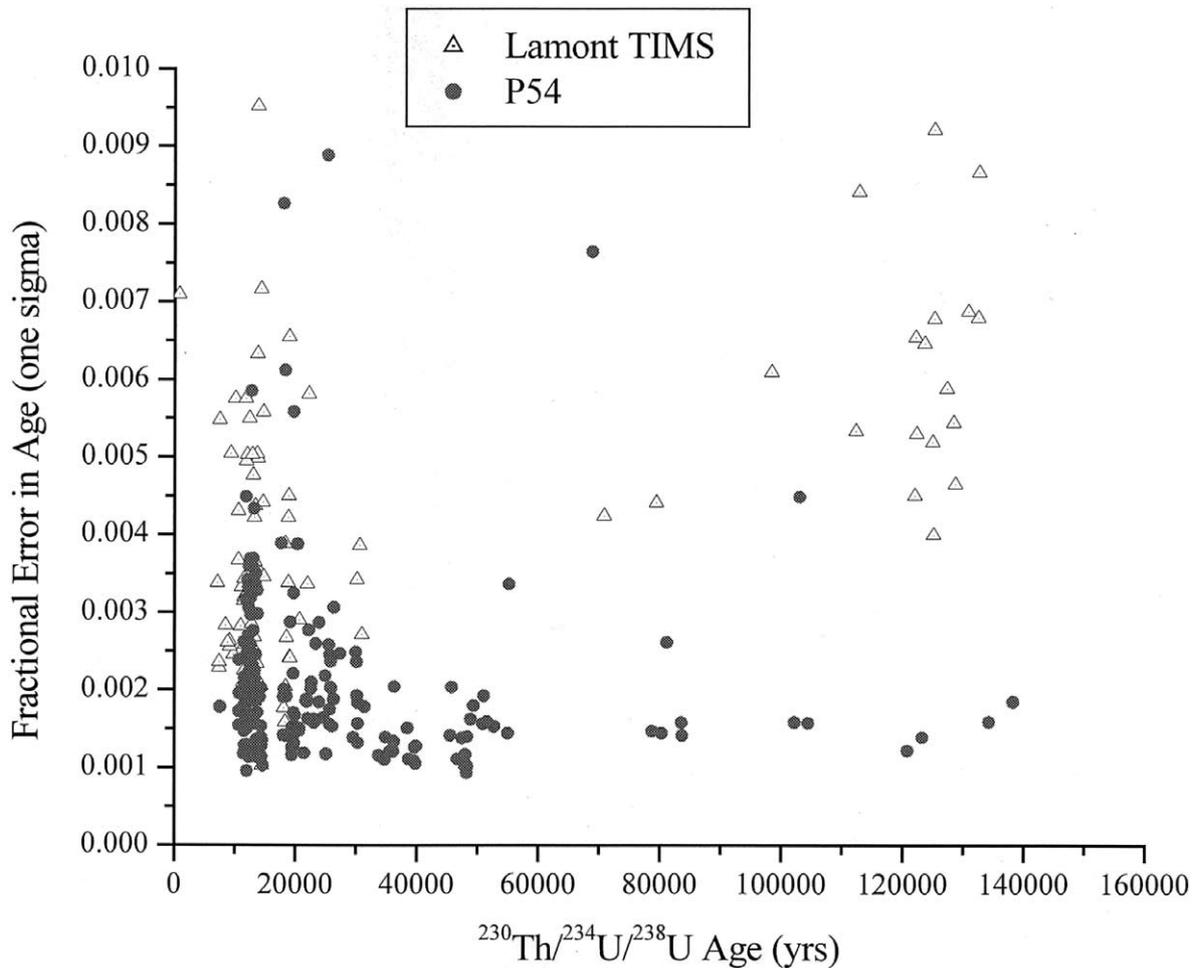


Fig. 2. Fractional error in age vs. $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ age for Lamont TIMS (triangles) and Plasma 54 (filled circles) measurements. Samples are from Barbados, Kiritimati Island, and Araki Island.

constant. As a check on measurement precision of the $^{233}\text{Pa}/^{231}\text{Pa}$ ratio and our chemical separation methods, we prepared a mixed ^{233}Pa and ^{231}Pa standard of $\sim 11 \text{ pg g}^{-1}$ and 3 pg g^{-1} , respectively. The mixed standard was prepared immediately following “milking” of ^{233}Pa from ^{237}Np and subsequent purification of ^{233}Pa from ^{233}U . Replicate measurements of the 233/231 mass ratios in the mixed standard were made 6 to 150 days after preparation of the standard. The concentration of ^{233}Pa in the mixed standard at any given time can be described by the following equation:

$$^{233}\text{Pa} = ^{233}\text{Pa}_0 * e^{-\lambda_{233} * t} \quad (1)$$

where $^{233}\text{Pa}_0$ is the initial concentration ($\sim 11 \text{ pg g}^{-1}$) and $\lambda_{233} = 2.570 \times 10^{-2} \text{ days}^{-1}$ is the decay constant of ^{233}Pa (Jones et al., 1986). Thus, the calculated concentration of ^{233}Pa in the standard was $\sim 9 \text{ pg g}^{-1}$, 4 pg g^{-1} , and 0.2 pg g^{-1} at 7, 40, and 150 days, respectively. Aliquots of the 40-day-old mixed standard were treated by the column chemistry described in Table 1. Assuming no fractionation of Pa from U during storage and assuming Pa and U behave similarly during sample nebulization, ionization in the plasma, and during transport and ion detection, the 233/231 mass ratio in the mixed standard should be constant with time regardless of the decay of ^{233}Pa to ^{233}U . Conversely, the $^{233}\text{Pa}/^{231}\text{Pa}$ ratio of the pure mixed standard in which the daughter product of ^{233}Pa (^{233}U) was removed (i.e., column chemistry) will have a $^{233}\text{Pa}/^{231}\text{Pa}$ ratio equal to the following:

$$233/231 = 233/231_0 * e^{-\lambda t} \quad (2)$$

Where 233/231₀ is the ratio in the parent solution, λ is the decay constant for ^{233}Pa , and t is the time elapsed between preparation of the mixed standard and the final column separation of Pa from U.

The 233/231 mass ratio in two aliquots of standard in which we separated ^{233}Pa from ^{233}U 40 days after initial purification measured 1.2056 and 1.2100. Solving for 233/231₀ in Eqn. 2, the decay-corrected 233/231 ratios of these solutions are equal to 3.367 and 3.379, respectively (Table 4), which are indistinguishable from the measured mean value of 3.374 ± 0.007 (2 SD; $n = 3$). The data in Table 4 suggest that the 233/231 ratio of the mixed standard measured at day 40 is $\sim 1\%$ lower than the ratio measured at either day 6 or day 150. We do not have an explanation for the offset but suggest an increase in background current (dark noise) resulting from the accumulated exposure of the Daly knob to ^{233}Pa might be responsible. Accumulated exposure would be presumed to have been at a minimum during analysis at day 6 (first exposure) and day 150 (minimum ^{233}Pa activity). In light of this anomaly, it is advisable to monitor background counts to determine if background current increases from prolonged exposure to β -decaying ^{233}Pa nuclide. Nevertheless, the consistency between values with and without column chemistry and analyses of procedural blanks provides convincing evidence for complete chemical separation of U and Pa. More importantly, the overall consistency between the 233/231 mass ratios in solutions across a *twenty-fold* range in ^{233}Pa concentration suggests negligible (less than 1%) differences between ^{233}U and ^{233}Pa during sample introduction and detection by MC-MS-ICPMS. Evidently, interference of ^{233}Pa by ^{233}U is not observed during ratio measurements. This

Table 4. Measured 233/231 mass ratios in a mixed standard originally containing approximately 11 pg g^{-1} ^{233}Pa and 3 pg g^{-1} ^{231}Pa .

Days after purification	Measured 233/231 ratio	Column Separation	Calculated 233/231 ratio
6	3.4235 (0.0342)	None	—
7	3.4239 (0.0311)	None	—
8	3.4161 (0.0342)	None	—
40	1.2056 (0.0086)	YES	3.3671 (0.0240)
40	1.2100 (0.0055)	YES	3.3795 (0.0187)
43	3.3736 (0.0405)	None	—
44	3.3715 (0.0223)	None	—
43	3.3781 (0.0276)	None	—
150	3.4297 (0.0361)	None	—
150	3.4239 (0.0236)	None	—
150	3.4403 (0.0143)	None	—

Ratio measurements were made 6 to 150 days after the initial purification of ^{233}Pa in the mixed standard. The measured 233/231 ratios at day 40 have been recalculated by correction of the decay of ^{233}Pa (Eqn. 2). Numbers in quotes represent the analytical errors (2 SD) in the measured ratio or the estimated error in the recalculated ratio.

observation reaffirms several clear advantages of MC-MS-ICPMS. Since it is not necessary to minimize in growth of ^{233}U from decay of ^{233}Pa , isotopic measurements of samples do not have to be made soon after (days to weeks) the column separation of Pa from U. Nor is the accuracy of $^{231}\text{Pa}/^{233}\text{Pa}$ ratio measurements dependent on the efficiency of uranium “burn-off” from filaments, as required by TIMS. It is highly recommended, however, that consistency standards (with and without column chemistry) and blanks be processed and analyzed simultaneously with samples so that potential errors introduced during chemical processing, or from changes in instrument performance, can be immediately identified.

Having established an initial estimate of the precision and accuracy in $^{233}\text{Pa}/^{231}\text{Pa}$ measurements, we determined the $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages of four Barbados fossil corals (30 ka) by the methods described in this work (Table 5). These samples were chosen as a test of the U-Th-Pa methodology because X-ray diffraction indicated detectable calcite at $<0.3\%$, and $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages of these samples were determined previously by MC-MS-ICPMS. While the sea level record (Fairbanks, 1989; Fairbanks, 1990) suggests that these corals were exposed to percolating vadose freshwater for $\sim 15,000$ yr, these samples were expected to yield concordant $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages based on the general absence of diagenesis on Barbados coral samples younger than 82,000 yr before present (BP).

Replicate $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages were determined from individually cored pieces (A and B). The same stock ^{233}Pa spike was used to prepare each set of samples and reference standard. A and B samples were spiked, processed, and analyzed approximately one month apart. We chose a Yemen speleothem, Y99-7Ra, as our ^{231}Pa and U reference standard. The age of the Yemen speleothem (585 ± 53 ka; determined by $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ method), its uranium content (3 ppm), and negligible ^{232}Th content (60 pg g^{-1}) make it an ideal standard since it can be assumed that Pa and U are in secular equilibrium ($[^{231}\text{Pa}/^{235}\text{U}] \text{ activity} = 1$) and the uranium content is close to that of corals. The ^{233}Pa spike concentration was calculated from the measured $^{233}\text{Pa}/^{231}\text{Pa}$ activity ratio and the

Table 5. $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages and initial $\delta^{234}\text{U}$ from Barbados coral samples.

Sample	U-Th age (yr)	U-Pa age (yr)	$\delta^{234}\text{U}_i$ (initial)	U-Th age* (yr)	$\delta^{234}\text{U}_i$ * (initial)
RGF12-28-6a	29,844(76)	27,068(581)□	142		
RGF12-28-6b	29,641(88)	29,877(430)	141		
Average	29,742(203)	29,877(430)		29,590 (82)	137
RGF12-28-7a	30,028(60)	29,860(489)	145		
RGF12-28-7b	29,708(68)	29,669(459)	143		
Average	29,868(320)	29,765(191)		30,158 (123)	139
RGF12-29-2a	30,290(73)	30,035(488)	142		
RGF12-29-2b	30,011(68)	30,645(338)	140		
Average	30,150(279)	30,340(610)		30,275 (80)	138
RGF12-30-3a	30,679(54)	30,220(579)	144		
RGF12-30-3b	30,515(75)	31,123(419)	145		
Average	30,597(164)	30,672(900)		30,292 (95)	140

All coral species are *Acropora palmata* and are listed in stratigraphic sequence. $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages were determined from the same dissolved fragment. A and B designate replicates from different fragments. $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages denoted by * were previously determined by methods without Pa spiking and with chemical separation of U and Th only. Numbers in quotes represent the analytical error (2 SD) or the difference between replicates.

□ denotes sample outliers and are not included. Ages were calculated using the following equations (Ivanovich et al., 1992):

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

$$\left[\frac{^{231}\text{Pa}}{^{235}\text{U}} \right] = 1 - e^{-\lambda_{231} * t_2}$$

In all calculations, we use decay constants of $\lambda_{230} = 9.1577 \times 10^{-6} \text{ year}^{-1}$, $\lambda_{231} = 2.1158 \times 10^{-5} \text{ year}^{-1}$, and $\lambda_{234} = 2.8263 \times 10^{-6} \text{ year}^{-1}$, (Cheng et al., 2000; Roberts et al., 1969).

U concentration of the speleothem. The ^{233}Pa spike concentrations used with sample set A and B were calculated to be 10.30 pg g⁻¹ and 4.24 pg g⁻¹, respectively.

We estimate the uncertainty in the $^{231}\text{Pa}/^{235}\text{U}$ age in Table 5 to be about $\pm 2.5\%$ by combining the analytical precision with an estimate of the external error ($\pm 1\%$: Table 4), and the uncertainty in the decay constant for ^{231}Pa ($\pm 0.6\%$).

$^{231}\text{Pa}/^{235}\text{U}$ ages of the four Barbados samples are stratigraphically consistent and are consistent with the paired $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages (Table 5). Excluding one discordant $^{231}\text{Pa}/^{235}\text{U}$ age (RGF12-28-6A), the average $^{231}\text{Pa}/^{235}\text{U}$ age is identical to the $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ age, and so we conclude that this procedure can be used to obtain $^{231}\text{Pa}/^{235}\text{U}$ ages to the precision necessary to confirm the reliability of closed system $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages.

4. DISCUSSION

High-precision and high-accuracy $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages paired with AMS radiocarbon dates of corals and speleothems (Edwards et al., 1993; Bard, 1998; Burr et al., 1998; Beck et al., 2001) and radiocarbon dating of microfossils samples from varved sediments (Goslar et al., 2000; Hughen et al., 2000) provide the opportunity to extend the record of $\Delta^{14}\text{C}$ from 12,000 to 50,000 yr. High-precision and high-accuracy $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages on corals from submerged fossil reefs and elevated terraces permit reconstructions of the magnitude and timing of past sea level changes (Edwards et al., 1987; Bard et al., 1990; Fairbanks 1990; Chappell et al., 1996; Yokoyama et al., 2001; Gallup et al., 2002; Cutler et al., 2003). Corals exposed to freshwater during sea level regressions may experience gain or loss of U and Th. The increased likelihood that corals have been exposed to freshwater, in either the vadose or

phreatic zone before the last glacial maximum low stand, presents challenges to both extending the ^{14}C calibration and to precise and accurate dating of past sea level changes. The $\delta^{234}\text{U}_i$ measured in a fossil coral relative to that of modern seawater is the first indicator of open system $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages. There are, however, limitations with the use of $\delta^{234}\text{U}_i$ as an a priori criterion. The historical data compiled for seawater and modern corals defines a range of generally accepted $\delta^{234}\text{U}_i$ values of between 140 and 150‰, rather than a single accepted value. Although conservative behavior of U and $\delta^{234}\text{U}_i$ in seawater has been firmly demonstrated (Delanghe et al., 2002), it has been suggested that the $\delta^{234}\text{U}_i$ of seawater may not be constant through time. (Hamelin et al., 1991; Richter and Turekian, 1993; Esat and Yokoyama, 2000). Despite these findings, it clear is that departures in excess of 10‰ in fossil coral $\delta^{234}\text{U}_i$ from a seawater value of $\sim 145\%$ suggest diagenetic alteration. In cases where coral samples have been exposed to freshwater and the $\delta^{234}\text{U}_i$ is within 10‰ of modern seawater, it is necessary to have an additional chronometer to test for age concordance. $^{231}\text{Pa}/^{235}\text{U}$ dating can confirm the accuracy of $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages. The 30 ka Barbados samples dated in this study represent the youngest of the Barbados corals believed to have been exposed to freshwater from the lowering of sea level at the last glacial. Verification of MC-MS-ICPMS techniques and closed system $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ ages for these samples demonstrates the potential for extending an accurate and precise radiocarbon calibration and sea level record from corals.

5. CONCLUSIONS

The precise and accurate determination of $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages from a single fossil coral fragment has

been demonstrated by multi-collector magnetic sector inductively coupled mass spectrometry (MC-MS-ICPMS). The ICP-MS method simplifies analytical procedures, reduces sample size, significantly reduces sample handling, and increases sample throughput when compared to TIMS. The MC-MS-ICPMS method makes redundant dating of corals by $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ a routine procedure. Although ionization efficiencies for U, Th, and Pa are superior by TIMS methodology, routine precision for our $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ dates is (0.3%; 2 RSD) comparable to the most precise measurements reported by TIMS. The analytical precision in determining $^{231}\text{Pa}/^{235}\text{U}$ by MC-MS-ICPMS is similar to that achieved by TIMS. Our estimate of the uncertainty in our $^{231}\text{Pa}/^{235}\text{U}$ dates is $\pm 2.5\%$ (2 RSD) and includes estimates in the uncertainty of λ_{231} and an unidentified external error. Further tests of replicate samples and of a homogenized coral standard will assist in identifying and substantially reducing the sources of external error. Our MC-MS-ICPMS methodology is sufficient to test for concordance of $^{230}\text{Th}/^{234}\text{U}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ages in the age range of 10 ka to 150 ka.

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