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^{238}U-^{234}U-^{230}Th-^{232}Th systematics and the precise measurement of time over the past 500,000 years

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We have developed techniques to measure the ^{230}Th abundance in corals by isotope dilution mass spectrometry. This, coupled with our previous development of mass spectrometric techniques for ^{234}U and ^{232}Th measurement, has allowed us to reduce significantly the analytical errors in ^{238}U-^{234}U-^{230}Th dating and greatly reduce the sample size. We show that 6×10^8 atoms of ^{230}Th can be measured to $\pm 30‰$ (2σ) and 2×10^{10} atoms of ^{230}Th to $\pm 2‰$. The time over which useful age data on corals can be obtained ranges from a few years to ~ 500 ky. The uncertainty in age, based on analytical errors, is ± 5 y (2σ) for a 180 year old coral (3 g), ± 44 y at 8294 years and ± 1.1 ky at 123.1 ky (250 mg of coral). We also report ^{232}Th concentrations in corals (0.083–1.57 pmol/g) that are more than two orders of magnitude lower than previous values. Ages with high analytical precision were determined for several corals that grew during high sea level stands ~ 120 ky ago. These ages lie specifically within or slightly postdate the Milankovitch insolation high at 128 ky and support the idea that the dominant cause of Pleistocene climate change is Milankovitch forcing.

1. Introduction

As for most isotopic measurements of radioactive and radiogenic nuclides, studies of ^{238}U-^{234}U-^{230}Th-^{232}Th systematics have two primary aims: to determine the age and/or some aspect of the mechanisms of origin of a geologic material. This system differs from the commonly used isotope systems because ^{234}U and ^{230}Th have relatively short mean lives ($\sim 10^5$ years) and, as intermediate daughters in the ^{238}U decay chain, are both radioactive and radiogenic. Because of the short mean lives, this system is appropriate for the investigation of processes which have occurred in the last $\sim 5 \times 10^5$ years. Much of this time period is inaccessible by other methods. Conventional ^{14}C dating has a range of up to $\sim 4 \times 10^4$ years. Measurement of ^{14}C by accelerator mass spectrometry has recently extended this range to $\sim 7 \times 10^4$ years (see [1]). K-Ar techniques [2–4] (and rarely Rb-Sr [2]) have been used to date K-rich volcanics about 10^5 years old, but the availability of such materials is limited and the analytical uncertainty for these young materials is large.

Because ^{234}U and ^{230}Th are α-emitters and because of their short mean lives, analysis is typically done by isotope dilution α-spectrometry. Over the past several decades, investigators have extensively examined the ^{238}U-^{234}U-^{230}Th-^{232}Th systematics of a variety of geologic materials using these techniques (see [5]). These efforts have focused on two major problems, the study of source region characteristics and fractionation processes during magma generation [6–13], and the dating of marine and lacustrine precipitates [14–20]. The former line of investigation is valuable because in principle ^{238}U-^{234}U-^{230}Th-^{232}Th systematics can be used to determine the U/Th ratio in a young volcanic rock as well as its source region. This provides a test for models of trace element fractionation during magma generation. The latter line of investigation is particularly important because the absolute chronology of the late Pleistocene (< 150 ky; 1 ky = 10^3 years) high sea level stands is based on ^{238}U-^{234}U-^{230}Th dating of corals. There is an apparent correlation between the ages of a number of coral terraces thought to represent high sea level stands and the

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times of high summer solar insolation in the northern hemisphere as calculated from known changes in the geometry of the earth's orbit and rotation axis [21–23]. This relationship is one of the major observations in support of the astronomical or Milankovitch theory of climate change [24] which states that the fluctuations in Pleistocene climate are caused by the changes in the distribution of solar energy received by the earth due to changes in the obliquity of the ecliptic, changes in the eccentricity of the earth's orbit and the precession of the earth's rotation axis.

Both of these important lines of investigation have been limited by (1) the analytical uncertainty obtainable by α-counting methods, and (2) the diagenetic changes of the host minerals. Studies of ^{238}U-^{234}U-^{230}Th-^{232}Th systematics in volcanics are critically dependent on the ability to determine the difference between the measured $^{230}Th/^{238}U$ activity ratio and unity. Yet, there appears to be some doubt as to whether any unaltered silicic volcanic rocks have $^{230}Th/^{238}U$ activity ratios measurably different from unity [12]. Similarly, the major issue in coral dating studies is whether ages of terraces thought to represent high sea level stands correspond to periods of high solar insolation in the northern hemisphere. Most coral terraces dated by ^{238}U-^{234}U-^{230}Th methods which are pertinent to the study of climatic fluctuations in the Pleistocene have ages between 70 and 150 ky. In this age range, a typical α-counting analysis gives a 2σ error of about ± 10 ky (see [25]). Since the time between successive peaks in the Milankovitch insolation curve is ~ 20 ky, if sea level highs correspond to Milankovitch insolation highs, then the ages of two successive terraces are barely resolveable at the 2σ level just considering analytical uncertainties. The time difference between a high point and an adjacent low point in the Milankovitch curve is ~ 10 ky. Therefore, a clear correlation between times of high insolation and ages of coral terraces representing high sea level stands cannot presently be made. For corals significantly older than 100 ky, ages of successive coral terraces cannot, in general, be resolved by α-counting.

We have therefore undertaken this study to examine the possibility of measuring ^{230}Th to high precision by isotope dilution mass spectrometry. We have recently shown that it is possible to routinely measure 5×10^9 atoms of ^{234}U to better than $\pm 5‰$ (2σ), 8×10^{12} atoms of ^{238}U to $\pm 2‰$ (2σ), and 3×10^{11} atoms of ^{232}Th to $\pm 20‰$ (2σ) using mass spectrometric methods [26–29]. The addition of high-precision ^{230}Th measurements to this group of nuclides would allow the application of ^{238}U-^{234}U-^{230}Th-^{232}Th systematics to a wide range of geologic problems. Among these is the potential to delineate the detailed chronology of events in the late Pleistocene and Holocene. The purpose of this study is: (1) to develop an accurate, high-precision technique to measure ^{230}Th in small amounts of coral by isotope dilution mass spectrometry; (2) to develop a procedure to separate U and Th from corals with high chemical yields and low procedural blanks; (3) to analyze ^{238}U, ^{234}U, ^{230}Th and ^{232}Th in a number of corals to determine the precision with which corals of different ages can be dated and compare these dates to those obtained by other methods; and (4) to use these techniques to date several corals thought to have grown during (a) high sea level stand(s) 120–150 ky ago and compare these ages to the time of the Milankovitch insolation high at 128 ky. The basic problem with the mass spectrometric determinations is the low level of ^{230}Th and the possible high ^{232}Th signal causing a contribution at mass 230. The more fundamental question of whether corals can be selected which represent truly closed systems must await more extensive studies.

2. Experimental methods

2.1. Instrumental procedure

Mass spectrometric procedures used in this laboratory for measuring small uranium samples [30,31] and for measuring ^{237}U [26] have been described earlier. The approach used here is virtually identical to the "isotopic composition" run described in the latter reference. We use a double spike with $^{233}U/^{236}U \approx 1$ and spike the sample so that $^{235}U/^{236}U \approx 10$. The measurements are carried out on the Lunatic I (LI) mass spectrometer using an electron multiplier with a gain of 4×10^3 in the analogue mode and an electrometer (Cary 401) with a 10^9 Ω feedback resistor [32]. Data are acquired in the sequence ^{236}U-^{235}U-^{234}U-^{234}U-^{233}U. Zeros are measured 0.5 mass units above and below each mass. Integration time for zeros

TABLE 1

Comparison between mass spectrometric and α-counting methods for measuring ^{230}Th and ^{234}U in a ~120 ky old coral

Method	Sample size	Number of ions or alpha particles measured/run		2σ uncertainty [a]		
		^{230}Th	^{234}U	^{230}Th/^{238}U	^{234}U/^{238}U	age (ky)
Mass spec.	200 mg coral	5×10^6	2×10^6	±2‰	±5‰	±1
α-counting	10 g coral	3×10^3	5×10^3	±40‰	±30‰	±10

[a] The α-counting uncertainties are taken from Harmon et al. [25] and are based on counting statistics.

and peaks are one second for all masses except ^{234}U. ^{234}U peaks are measured for four seconds and zeros for two seconds. Data acquisition takes ~ two hours and 100–200 ratios (50–100 cycles with two ^{234}U measurements/cycle) are measured. Data are acquired at filament temperatures of 1640–1800°C. The $^{234}U^+$ current ranges from 1500 to 3000 ions/s. The total number of ^{234}U ions collected in one run is $\sim 2\times10^6$. The main difference between the procedure used in this study and the one described in [26] is that 3×10^{10} atoms of ^{234}U are loaded on the filament instead of 5×10^9 atoms. This has the effect of lowering the temperature at which data is acquired by ~50°C and increasing the length of time the beam remains at high intensity by about a factor of 2. Consequently, the errors in ^{234}U/^{238}U shown in Table 4 tend to be slightly lower than those from our previous study. The ionization efficiency (ions produced/atoms loaded) for this procedure is $U^+/U \sim 5\times10^{-4}$ due to large sample size.

All data sets of ten ratios are normalized using the power law (see [33]) and the mean ^{233}U/^{236}U ratio for that set of ten ratios. The isotopic ratios and deviations of these ratios are then reduced using the full double spike equations. All quoted errors are 2σ of the mean ($2\sigma_M$). ^{234}U/^{238}U ratios are calculated for normalized ^{234}U/^{235}U ratios and ^{238}U concentrations calculated from the normalized ^{235}U/^{236}U ratios using $^{238}U/^{235}U = 137.88$. For a single run, $2\sigma_M$ for the ^{234}U/^{238}U ratio is typically ±4 to 5‰ and for the ^{238}U concentration is typically ±2 to 3‰ (see Tables 1, 3, 4).

Measurement of the Th isotopes is also carried out on the LI spectrometer using the same detector system. The sample is spiked with a ^{229}Th tracer so that each run contains $\sim 2\times10^{11}$ atoms of ^{229}Th. The number of ^{230}Th atoms loaded on the filament ranges from 6×10^8 for a 180 year old sample to 6×10^{10} for a sample of several hundred ky as shown in Table 2. Analogue scans of the Th spectrum for a young and old sample are shown in Figs. 1 and 2. At running conditions, the $^{229}Th^+$ current is $\sim 1\times10^5$ ions/s and the $^{230}Th^+$ current ranges from 4×10^2 to 4×10^4 ions/s. Data is acquired at filament temperatures of 1810–1870°C. The isotopes are measured in the sequence ^{229}Th-^{230}Th-^{230}Th-^{232}Th. Zeros are measured 0.5 mass units above and below each mass. Integration time for the ^{230}Th peaks is 4 seconds; for the ^{230}Th zeros and ^{229}Th peak, 2 seconds; and for the remaining peak and zeros, 1 second. Data acquisition takes ~40 minutes and 40–60 ratios (20–30 cycles with two ^{230}Th measurements/cycle) of ^{230}Th/^{229}Th are measured. The total number of $^{230}Th^+$ ions collected in a run ranges from 6×10^4 for the 180-year sample to 6×10^6 for the oldest sample. For the ^{230}Th/^{229}Th ratio, the value of $2\sigma_M$ for one run ranges from ±30‰ for the very young sample (180 years) to ±2‰ for samples ~100 ky old. These uncertainties are only a factor of 2–3 times the error

TABLE 2

Number of ^{230}Th atoms per analysis and weight of coral analyzed

Run	^{230}Th atoms $\times10^{-10}$	Coral weight (g)
TAN-E-lg	0.058	2.8
CWS-F-1	0.43	4.6
CH-8	3.2	4.1
AFS-12 A	2.4	0.25
AFS-12 B	3.8	0.39
AFS-12 C	2.7	0.28
E-L-3	2.3	0.26
E-T-2	2.2	0.28
VA-1	6.2	0.38

due to counting statistics alone when the ions making up the background under the ^{230}Th peak and the counting statistics associated with the ^{229}Th peak are included in the calculation.

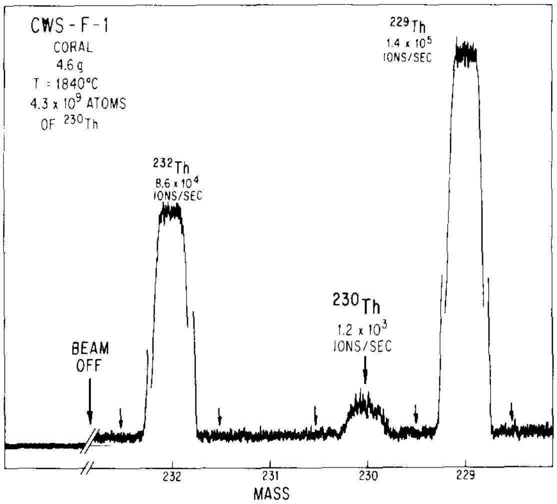

Fig. 1. Analogue scan of the Th spectrum for CWS-F-11 (845 years old) at a filament temperature of 1840°C. The sample was spiked with ^{229}Th. 4.3×10^9 atoms of ^{230}Th which had been extracted from 4.6 g of coral were loaded on the filament. The ionization efficiency was 0.8‰. Arrows show the position where zeros were measured. The background with the accelerating voltage on is slightly higher than the background with the accelerating voltage off due to the reflection of the ^{187}Re and ^{185}Re beams off the flight tube. The ^{230}Th abundance was determined to ±8‰ (2σ). Note the change in scale for ^{229}Th and ^{232}Th.

2.2. *Multiplier linearity and electrometer noise*

We have previously shown that the multiplier on the LI mass spectrometer is linear to ±2‰ for currents of up to 3×10^6 ions/s and isotopic ratios up to $\sim10^2$ and that the response time of the electrometer is such that within one second after an ion beam is taken off the multiplier, the signal is $<10^{-4}$ times the original signal [26,31]. For our Th measurements, the isotope ratios (^{229}Th/^{230}Th = 5–200) and ion currents (up to 1.6×10^5 ions/s) are not large enough to cause problems associated with electrometer response time or non-linearity problems that are significant. The noise level of the multiplier and amplifier under normal operating conditions is equivalent to ±12 ions/s where the uncertainty given is 2σ of the distribution for a series of 4-second noise measurements. The 2σ error for one ^{230}Th measurement including the background subtraction is ±17 ions/s. Since the ^{230}Th current is measured ~40 times in one run, the total error due to electrometer noise is $\pm17/\sqrt{40} = \pm3$ ions/s. For a ^{230}Th$^+$ current of 4×10^2 ions/s, this is about a quarter of the ±30‰ observed error. For larger samples, the error due to noise is smaller.

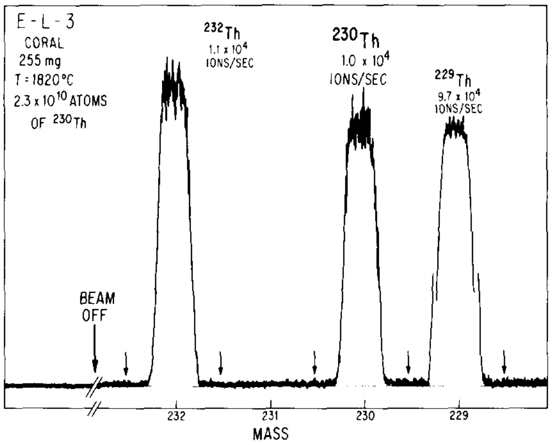

Fig. 2. Analogue scan of the Th spectrum similar to Fig. 1, but for a much older sample (E-L-3, 125.5 ky). 2.3×10^{10} atoms of ^{230}Th which had been extracted from 255 mg of coral were loaded on the filament. The ionization efficiency was 0.9‰ and the ^{230}Th abundance was determined to ±2‰. Note the change in scale for ^{229}Th.

2.3. *Background characteristics*

Under normal operating conditions, the background under the Th spectrum is slightly higher than the background with the accelerating voltage off (cf. Figs. 1 and 2). This difference is typically ~150 ions/s and is due to the reflection of the ^{187}Re$^+$ and ^{185}Re$^+$ beams off the flight tube. In the vicinity of the ^{230}Th peak, the background due to the reflected peak is effectively linear. For larger (i.e. older) samples, the background current is only a few permil of the ^{230}Th$^+$ current and does not introduce significant errors. For smaller samples, the background current is > 10% of the ^{230}Th$^+$ beam. This has the effect of lowering the precision of the ^{230}Th measurement slightly since the measurement of the ^{230}Th zero and the ^{230}Th peak are subject to the counting statistics associated with the ~150 ions/s. However, the Re beam is reasonably stable and does not change by large amounts during the course of a run. Since a ^{230}Th zero is measured immediately before and immediately after each ^{230}Th peak measurement, we do not believe that significant inaccuracy or imprecision other than that associated with counting statistics is introduced by the background current.

2.4. Fractionation

Fig. 3 shows the change in the measured ^{229}Th/^{232}Th during the course of a spike calibration run. This shows that, not including the very end of the run, Th fractionates by a total range of only 1.5‰ per mass unit in the course of a run. This is much less than the ±2‰ error of the highest precision ^{230}Th measurements as shown by the "$+2\sigma$" and "-2σ" lines in Fig. 3. For the data reported here, ratios measured at the end of a run when the beam is decaying by more than 5%/minute are not included. Reproducible results for several spike calibration runs indicate that instrumental fractionation does not introduce errors larger than the ±2‰ error of the individual runs even for isotopes different in mass by 3 amu. Fractionation at the multiplier is corrected for by multiplying the measured ^{n}Th/^{m}Th ratio by $(n/m)^{1/2}$, where n and m are the mass numbers. It has been shown previously by measuring the same sample with the multiplier and collector, that this relationship adequately corrects for multiplier fractionation on the LI system [34].

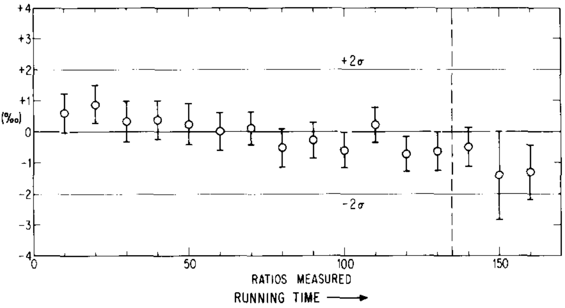

Fig. 3. This shows the measured ^{229}Th/^{232}Th ratio versus time for a spike calibration run. $D = \{[(^{229}\text{Th}/^{232}\text{Th})_{\text{TEN}}/(^{229}\text{Th}/^{232}\text{Th})_{\text{GM}}]^{1/3} - 1\} \times 10^3$ where the subscript TEN refers to the mean of a set of ten ratios and GM refers to the grand mean of all the ratios in the run. D is a measure of the deviation per mass unit of a given set of ten ratios from the grand mean in parts per thousand. The horizontal axis represents the time of data acquisition (~ 1 hour) and is scaled in cumulative ratios. The error bars for the individual points are $2\sigma_M$ for that set of ten ratios. The vertical dashed line represents the time that the beam began to decay by more than 5% per minute. Data to the right of this line is discarded. 10^{13} atoms of Th were loaded on the filament for this run. This is somewhat larger than typical filament loads for corals (10^{12} Th atoms). The horizontal lines labeled "$+2\sigma$" and "-2σ" represent the 2σ error in ^{230}Th/^{229}Th for high-precision coral runs. The total range of fractionation is well within these bounds, showing that error due to fractionation is small.

2.5. Ionization efficiency

The ionization efficiency for a number of Th runs on standards and Th separated from corals is shown plotted as a function of total Th loaded in Fig. 4. This shows that ionization efficiency decreases with increasing Th loaded on the filament using this approach. For the corals analyzed, total Th loads were $< 10^{12}$ atoms and ionization efficiencies were 0.7–1.3‰. As discussed below, corals have relatively high ^{230}Th/^{232}Th ratios (see Table 4), so for a fixed amount of ^{230}Th loaded on the filament, very little ^{232}Th is also loaded on the filament. Most geologic materials have ^{230}Th/^{232}Th ratios which are several orders of magnitude lower than corals, so for the same amount of ^{230}Th loaded, large amounts of ^{232}Th are also loaded. The relationship in Fig. 4 suggests that mass spectrometric ^{230}Th measurements on these materials would have significantly lower ionization efficiencies and, consequently, larger uncertainties than obtained here.

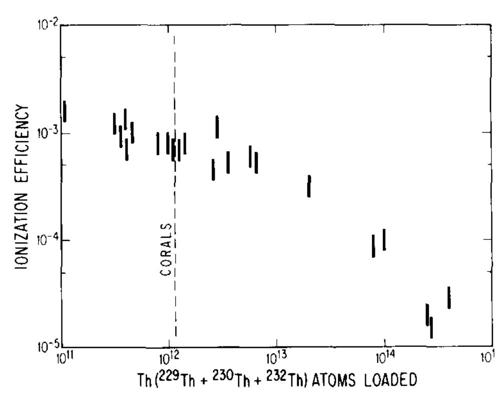

Fig. 4. This shows a log-log plot of the ionization efficiency vs. the total number of Th atoms loaded on the filament for corals and for standards. Ionization efficiency decreases with increasing Th loads. The coral runs all lie to the left of the dashed line marked "corals" and have ionization efficiencies of 0.7–1.3‰.

2.6. Spikes and standards

The ^{229}Th spike was obtained from Oak Ridge National Laboratory in solution in nitrate form. This was diluted with 1N HNO_3 and stored in a teflon bottle. Mass spectrometer runs to determine the isotopic composition of the spike showed that it was essentially pure ^{229}Th ($^{230}Th/^{229}Th < 2 \times 10^{-5}$ and the amount of ^{232}Th was indistinguishable from the filament loading blank, $^{232}Th/^{229}Th < 7 \times 10^{-4}$). Analogue scans showed that none of the U isotopes were present in appreciable amounts. A ^{232}Th standard solution was prepared (T. Wen, September 1976) from 99.998% pure ThO_2 powder (Johnson and Matthey) which was heated to 700°C, weighed, dissolved in a solution of 2.5N HNO_3 and 0.01N HF and stored in a 1-liter teflon bottle. This bottle has been weighed recently. Comparison with the original weight indicates that evaporative losses could not have increased the ^{232}Th concentration of the solution by more than 0.7‰ over the past ten years. The original ^{232}Th solution was diluted twice with ~ 1N HNO_3 in 1985. The dilute solutions had volumes of 1 liter and 500 ml and were stored in tightly capped, nearly full teflon bottles. In isotopic composition, these solutions had $^{230}Th/^{232}Th = 6.8 \pm 0.2 \times 10^{-5}$ and $^{229}Th/^{232}Th < 10^{-5}$. The ^{229}Th spike was calibrated against the most dilute ^{232}Th standard solution. The ^{229}Th concentration of this spike is $(5.508 \pm 0.006) \times 10^{11}$ atoms/g (mean and $2\sigma_M$ for four experiments). The error for each experiment ranged from ±0.9‰ to ±2.0‰. None of four experiments gave a concentration which differed from the average value by more than 1.5‰.

As a further check, another ^{232}Th solution was prepared recently from a Th metal powder which was significantly less pure than the ThO_2 powder. An aliquot of this solution was mixed with a ^{229}Th tracer and the $^{232}Th/^{229}Th$ ratio was measured. The ^{229}Th concentration determined using the Th metal standard agreed to ~ 1% with that determined using the Th oxide standards and showed that processes such as adsorption of Th onto the walls of the bottle, or precipitation of Th salts, which would lower Th concentration, have not occurred to any significant extent for the Th oxide standard over the past ten years. U standards and spikes are as discussed by Chen and Wasserburg [31].

2.7. Chemical separation of U and Th

Procedures for purification of U and Th are similar to those described in [26]. Coral samples (with the exception of some of AFS-12 which was provided to us in powdered form) were prepared by breaking the sample into pieces several millimeters in diameter with a stainless steel chisel. These fragments were examined under a binocular microscope and any pieces that showed signs of secondary alteration were discarded. The remaining pieces were ultrasonically cleaned in distilled water twice. The large pieces were then rinsed individually in distilled water, dried and weighed. The fine pieces were discarded. Samples of 2.8–4.6 grams of young (< 10 ky) coral or ~ 500 mg of old (> 10 ky) coral were dissolved by first adding several milliliter of distilled water, then slowly adding concentrated HNO_3 over the course of ~ 1 hour. The solution was heated under a heat lamp for ~ 1 hour. This resulted in the oxidation of any remaining organic matter and changed the color of the solution from slightly brown to clear. The sample was then spiked and, in order to insure sample-spike equilibration, dried, fumed with concentrated $HClO_4$, and dried. It was then dissolved in ~ 1N HCl and ~ 8 mg of Fe in chloride solution was added. The U and Th were then co-precipitated with Fe by the addition of ammonium hydroxide until the color of the solution changed from yellow to clear. The mixture was centrifuged and the supernate discarded. The residue was then rinsed twice with distilled water, dissolved in concentrated HNO_3, dried and redissolved in concentrated HNO_3 twice, dried and dissolved in 0.5 ml of 7N HNO_3. This solution was loaded on an anion exchange column (Dowex AG 1 × 8 resin) with a volume of 0.5 ml. Fe was eluted using 7N HNO_3. The Th fraction was then eluted with 6N HCl and the U fraction with 1N HBr. The U fraction was dried, dissolved with HNO_3, dried, dissolved in HNO_3, dried and dissolved in 0.1N HNO_3. An aliquot containing ~ 3 × 10^{10} atoms of ^{234}U (corresponding to ~ 70 mg coral) was loaded on a graphite-coated zone refined Re filament as described in [31]. The Th fraction was further purified by drying it down, dissolving it in HNO_3, drying it and dissolving it in 0.15 ml of 7N HNO_3. This solution was loaded on a column similar to the first column but with a volume of 0.15 ml. A similar elution scheme was followed. The subsequent Th fraction was dried, dissolved in HNO_3, dried and dissolved in 0.1*N* HNO_3. For samples younger than 10 ky, the whole Th fraction was loaded, and for samples older than 10 ky, half the Th fraction (corresponding to 250–390 mg of coral) was loaded on a graphite-coated zone refined Re filament. The loading technique is similar to the U loading technique. For the complete procedure, the U yield is > 95% and the Th yield is 93–98%. The amount of U in the Th fraction is $< 10^{-5}$ times the total U processed.

2.8. *Analytical blank*

We use zone refined, highly annealed Re filaments (REMBAR Co., Inc.) that have been outgassed at ~ 2000°C for 2 hours. Examination of one batch of Re ribbon showed that outgassed filaments coated with graphite following our standard procedure produced $^{232}Th^+$ currents of 6×10^2 to 4×10^5 ions/s and $^{238}U^+$ currents of < 60 to 3×10^3 ions/s when heated to typical temperatures at which data were acquired. Since typical sample currents are 3×10^7 ions/s for ^{238}U and 8×10^4 ions/s for ^{232}Th, many of the $^{232}Th^+$ filament currents were unacceptably high. Outgassing for longer periods of time or at slightly higher temperatures did not appreciably lower the currents. A second batch of Re ribbon from the same supplier gave filament currents of < 60 to 1×10^4 for $^{232}Th^+$ and < 60 to 2×10^3 for $^{238}U^+$. Out of 53 filaments, all but three had $^{232}Th^+$ currents below 1×10^3 ions/s. Since occasionally, filaments in this batch have high $^{232}Th^+$ currents, as standard procedure, we check every filament in the mass spectrometer before loading a sample on it. Filaments with $^{232}Th^+$ currents higher than 10^3 ions/s are not used.

The total procedural blank including the filament blank is 1.2×10^{10} atoms of ^{238}U and 1.0×10^{10} atoms of ^{232}Th with upper limits of 9×10^6 atoms of ^{234}U and 6×10^6 atoms of ^{230}Th. The blanks were determined using standard mass spectrometer runs with digital data acquisition and standard integration times. Blank levels of ^{234}U are presumably ~ 10^{-4} times ^{238}U and levels of ^{230}Th around 10^{-5} times ^{232}Th. In order to avoid introducing ^{230}Th and ^{229}Th contamination from previous samples, all re-usable labware, including ion exchange columns, which come in contact with coral solutions are divided into two groups. One group is used for young corals (< 10 ky) which have low ^{230}Th concentrations and, when spiked, have low $^{230}Th/^{229}Th$ ratios, and the other group for old corals (> 10 ky) which have high ^{230}Th concentrations and higher $^{230}Th/^{229}Th$ ratios. The two groups of labware are cleaned and stored separately. Ion exchange resin is discarded after every use. Between samples, ion exchange columns are rinsed with 7*N* HNO_3 and distilled water, stored (in separate groups) in 7*N* HNO_3, and rinsed with 7*N* HNO_3 and distilled water before the next use.

2.9. *Resolution of small differences in ^{230}Th abundance and time*

For one run, the 2σ error in $^{234}U/^{238}U$ is ±4–5‰. The error in the ^{238}U abundance is ±2–3‰ and the error in the ^{230}Th abundance ranges from ±30‰ for the 180 year old sample (TAN-E-lg) to ±2‰ for a 123.1 ky old sample (AFS-12; see Tables 1, 3, 4). The error in $^{230}Th/^{238}U$ therefore ranges from ±30‰ to ±3‰. When the analytical errors in $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ are propagated through the age equation (equation (1), discussed below), errors in age of ±5 years for TAN-E-lg and ±1.1 ky for AFS-12 A are calculated. Based on these errors, one would expect to be able to resolve the ages of two young (~ 200 year old) corals different in age by ~ 10 years and two old (~ 120 ky old) corals different in age by ~ 2 ky.

In order to confirm this age resolution estimate, we carried out the following experiment. About 3 g of AFS-12 were dissolved and the solution divided into five aliquots, four aliquots containing ~ 0.5 g of coral and the remaining aliquot kept in reserve. Known amounts of ^{230}Th from a ^{230}Th standard solution were added to three of the four aliquots. This increased the ^{230}Th concentrations in these aliquots by ~ 8‰, 16‰ and 32‰. This is equivalent to shifts in age of ~ 2, 4 and 8 ky. All four aliquots were then spiked, processed, and the Th isotopes measured as described above. The U isotopes were measured in one aliquot. The results are shown in Fig. 5 where the ^{230}Th abundance determined on the mass spectrometer is plotted against the gravimetrically determined ^{230}Th abundance. The ages corresponding to the ^{230}Th concentrations are also shown. These are calculated using equation (1) (see discussion below) and

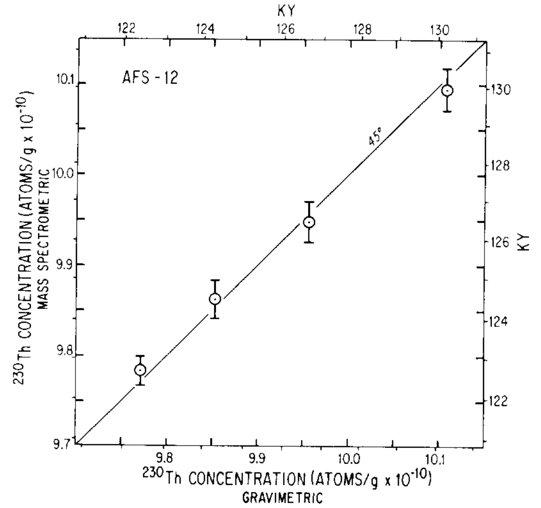

Fig. 5. This shows the mass spectrometrically determined ^{230}Th abundance (^{230}Th atoms/g) plotted vs. the gravimetrically determined ^{230}Th abundance for AFS-12 B and aliquots of AFS-12 B to which known amounts of ^{230}Th have been added. The axes are also scaled in ky using the measured ^{238}U abundance, ^{238}U/^{234}U ratio and equation (1). The error bars are $2\sigma_M$. None of the points deviate by more than 1.2‰ or 0.3 ky from a 45° line through the origin. The diagram shows that just considering the error in the ^{230}Th measurement, differences in age of < 2 ky are clearly resolvable for a coral ~ 120 ky old.

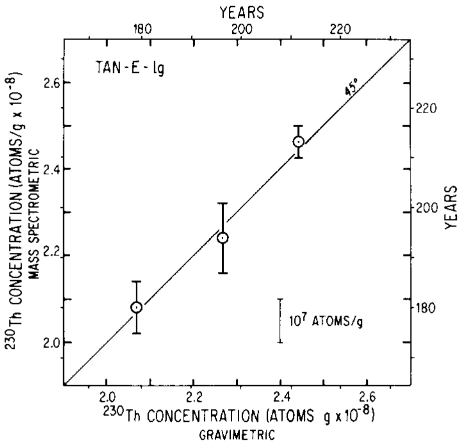

Fig. 6. This is similar to Fig. 5 but for a much younger coral (TAN-E-lg, 180 years). In addition to ^{230}Th atoms/g, the axes are also scaled in years. None of the points deviate from the 45° line by more than 12‰ or 2.4 years. The diagram shows that for corals ~ 200 years old, differences in ^{230}Th concentration of ~ 10^7 atoms/g, corresponding to differences in age of 17 years, are clearly quantitatively resolvable.

the results of the U analysis. The ^{230}Th concentration of the initial solution used in the calculation of the gravimetric ^{230}Th concentration is an average of the four ^{230}Th determinations after the known enrichments of ^{230}Th have been subtracted. All four points plot within 1.2‰ or 0.3 ky of a 45° line through the origin, indicating agreement between the mass spectrometric and gravimetric determinations will within the error of each individual measurement. Based on this experiment and assuming no error in the U analysis, it is clear that, for ~ 120 ky old corals, differences in age of 2 ky are analytically resolvable.

A similar experiment was performed to determine the age resolution for very young corals. About 15 g of TAN-E-lg was dissolved and the resulting solution divided into four aliquots. Three aliquots contained ~ 3 g of coral each, and the remainder was kept in reserve. ^{230}Th was added to two of the aliquots in order to increase the ^{230}Th concentration by 90‰ and 170‰, respectively. The number of ^{230}Th atoms added was 2×10^7 and 4×10^7. This corresponds to shifts in age of 17 and 33 years. The Th isotopes were measured in all three aliquots and the U isotopes in one aliquot. The results of this experiment are shown in Fig. 6. None of the points differ by more than 12‰ or 2 years from the 45° line, again well within the error of the individual measurements. This experiment shows that, for corals ~ 200 years old, differences in age of 17 years are clearly resolvable analytically.

3. Samples

We analyzed samples which had a variety of ages as well as samples which would provide information on the timing of the sea level high(s) at around 120 ky. Perhaps the most extensively studied coral terraces of this age are from Barbados [20–22], the Huon Peninsula in New Guinea [23,35] and islands in the New Hebrides Arc [36–38]. We have analyzed samples from Barbados and the New Hebrides as well as one coral from Hispaniola. Sample numbers, genus, species when known, locality, and references where more information concerning the samples can be found are listed in Table 3. TAN-E-lg, CWS-F-1 and CH-8 were provided to us by F.W. Taylor, AFS-12 (powder) by T.L. Ku, AFS-12 (rock fragment) and VA-1 by R.K. Matthews, and E-T-2 and E-L-3 by

TABLE 3

^{238}U and ^{232}Th concentrations in corals

Sample [a]	Genus and species	Locality	^{238}U (nmol/g) [b,c]	^{232}Th (pmol/g) [c,d]	(^{232}Th/^{238}U) $\times 10^5$
TAN-E-lg	*Platygyra* –	Tangoa Is., S. of Santo Is., New Hebrides Arc (F.W. Taylor, written communication)	10.80 ±0.04	0.083 ±0.003	0.77±0.03
CWS-F-1	*Platygyra* –	W. coast of Santo Is., New Hebrides Arc, (F.W. Taylor, written communication)	10.21 ±0.01	0.147 ±0.002	1.44±0.02
CH-8	*Siderastua radians*	Canada Honda, shore of Lago Enriquillo, SW Dominican Republic [39]	9.68 ±0.01	0.279 ±0.002	2.88±0.02
AFS-12 A	*Acropora palmata*	Rendezvous Hill, Christ Church Ridge, Barbados [20]	12.66 ±0.02	1.40 ±0.05	11.1 ±0.4
B	–	–	12.62 ±0.03	1.57 ±0.03	12.4 ±0.2
C	–	–	12.43 ±0.03	1.37 ±0.03	11.1 ±0.2
E-T-2	*Oulophyllia crispa*	Port Havannah, Efate Is., New Hebrides Arc, [40]	9.75 ±0.01	0.12 ±0.03	1.2 ±0.3
E-L-3	*Porites lutea*	Port Havannah, Efate Is., New Hebrides Arc, [40]	11.39 ±0.03	0.12 ±0.03	1.1 ±0.3
VA-1	*Acropora palmata*	Hill View Terrace, St. George's Valley, Barbados [20]	13.37 ±0.02	1.08 ±0.02	8.1 ±0.2
Open ocean surface water [e]	–		0.01383±3	0.00051±3	3.7 ±0.2

[a] A, B and C indicate replicate analyses; for AFS-12, A and B represent different fractions of the same powder and C represents separate coral fragments.

[b] Calculated using ^{238}U/^{235}U = 137.88.

[c] All errors are $2\sigma_M$. 1 nmol/g = 10^{-9} mol/g; 1 pmol/g = 10^{-12} mol/g.

[d] Corrected for the procedural blank of 0.02±0.01 pmoles ^{232}Th; most of the error is due to the uncertainty in the blank correction.

[e] Atlantic surface water from [26].

A.L. Bloom. All samples have been previously dated by ^{14}C, ^{230}Th/^{234}U (α-counting) or U-He (see Table 5). Except for VA-1, all samples were shown by previous workers, using X-ray diffraction techniques, to contain less than 1% calcite. TAN-E-lg was alive when sampled and the portion which we analyzed represents the annual growth bands from 1804 to 1810. All samples grew in marine environments except possibly CH-8, which was collected along the shore of Lago Enriquillo, a lake on Hispaniola [39]. This sample is close to the base of a marine transgressive sequence. Based on faunal assemblages, it is thought that the body of water from which CH-8 grew was connected to the ocean. AFS-12 is from the reef crest facies of the Rendezvous Hill or Barbados III terrace which is thought to have formed during a high sea level stand and has an age of 129 ± 9 ky

(^{230}Th/^{234}U, α-counting, 2σ; Ku, unpublished). E-T-2 and E-L-3 are from a terrace doublet on Efate Island in the New Hebrides Arc. E-T-2 is from the flower terrace and E-L-3 is from the upper terrace. Assuming that progressively higher terraces are older, E-L-3 would be the older of the two terraces. These have both been dated at 141 ± 16 ky (2σ, ^{230}Th/^{234}U (α-counting), [40]). They are thought to correlate with the terrace doublets of about the same age on the Huon Peninsula of New Guinea [36,40] and may correlate with a terrace doublet also of similar age on Loh Island in the New Hebrides [38]. It has been suggested that the double terraces in New Guinea represent two sea level highs ~ 125 ky and ~ 140 ky ago [41,42] (see [43]). The older of these two terraces would pre-date the nearest Milankovitch insolation high by some 10 ky and therefore could not be caused by this phenomenon. VA-1 (Hill View Terrace, Saint George's Valley, Barbados) has a U-He age of 520 ky [20] and was chosen in order to determine the isotopic characteristics of a very old sample. An extensive study [20] of these old terraces using U-He and ^{238}U-^{234}U-^{230}Th techniques has shown that many of the corals have ^{234}U/^{238}U initial values much higher than would be expected for a marine environment and some of them had ^{230}Th/^{234}U ratios slightly higher than the maximum possible value for a closed system.

4. Results

Our data for ^{238}U and ^{232}Th concentrations are shown in Table 3. ^{238}U concentrations in different corals are similar to those reported by previous workers. ^{232}Th concentrations vary by over an order of magnitude from 0.083 to 1.57 pmol/g and have errors of ±8‰ to ±250‰. The errors are largely due to the uncertainty in the blank correction (0.02 ± 0.01 pmoles ^{232}Th). Previous determinations of ^{232}Th in corals have not obtained such low values. The samples from Barbados (AFS-12 and VA-1) have distinctly higher ^{232}Th concentrations (1.08–1.57 pmol/g) than the other corals. ^{232}Th/^{238}U ratios are extremely low and range from 0.77×10^{-5} to 12.4×10^{-5}. These values are comparable to the ^{232}Th/^{238}U ratio of surface water in the open ocean (3.7×10^{-5}; [26,44–48]).

The isotopic data and the calculated ages are presented in Table 4. The ^{234}U/^{238}U atomic ratios have been reformulated into δ-notation, which denotes the fractional enrichment in ^{234}U/^{238}U relative to the ^{234}U/^{238}U ratio at secular equilibrium in parts per thousand. The observed value is given by $\delta^{234}\text{U}(0) = \{[(^{234}\text{U}/^{238}\text{U})/(^{234}\text{U}/^{238}\text{U})_{eq}] - 1\} \times 10^3$ where $(^{234}\text{U}/^{238}\text{U})_{eq}$ is the atomic ratio at secular equilibrium (5.472×10^{-5}). The initial value is $\delta^{234}\text{U}(T)$ and is calculated using equation (2) (below). ^{230}Th/^{238}U atomic ratios have also been represented as activity ratios $[^{230}\text{Th}/^{238}\text{U}\}_{act}$ by multiplying the ^{230}Th/^{238}U atomic ratio by $\lambda_{230}/\lambda_{238}$. The age is calculated from the ^{238}U-^{234}U-^{230}Th age equation (equation (1), below) using $\delta^{234}\text{U}(0)$ and $[^{230}\text{Th}/^{238}\text{U}]_{act}$.

Except for one sample, $\delta^{234}\text{U}(0)$ ranges from 103 for an older sample (E-T-2) to 152 for a younger coral (CWS-F-1). CH-8 has a distinctly lower $\delta^{234}\text{U}(0)$ (= 82) than the other samples. Errors are ± 4–6 δ-units. Except for CH-8 and VA-1, $\delta^{234}\text{U}(T)$ falls in a narrow range between 149 and 162. The range of these values is slightly higher but overlaps the range for present-day open ocean water of various depths (140–150; [26]). For CH-8, $\delta^{234}\text{U}(T) = 84$. For VA-1, $\delta^{234}\text{U}(T)$ is 530 using the U-He age (= 520 ky, [20]) and is much higher than the present seawater value. Not including VA-1, errors in $\delta^{234}\text{U}(T)$ range from ±4 to 9 δ-units and are somewhat larger than those for $\delta^{234}\text{U}(0)$.

^{230}Th/^{232}Th atomic ratios vary from 0.0042 for the youngest coral (TAN-E-lg) to 1.2 for an older coral (E-L-3). These values are extremely high compared to most geologic materials (^{230}Th/^{232}Th ~ 10^{-5}). This is due to the extremely low ^{232}Th/^{238}U ratio in corals. The error in these values, ±9‰ to ±250‰, is due largely to uncertainty in the blank correction for ^{232}Th.

^{230}Th/^{238}U atomic ratios range from 3.20×10^{-9} to 2.0144×10^{-5}, corresponding to activity ratios of 0.00190–1.1940. Errors range from ±30‰ for very low ratios to ±2‰ for higher ratios. VA-1 has ^{230}Th/^{238}U higher than the maximum possible value for closed system evolution from seawater, confirming observations by Bender et al. [20]. For the other samples, the ages and 2σ uncertainties in age have been calculated from equation (1), $\delta^{234}\text{U}(0)$ and $[^{230}\text{Th}/^{238}\text{U}]_{act}$ and are shown in Table 4. Replicate analyses have been

TABLE 4

U and Th isotopic composition of corals and seawater and coral ages [a]

Sample	$(^{234}U/^{238}U) \times 10^5$	$\delta^{234}U(0)$ [b,c]	$\delta^{234}U(T)$ [b,c]	$^{230}Th/^{232}Th$ [d]	$(^{230}Th/^{238}U) \times 10^5$	$[^{230}Th/^{238}U]_{act}$	Age [b,f]
TAN-E-lg	6.285 ± 31	149 ± 6	149 ± 6	0.0042 ± 2	0.00320 ± 9	0.00190 ± 5	180 ± 5 y
CWS-F-1	6.306 ± 22	152 ± 4	153 ± 4	0.0105 ± 2	0.01506 ± 13	0.00893 ± 8	845 ± 8 y
CH-8	5.920 ± 20	82 ± 4	84 ± 4	0.0465 ± 4	0.13415 ± 48	0.07951 ± 28	8,294 ± 44 y
AFS-12 A [g]	6.066 ± 22	109 ± 4	153 ± 6	0.116 ± 4	1.2811 ± 47	0.7593 ± 28	122.1 ± 1.1 ky
B	6.080 ± 35	111 ± 5	157 ± 7	0.103 ± 2	1.2874 ± 42	0.7631 ± 25	122.7 ± 1.3 ky
C	6.068 ± 25	109 ± 5	155 ± 6	0.117 ± 2	1.2957 ± 47	0.7680 ± 28	124.5 ± 1.3 ky
E-T-2	6.036 ± 22	103 ± 4	149 ± 6	1.1 ± 0.2	1.3179 ± 28	0.7811 ± 17	129.9 ± 1.1 ky
E-L-3	6.093 ± 26	113 ± 5	162 ± 7	1.2 ± 0.3	1.3071 ± 40	0.7748 ± 24	125.5 ± 1.3 ky
VA-1	6.136 ± 32	121 ± 6	–	0.249 ± 5	2.0144 ± 65	1.1940 ± 39	–
Open ocean water [h]	6.239 ± 26 to 6.292 ± 26	140 ± 5 to 150 ± 5	–	7×10^{-6} to 2×10^{-5}	3×10^{-5} to 7×10^{-5}	1×10^{-5} to 4×10^{-5}	–

[a] All errors are $2\sigma_M$; all isotope ratios are atomic ratios unless otherwise specified.

[b] $\lambda_{238} = 1.551 \times 10^{-10}\ y^{-1}$ [61]; $\lambda_{234} = 2.835 \times 10^{-6}\ y^{-1}$ [59,60]; $\lambda_{230} = 9.195 \times 10^{-6}\ y^{-1}$ [58].

[c] $\delta^{234}U = \{[^{234}U/^{238}U)/(^{234}U/^{238}U)_{eq}] - 1\} \times 10^3$ where $(^{234}U/^{238}U)_{eq}$ is the atomic ratio at secular equilibrium and is equal to $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$. $\delta^{234}U(0)$ is the measured value. $\delta^{234}U(T)$ is the initial value calculated using the ^{238}U-^{234}U-^{230}Th age (equation (1)) and equation (2).

[d] Corrected for the ^{232}Th blank of 0.02 ± 0.01 pmoles; most of the error is due to the uncertainty of the blank correction.

[e] $[^{230}Th/^{230}U]_{act}$ is the activity ratio calculated by dividing $^{230}Th/^{238}U$ by the $^{230}Th/^{238}U$ atomic ratio at secular equilibrium; $(^{230}Th/^{238}U)_{eq} = \lambda_{238}/\lambda_{230} = 1.6871 \times 10^{-5}$.

[f] Age refers to the age of the sample in 1986; 1 ky $= 10^3$ years.

[g] A, B and C indicate replicate analyses; A and B are different fractions of the same powder; C is a rock fragment from the same sample.

[h] Values for the U isotopic composition and the ^{232}Th and ^{238}U abundances are from [26]; the ^{230}Th abundance is from surface water values in [55].

performed for AFS-12. Analyses "A" and "B" are from different splits of the same powder and "C" is from a separate rock fragment. All three analyses give $\delta^{234}U(0)$, $[^{230}Th/^{238}U]_{act}$ and age which are in excellent agreement within the error of the measurements. The ages which we obtained for E-L-3 and E-T-2 suggest that E-L-3 is younger than E-T-2. This is in apparent disagreement with the field evidence [40], which suggests that since E-L-3 is from the higher terrace, it should be older. The reason for this discrepancy is not apparent to us.

5. Discussion

5.1. The ^{238}U-^{234}U-^{230}Th age equation and the uncertainty in age

^{234}U and ^{230}Th are the longest lived intermediate daughters in a decay series that starts with ^{238}U and ends with ^{206}Pb. The ^{238}U decay series with only the nuclides pertinent to this discussion is shown below:

$$^{238}\mathrm{U} \xrightarrow[6.446\times10^{9}\ \mathrm{y}]{} {}^{234}\mathrm{Th} \xrightarrow[34.8\ \mathrm{days}]{} {}^{234}\mathrm{U} \xrightarrow[352.7\times10^{3}\ \mathrm{y}]{}$$

$$^{230}\mathrm{Th} \xrightarrow[108.8\times10^{3}\ \mathrm{y}]{} {}^{206}\mathrm{Pb}$$

The times below the arrows are mean lives. The mean life of ^{238}U is several orders of magnitude longer than any of the intermediate daughters so that any closed system, regardless of the initial state, will approach a state of "secular equilibrium". In this state, the activities of all the intermediate daughters are the same and are equal to the ^{238}U activity. Any process which removes or adds nuclides in the decay chain will disrupt the equilibrium. The subsequent growth or decay of the intermediate nuclides toward a new equilibrium state can be used to date geological materials [14–17,49–54] ^{238}U-^{234}U-^{230}Th dating of corals is possible because of the extreme fractionation of U from Th in seawater ($^{232}Th/^{238}U$

is ~ 10^5 times lower than in igneous rocks). The $^{232}Th/^{238}U$ ratio in corals as shown in Table 3 is similar to that in seawater. The $^{230}Th/^{238}U$ ratio in seawater is similarly low. ^{230}Th measurements in surface water from the open ocean [55] indicate that this ratio is typically 3×10^{-10} to 7×10^{-10} or 2×10^{-5} to 4×10^{-5} times the equilibrium $^{230}Th/^{238}U$ ratio. If ^{230}Th does not fractionate greatly from ^{238}U during coral growth as appears to be the case from $^{232}Th/^{238}U$, then the initial $^{230}Th/^{238}U$ ratio must be negligible. Using this initial condition and the assumption that a coral remains a closed system with respect to U and Th, the equations for radioactive production and decay of ^{238}U, ^{234}U and ^{230}Th yield

Equation (1):

$$1-\left[\frac{^{230}\mathrm{Th}}{^{238}\mathrm{U}}\right]_{\mathrm{act}} = e^{-\lambda_{230}T} - \left(\frac{\delta^{234}\mathrm{U}(0)}{1000}\right)\left(\frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}}\right) \times \left(1-e^{(\lambda_{234}-\lambda_{230})T}\right)$$

(modified from Kaufman and Broecker, [17]).

Equation (2):

$$\delta^{234}\mathrm{U}(T) = \delta^{234}\mathrm{U}(0)e^{\lambda_{234}T}$$

where the λ's denote the decay constants and T is the age. Equation (1) is plotted in Fig. 7 which shows $[^{230}Th/^{238}U]_{act}$ plotted as a function of T and contoured in units of $\delta^{234}U(T)$. This shows that as T becomes large, $[^{230}Th/^{238}U]_{act}$ approaches unity. The second term on the right-hand side of the equation accounts for the fact that $\delta^{234}U$ in seawater and $\delta^{234}U(T)$ in corals are not equal to zero. Equation (1) shows that the age of a coral can be calculated if $\delta^{234}U(0)$, $[^{230}Th/^{238}U]_{act}$ and the decay constants are known. Equation (2) relates the observed $\delta^{234}U(0)$ to the initial state when the system was isolated with $^{230}Th = 0$.

In order to calculate the age accurately, accurate values for the decay constants must be known. Previous studies have used mean lives of 108,500 years for ^{230}Th and 357,800 years for ^{234}U, based on the studies of Attree et al. [56] and presumably Fleming et al. [57], respectively. We have chosen to use the more recent determinations of 108,750 ± 850 years (2σ; [58]) for the mean life of ^{230}Th

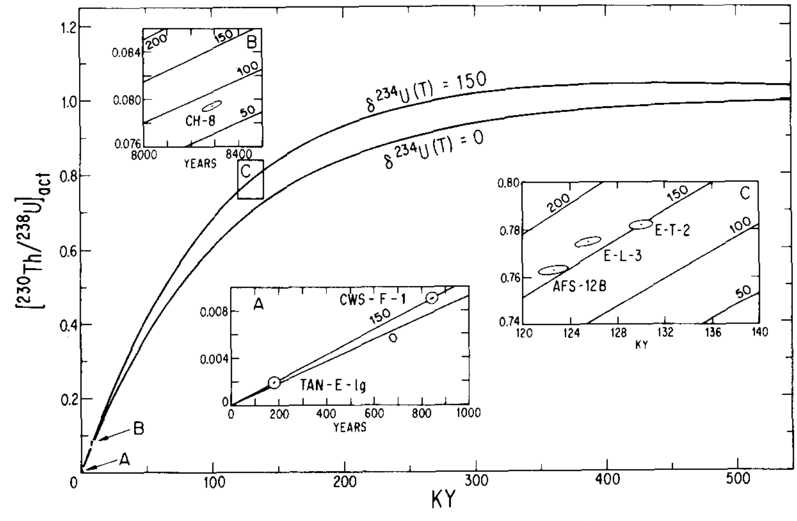

Fig. 7. This shows the change in $[^{230}Th/^{238}U]_{act}$ with time for different initial $\delta^{234}U$ values and is calculated assuming a closed system and assuming initial $^{230}Th = 0$ (equations (1) and (2)). $\delta^{234}U = 150$ is close to the present-day seawater value. Insets A, B and C are blowups of different areas of the graph. Note that the horizontal axes for A and B are scaled in years. All the contours are $\delta^{234}U(T)$ values. With the exception of VA-1 which cannot be plotted in this diagram, all the corals are plotted with their respective 2σ error ellipses. Note that for inset A, the analytical error is shown by the small black ellipses inside the open circles. The circles are drawn for clarity only. For insets B and C, the 2σ error is shown by the open ellipses and the mean value is represented by the centroid. With the exception of CH-8, which presumably grew in an environment restricted from the open ocean, all points lie on or close to the $\delta^{234}U(T) = 150$ line.

and 352,740 ± 710 years (2σ; [59,60]) for the mean life of ^{234}U. Within error, the earlier ^{230}Th value is the same as the more recent value, but the analytical uncertainty of the more recent value is much smaller. The value for ^{234}U is the average of the two 1971 references. These two values are different by 200 years. The 2σ error which we quote is from the latter reference. For ^{238}U, we use $(6.4464 \pm 0.0069) \times 10^9$ years (2σ; [61]).

The fractional errors in the decay constants are as follows: λ_{238}, ±1‰; λ_{234}, ±2‰; and λ_{230}, ±8‰. Errors in the decay constants will yield systematic errors in T. Errors in λ_{238} and λ_{234} are insignificant compared to our analytical errors for all T. For $\lambda_{230}T \ll 1$, λ_{230} is not an important term and does not introduce significant error in T. As T increases, λ_{230} becomes a more important term and the uncertainty in T increases. For $T < 150$ ky, the error in T due to error in λ_{230} is less than the error in T due to the analytical uncertainty. For T larger than 150 ky, the error in T due to error in λ_{230} is up to 1.5 times larger than the error due to analytical uncertainty. The error in years due to errors in λ's is ±0.4 for $T = 200$ years, ±2 for $T = 1000$ years, ±22 for $T = 10$ ky, ±800 for $T = 120$ ky, and ±17,000 years for $T = 300$ ky and is therefore insignificant compared to analytical error except at large T.

Uncertainties in T are also introduced by uncertainties in δ^{234}U(0) and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$. These uncertainties were the dominant source of error in earlier studies. We showed in the experimental method section that, based on the addition of a known quantity of ^{230}Th atoms, we could resolve the ages of two ~ 200 year old corals different in age by 17 years and could resolve the ages of two ~ 120 ky old corals different in age by 2 ky. We now examine the error in T, ΔT, introduced by analytical error, as a function of T. We have analyzed a number of corals of different ages. The calculated ages using equation (1) and the 2σ errors in age based on the propagation of the analytical errors in δ^{234}U(0) and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ through equation (1) are listed in Tables 4 and 5 and plotted in Fig. 7. The coral data are also plotted on a $\Delta T/T$ versus T plot (Fig. 8). We have drawn an error envelope through these points. This envelope has been extrapolated to larger and smaller T using the following assumptions: For extrapolating to large T, we have assumed that the analytical uncertainty for older corals is the same as the analytical uncertainty for ~ 120 ky corals. This assumption is reasonable since the number of atoms/gram of ^{230}Th and ^{234}U for an infinite age coral are both within 50% of their values for a ~ 120 ky old coral. For extrapolating to T younger than 180 years, we have assumed that the fractional error is inversely proportional to the square

TABLE 5

Coral ages using different methods or techniques [a]

Sample	^{14}C [b] (conventional)	^{14}C [c] (corrected)	Ring counting	^{238}U-^{234}U-^{230}Th (α-counting)	^{238}U-^{234}U-^{230}Th (this study)
TAN-E-lg	270 ± 120 y (1)	30–70, 180–270, or 300–500 y	176–182 y (1)	–	180 ± 5 y
CWS-F-1	980 ± 120 y (1)	780–1010 y	–	–	845 ± 8 y
CH-8	8990 ± 120 y (2)	~ 10,000 y	–	–	8294 ± 44 y
AFS-12 A	–	–	–	129 ± 9 ky (3)	122.1 ± 1.1 ky
B				129 ± 9 ky (3)	122.7 ± 1.3 ky
C				129 ± 9 ky (3)	124.5 ± 1.3 ky
E-T-2	–	–	–	141 ± 16 ky (4)	129.9 ± 1.1 ky
E-L-3	–	–	–	141 ± 16 ky (4)	125.5 ± 1.3 ky

[a] All errors are 2σ. Ages refer to the ages in 1986 (C.E.). Numbers in parentheses refer to the following sources: (1) F.W. Taylor (written communication), (2) Taylor et al. [39], (3) Ku (unpublished), (4) Bloom et al. [40].

[b] ^{14}C ages are as reported by the sources in radiocarbon years using the 8033 year mean life; no corrections have been made for natural fractionation of carbon isotopes, the difference between ^{14}C/C in surface water and the atmosphere, or differences in initial ^{14}C/C.

[c] ^{14}C ages have been corrected by us to dendroyears using the curves of Stuiver [68] for TAN-E-lg and CWS-F-1 and assuming a ^{14}C/C initial ratio from Klein et al. [69] for tree rings ~ 8000 years old. No corrections have been made for natural fractionation of carbon isotopes or the difference between ^{14}C/C in the surface water and the atmosphere.

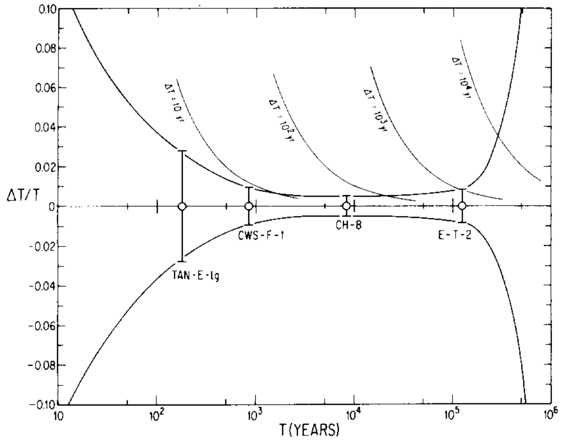

Fig. 8. This shows $\Delta T/T$ plotted versus time, where T is the age and ΔT is the 2σ error in age based on the propagation of analytical errors through equation (1). T is plotted on a log scale. Between 180 years and 129.9 ky, the error envelope is drawn through the observed values for several corals. The error envelope is extrapolated to younger and older T as described in the text. The lowest values of $\Delta T/T$ are at $\sim 10^4$ years and values of $\Delta T/T < 0.10$ can be obtained over the range $T = 15$ years to $T = 500{,}000$ years. Parts of the diagram are contoured in ΔT. The intersection of the $\Delta T = 10^4$ contour with the error envelope shows that $\Delta T < 10^4$ years for all $T < 3 \times 10^5$ years.

root of the number of ^{230}Th atoms per analysis. This error envelope shows that the smallest fractional errors in age of ~ ±5‰ are obtained for corals several thousand to several tens of thousands of years old. These samples are old enough to have enough ^{230}Th atoms for a high precision analysis (using small amounts of coral) yet are young enough ($\lambda_{230}T < 1$) to fall on the initial linear part of the $[^{230}\mathrm{Th}/^{238}\mathrm{U}]_{\mathrm{act}}$ growth curve (see Fig. 7). The error envelope also shows that $\Delta T/T < 0.10$ for corals as young as 15 years old and as old as 500,000 years old. Corals as old as 600 ky have ages distinguishable from infinity at the 2σ level. Fig. 8 is also contoured in absolute error, ΔT. Examination of the $\Delta T = 10^4$ years contour shows that, for all $T < 300$ ky, $\Delta T < 10$ ky. If sea level highs are separated by ~ 20 ky, it follows that all coral terraces representing sea level highs which are younger than 300 ky have analytically resolvable ages.

The analyzed corals have previously been dated by the counting of coral growth rings, ^{14}C, and/or ^{238}U-^{234}U-^{230}Th using α-counting methods and are compared in Table 5. TAN-E-lg was dated by ^{14}C and by counting of growth rings (F.W. Taylor, written communication). It was determined using the latter method that the portion of the coral which we analyzed grew between 1804 and 1810 (176–182 years old). Our date of 180 ± 5 years (at the time the sample was analyzed, June 1986) is in excellent agreement with this result. TAN-E-lg, CWS-F-1 and CH-8 have all been dated by ^{14}C (F.W. Taylor, written communication, [39]). For CH-8, the corrected age has been given as an approximation without uncertainties because the precise correction at this time does not appear to be known. The corrected radiocarbon ages and our ages for TAN-E-lg and CWS-F-1 are consistent within the errors of the measurements. However, there is a substantial difference between the corrected ^{14}C age and our age for CH-8. The reality of this discrepancy requires serious comparison of both methods, particularly for samples older than 8000 years where the availability of samples dated by dendrochronology is limited. We note that the analytical precision of the ^{238}U-^{234}U-^{230}Th dates is several times higher than the ^{14}C dates.

AFS-12, E-T-2 and E-L-3 have been dated previously using the ^{238}U-^{234}U-^{230}Th method by α-counting. Our determinations agree with the earlier results at the 2σ level of uncertainty of the errors quoted. However, the uncertainties in the present study are around an order of magnitude smaller. It is clear from Table 1 that the main reason behind the improved precision is that many more ions can be measured by mass spectrometry than α-particles by counting decays. We measured ~ 10^6 ions of ^{230}Th or ^{234}U per run, whereas in a typical α-counting run, ~ 10^3 α-particles are measured. The sample size which we use (250 mg of coral) is also ~ 40 times smaller than the typical sample sizes used for α-counting.

5.2. *^{232}Th concentrations and $\delta^{234}U(T)$*

Our ^{232}Th determinations in corals are extremely low (Table 3). Because of the extremely low values and the long mean life of ^{232}Th, α-counting studies have often not reported ^{232}Th. Examination of the reported ^{232}Th concentrations (cf. [16,18,62–66]) shows that the typical detection limit in the α-counting studies is about 100 pmol/g and that values as high as 10^4 pmol/g have been measured. Thus, the previous values (with the possible exception of [20]) are at least two orders of magnitude higher than the values which we report in Table 3. From an analytical standpoint, the low ^{232}Th concentrations found for corals mean that for a given amount of ^{230}Th loaded on the filament, relatively little ^{232}Th is also loaded on the filament. Thus, small amounts of total Th are loaded, ionization efficiency is high (see Fig. 4), and counting statistics for the ^{230}Th measurement are improved. The reliable determination of ^{232} Th also permits use of the ^{232}Th concentration as a geochemical tracer. From our results, it appears that $^{232}\mathrm{Th}/^{238}\mathrm{U}$ ratios in corals are about the same as open ocean surface water ([26]; Table 3), suggesting that these elements do not substantially fractionate from each other during coral growth. Substantial shifts in this ratio can therefore be used to indicate Th addition due to diagenesis (cf. [20]), metabolic effects, or growth from water with a different $^{232}\mathrm{Th}/^{238}\mathrm{U}$ ratio than open ocean water.

The precise $\delta^{234}\mathrm{U}(T)$ values are sensitive indicators of alteration or the environment in which a coral grew. All samples, with the exception of CH-8 and VA-1, have $\delta^{234}\mathrm{U}(T)$ values between 149 and 162. The range for open ocean water is $\delta^{234}\mathrm{U} = 140$–$150$ [26]. Considering errors, $\delta^{234}\mathrm{U}(T)$ for these samples is fully compatible with origin in a marine environment. This can be seen in insets "A" and "C" in Fig. 7 which show that these samples plot close to the $\delta^{234}\mathrm{U}(T) = 150$ contour. Based on the $\delta^{234}\mathrm{U}(T)$ values for the two youngest corals which are the least likely to have been altered, it appears that marine corals may initially have $\delta^{234}\mathrm{U}$ values that are at the high end or possibly higher than our values for open ocean water, possibly reflecting near-shore waters. For VA-1, $\delta^{234}\mathrm{U}(T) = 530 \pm 26$ (using the U-He age of 520 ky [20] for T). This is much higher than the seawater value and is clear evidence for diagenetic addition of ^{234}U, confirming previous observations [20]. CH-8 is thought to represent the initial stage of a marine transgression into the Enriquillo Valley [39]. However, the calculated $\delta^{234}\mathrm{U}(T) = 84$ (see inset "B", Fig. 7) is distinctly different from seawater, and cannot represent closed system evolution from normal seawater. It is possible that the sample was diagenetically altered or that CH-8 grew in a body of water that was restricted from the ocean and had a different uranium isotopic composition than the ocean. As Lago Enriquillo is reasonably shallow (~ 20 m deep), limited exchange with sediments could produce significant changes in uranium isotopic composition.

5.3. The Milankovitch curve and ages of corals ~ 120 ky old

Milankovitch [24] has calculated curves of the summer solar insolation at various latitudes as a function of time (cf. recalculations by Berger [67]). The curve for 65°N is appropriate for the initial growth of continental glaciers (see Fig. 9). This curve has low values between 166 and 137 ky, rises a maximum at 128 ky, then drops to a low value at 116 ky. According to the Milankovitch Theory, the height of sea level as a function of time should have a shape similar to the insolation curve. The dates of coral terraces representing sea level highs, should have ages close to or slightly younger than the 128 ky peak. Two successive coral terraces in New Guinea [23,35] have given ages determined by α-counting to be ~ 125 ky and ~ 140 ky and have led to the idea that the sea level curve may have had a double peak with ages corresponding

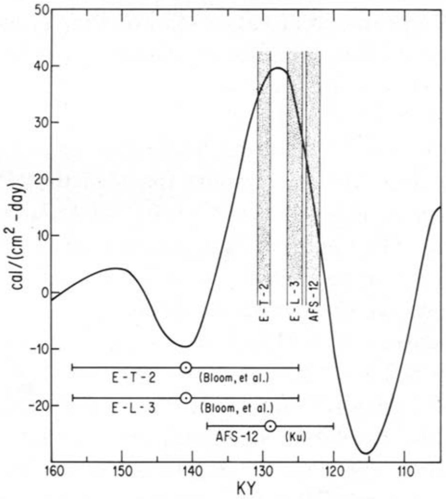

Fig. 9. The vertical axis represents the average solar insolation per day received at the top of the atmosphere at 65°N for the summer half year minus the present value. The curve is drawn for $T = 160$ ky to 105 ky and is taken from Berger [67]. The stippled bands represent the ages which we determined for E-T-2, E-L-3, and AFS-12. The error bars represent the ages of corals based on previous analyses (Bloom et al. [40], Ku (unpublished)). The ages which we have determined agree with the earlier values at the 2σ level but are much more precise and lie specifically within the Milankovitch band.

to the terrace ages [41,42]. A sea level high at ~ 140 ky would pre-date the 128 ky insolation peak by more than 10 ky and could not be the result of Milankovitch forcing. Kaufman [43] has argued, based upon a statistical analysis of a large number of dates, that if there were two peaks, they could not have been separated by more than 7.5 ky and that both peaks must have ages no older than 129 ky. The precise ages of these terraces should resolve this issue which is critical to our thinking about the causes of the Pleistocene glaciations.

AFS-12, E-L-3 and E-T-2 were known from previous work to have ages between 120 and 160 ky and are thought to have grown during periods of high sea level. E-L-3 and E-T-2 are from the upper and lower terraces of a terrace doublet in the New Hebrides which may correlate with the New Guinea terrace doublet [36,40]. Assuming the corals have not been altered, the ages of the terraces can be compared to the age of the insolation high. This is shown in Fig. 9 along with previous age data. The earlier data showed that the ages were in the general vicinity of 120–160 ky. Our data show that the ages lie specifically within the Milankovitch band. The age of E-L-3 (129.9 ky) appears to agree almost exactly with the 128 ky insolation high with a hint that it might be 2 ky older than the maximum. E-T-2 (125.5 ky) and AFS-12 (123.1 ky) appear to postdate the maximum by as much as 5 ky. The ages of E-L-3, E-T-2 and AFS-12 support the idea that Pleistocene sea level highs are the result of Milankovitch forcing. The apparent high position of sea level at 129.9 ky (represented by E-T-2) would require that, as the insolation curve increases, the phase lag between the Milankovitch and the sea level curves be very small (~ 1 ky or less). The age of AFS-12 suggests that sea level was still high, 5 ky after the insolation peak, suggesting that, as the insolation curve decreases, the phase lag is significantly larger. From the spread in ages between E-T-2 and AFS-12, it appears that sea level was high for at least 7 ky during the last interglacial period. Our data do not preclude the possibility of a double sea level peak at ~ 120 ky, but suggest that if there is a double peak, both occurred specifically within the band and could be explained in a general way by the Milankovitch mechanism.

6. Conclusions

We have shown that it is possible to measure 6×10^{8} ^{230}Th atoms to ±30‰ and 2×10^{10} ^{230}Th atoms to ±2‰ by isotope dilution mass spectrometry (2σ). This, coupled with the ability to measure 3×10^{10} ^{234}U atoms to ±5‰ and ^{238}U to ±2‰ [26], has allowed us to reduce significantly the analytical errors in ^{238}U-^{234}U-^{230}Th dating. This has allowed us to expand the time range over which useful age data on corals can be obtained to a range of a few years to ~ 500 ky. The uncertainty in age is ±5 years for a 180 year old coral (3 grams) and ±1 ky for a 123.1 ky old coral (250 mg). The ability to analyze small samples is very important with regard to studies of marine terraces. Reef forming corals are largely limited to the tropics. Solitary corals, however, grow in marine environments worldwide, and can be found in marine terraces of different latitudes, but only occur in small masses. Few marine terraces have yielded enough solitary coral for analysis by α-counting. The small sample size may also allow dating of materials such as foraminifera, clams and bones. Dating of these materials has been limited either by sample size requirements or sample alteration. The use of high dispersion mass spectrometers and ion counting detector systems will allow further refinement of these techniques, including extension to volcanics with high ^{232}Th contents. The precise measurements on corals which grew during sea level high(s) around 120 ky ago give ages which lie specifically within the 128 ky Milankovitch peak. Assuming closed system behavior, these ages support the idea that changes in Pleistocene climate are largely due to Milankovitch forcing.

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