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High precision Faraday collector MC-ICPMS thorium isotope ratio determination

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Abstract

Uranium-series dating of carbonate materials requires precise determination of the spike sample thorium isotope ratio, ^{230}Th/^{229}Th. This ratio is commonly measured using ion counting techniques, however the precision of analyses using ion counting devices suffers from beam intensity limitations, drift in multiplier gain and non-linearities in electron multiplier response. Here, we describe the application of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) to determine thorium isotope ratios at hitherto unattained precision. For the first time, thorium isotope analyses were performed using only Faraday collectors coupled to 10^{11} Ω feedback resistors in the amplifier system. Spiked thorium solutions were concentrated to produce ^{230}Th and ^{229}Th signal intensities of around 50 mV and 100 mV, respectively (across a 10^{11} Ω resistor) and are run at high intensity for a short period of time (~1 min). These analyses yield a ^{230}Th/^{229}Th external reproducibility of better than 0.3‰ for ~25–30 pg of consumed ^{230}Th. This is a factor of two better than the best published thermal ionisation mass spectrometry (TIMS) and MC-ICPMS techniques for similar sample sizes, and represents up to an order of magnitude improvement over many other established protocols. Combined with new techniques for high precision Faraday measurement of uranium isotopic composition [1], this permits improvements in the uncertainty of U-series ages to better than 0.1 thousand years (ka) at 100 ka and 1 ka at 300 ka. It should also be possible to resolve events to ~14 ka at 600 ka. Using these techniques, the U-series dating limit can be extended from 500–600 ka to 800 ka enabling a more detailed study of the frequency of late Pleistocene climate events.

Keywords: U-series dating; Coral; Faraday; Thorium; Th isotopes; Mass spectrometry; MC-ICPMS

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1. Introduction

Late Pleistocene carbonates such as corals and speleothems are important archives for paleoclimate studies, such as tracking sea-level changes through the glacial–interglacial cycles of the Quaternary and constraining records of continental climate change. Uranium-series analysis is a uniquely appropriate dating tool for this time period and takes advantage of the disequilibrium of isotopes within the uranium decay series at the time of deposition of the carbonate matrix [2]. Uranium is highly soluble in its oxidised (VI) state, compared to the relatively insoluble thorium. Providing there is no initial detrital contamination and the sample remains a closed system, the ^{230}Th/^{238}U activity ratio of the sample is initially zero and evolves towards unity as the system approaches secular equilibrium at a rate that is determined by the decay half-lives of ^{238}U's daughter isotopes ^{234}U and ^{230}Th (~245 ka and ~76 ka, respectively [3]). The dating limit of the U-series technique depends on the precision with which the relevant isotope ratios (^{234}U/^{238}U and ^{230}Th/^{238}U) can be determined. Precision of these analyses is limited by the very low abundance isotopes of ^{234}U and ^{230}Th, which are present in coral samples, for example, at levels of less than 200 pg/g and 50 pg/g, respectively.

The precision of U-series analytical techniques has undergone significant advancement since the introduction of α-spectrometry analyses in the 1950s, for which 10 g of a 120 ka coral sample (3 ppm U) would yield an age uncertainty of ±10 ka (not including uncertainties in decay half-lives) [4]. The development of U-series measurements using thermal ionisation mass spectrometry (TIMS) led to an order of magnitude improvement in age uncertainty (±1 ka at 120 ka) for much smaller sample sizes (200 mg of coral) [2]. Further improvement in mea-

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surement precision of thorium isotopes, using charge collection TIMS (CC-TIMS) [5,6], produced even smaller age uncertainties (0.4 ka at 120 ka).

Multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) offers a number of advantages over conventional TIMS techniques. In particular, the ICP source produces highly efficient ionisation of most elements, including those that are difficult to ionise by TIMS, such as thorium. Furthermore, the ionisation efficiency is not dependent on load size. Because the sample is introduced as a solution, the signal intensity can be adjusted simply by changing the concentration of the solution. Also, to a first approximation the instrumental mass discrimination in one element can be corrected for by admixing with another element [7]. The application of MC-ICPMS to U-series dating has led to improvements in measurement precision and reductions in both analysis time and sample size [8–12]. U-series age uncertainties of 0.2 ka (for a 120 ka sample) have been achieved for sample sizes similar to those used in TIMS analyses [9]. Continuing development and improvements in the design of the plasma source interface has led to further improvements in sensitivity of second-generation MC-ICPMS instruments.

Among the variety of modern TIMS and ICPMS analysis techniques currently employed in the measurement of uranium and thorium isotope ratios, most make use of single or multiple ion counting devices to obtain high precision data for the low abundance isotopes, ^{234}U and ^{230}Th. However, the accuracy and precision of measurements using ion counting devices are potentially threatened by limitations on maximum beam intensity, dead-time corrections, drifts in multiplier gain and non-linearities in electron multiplier response [3,13]. In contrast, Faraday collectors are characterised by high stability and linearity. Instead, their relatively high (Johnson) noise places a constraint on the minimum intensity of the ion beam that can be precisely measured.

In this study, the potential for measuring thorium isotope ratios in a single, static cycle analysis using only Faraday collectors is examined. It is demonstrated that the precision attained using this technique represents up to a factor of 10 improvement over many established protocols, while significantly reducing analysis time by two orders of magnitude. The improved precision of uranium and thorium isotope measurements using Faraday methods not only improves the uncertainty of a calculated U-series age, but also extends the dating limit of the technique.

2. Experimental procedures

2.1. Instrumentation

Analyses were conducted on a Nu Plasma MC-ICPMS (Nu Instruments, Wrexham) which uses variable mass dispersion zoom optics to direct the ion beams into a fixed-spacing array of Faraday collectors and ion counter(s). Each Faraday collector is coupled to a 10^{11} Ω feedback resistor in the amplifier system. The abundance sensitivity of the instrument, defined by the tailing contribution of ^{238}U at mass 237 varied between 2 ppm and 2.5 ppm at the time of our experiments. Sample solutions are introduced via an ARIDUS or CETAC MCN-6000 microconcentric nebuliser (uptake rate 70–110 μl/min).

2.2. Chemical preparation

The ratio of ^{230}Th/^{238}U is an important parameter for U-series dating and is determined by isotope dilution using a mixed ^{229}Th–^{233}U (^{229}Th–^{236}U) spike of known composition. The ^{232}Th concentration is a useful indicator of detrital contamination. During thorium analyses, the ^{230}Th and ^{232}Th signals are measured relative to a ^{229}Th spike. The Faraday analysis protocol described in this paper requires: (1) a high degree of separation of the uranium and thorium and (2) a very clean solution that is free of residual matrix elements and organics. First, the samples are dissolved and spiked with a ^{229}Th spike tracer. For high matrix samples, i.e., with uranium concentrations of $\leq$50 ppm, the uranium and thorium are concentrated from the matrix by iron co-precipitation. The sample is loaded in 1.5N HNO_3 onto a 0.5–0.6 ml TRU resin (Eichrom) column (after [8]). Matrix elements are eluted with 3N HCl and the uranium and thorium are then eluted together in 0.1N HCL + 0.3N HF. For a second cleaning step and final separation, the U–Th mix is loaded in 3N HNO_3 on a 0.5–0.6 ml column of UTEVA resin (Eichrom). Residual matrix is further eluted in 3N HNO_3 and the thorium is then eluted in two steps with a 3N HNO_3 + trace HF mix followed by 3N HCl. Finally, uranium is eluted with 0.1N HCL + 0.3N HF. This procedure yields excellent separation of the uranium and thorium (less than 0.2% of the uranium in the thorium fraction) and is virtually free of residual matrix elements. A fraction of the separated uranium is admixed with the thorium for instrumental mass bias correction during analysis (see Section 2.4 for details). Organic matter associated with the sample and/or resin is destroyed by rigorous treatment with mixed H_2O_2/HNO_3. Samples are dried down and then diluted in ∼0.2N HCL + 0.05N HF for analysis on the MC-ICPMS.

2.3. Data acquisition

Due to the low concentrations of ^{230}Th and ^{232}Th in coral samples (<50 pg/g), in conventional TIMS and MC-ICPMS thorium-analysis protocols the thorium isotopes are either: (1) cycled through a single ion counter (e.g., [2]) or (2) measured simultaneously with parallel ion counters (e.g., [10]). The instabilities and non-linearity effects associated with ion counting/electron multiplier devices are well recognised and place limitations on the accuracy and precision of ion counter analyses [3,13].

To avoid the problems associated with electron multiplier analyses, the measurement protocol described here uses multiple Faraday collectors (Table 1) to measure the thorium isotopes simultaneously in high concentration thorium solutions. On-peak analyses are conducted over a period of 1.0–1.5 min with a minimum ^{230}Th signal intensity of $\sim 5 \times 10^{-13}$ A (∼50 mV on a 10^{11} Ω resistor). Total ^{230}Th consumption during a 1 min analysis is approximately 25 pg. Admixed uranium from the

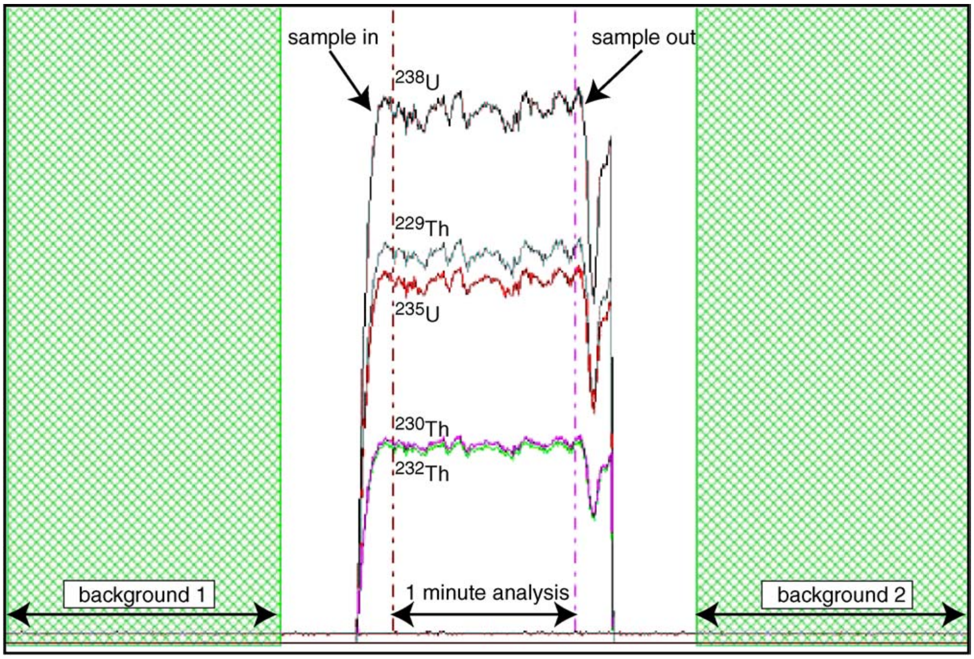


Fig. 1. Measurements are conducted using the "time-resolved" software supplied with the Nu Plasma MC-ICPMS. A 1 min on-peak analysis (0.2 s integration time) is bracketed by two 90 s background measurements with a deflected beam (^{238}U signal is not to scale). The interpolated background measurements are applied to the on-peak analysis.

sample, with a signal intensity of between 1×10^{-10} A and 1.5×10^{-10} A (10–15 V on a 10^{11} Ω resistor), is used to correct the thorium isotope ratios for instrumental mass discrimination in the ICPMS (discussed further in the following sections) (Fig. 1).

The contribution to each of the 50–100 mV thorium isotope signals from the ^{238}U peak tailing is very small, equivalent to less than 0.06‰ of the thorium beam intensity, and is effectively removed by normalising to the bracketing standard. Because of the very small thorium signals on the Faraday collectors, it is important to monitor the variability in the Faraday detector noise before and after the on-peak analysis. The background zero corrections, which represent the electronic noise of the detectors, are measured as "on-mass" zeros, while deflecting the ion beam off-axis. The magnitude of the drift in the detector noise of a given collector varies and if not reliably monitored and corrected for, can offset the measured thorium isotope ratios from the true values by up to 0.3‰. For this reason, an extended 90 s zero is monitored both before and after the sample analyses and a linear interpolation of the zero measurement is applied to the data set. This interpolation method improves the reproducibility of a set of analyses.

Table 1
MC-ICPMS collector configuration

Part (A)		Part (B)	
H6	238	Pos 1	(238)
–		Pos 2	
H5		Pos 3	236
H4	235	Pos 4	(235)
H3		Pos 5	
H2		Pos 6	233
H1	232	Pos 7	232
Ax		Pos 8	
L1	230	Pos 9	230
L2	229	Pos 10	229

(A) Collector configuration for the Nu Plasma instrument used in this study. The known ratio of ^{238}U/^{235}U in the admixed uranium is used to correct for instrumental mass bias. If the cup configuration of the instrument used for analysis does not allow for ^{238}U–^{235}U mass bias correction then an alternative collector configuration can be used (B) for which a ^{233}U–^{236}U double spike is used to correct for instrumental mass bias.

Memory effects are generally less of a problem in these Faraday analyses because the short duration, high intensity runs have a higher memory tolerance than long duration, low intensity analyses. To minimise the effects of residual thorium memory, the ^{230}Th/^{229}Th of each sample is matched to the ^{230}Th/^{229}Th of the bracketing standard. The most effective washout is achieved with progressive strengths of HCl + HF acid mixes. To ensure a negligible effect on the measured ^{230}Th/^{229}Th ratio, the required background signal of ^{230}Th prior to measurement is set to less than 1×10^{-16} A (500–600 cps on an ion counter), which is achieved very rapidly, within 5–10 min.

2.4. *Standard normalisation*

All thorium isotope analyses are measured relative to an in-house bracketing standard, which consists of an artificial mix of the thorium isotopes ^{229}Th, ^{230}Th and ^{232}Th (in the approximate ratio 2:1:1) with a uranium metal standard (CRM 145). The purpose of this bracketing standard is to monitor long-term reproducibility in thorium isotopic ratios. In most cases, the measurement "sessions" referred to in the following sections represent the new start up of the machine and tuning after a break of weeks or months.

The large mass discrimination in an ICP source and transfer region reflects the enhanced transmission of heavier isotopes over lighter ones (on the order of 0.5% per amu). The known isotopic composition of the admixed uranium ($^{235}U/^{238}U$) is used to calculate the instrumental mass bias and this correction is then applied to the measured thorium ratios. Because of the varying behaviour of different elements in the ICPMS, it may not always be appropriate to apply the mass bias factor of one element to another [14]. Generally, this effect is considered unimportant for Th–U external normalisation at the current levels of thorium isotope measurement precision, e.g., [10]. However, because of the improved precision attained using the Faraday method, the standard was monitored regularly throughout each measurement session in order to monitor the veracity of externally normalising Th measurements using U.

The absence of a certified thorium isotopic standard with a $^{232}Th/^{230}Th$ ratio similar to that of well preserved corals combined with the uncertainties arising from mass bias correction of thorium using admixed uranium creates difficulties in demonstrating the accuracy of an absolute thorium isotope ratio measurement. For the purposes of U-series dating, this uncertainty is overcome by using the in-house standard to bracket and normalise the thorium analyses of both the unknown samples and the spike calibration runs. The $^{229}Th/^{233}U$ ratio calibration of the spike is made by analysing a spiked sample with an assumed secular equilibrium $^{230}Th/^{238}U$ value. In this way, any shifts in the thorium isotopic ratios that are introduced by assuming the uranium and thorium mass bias factors to be equal is cancelled out in the final calculation of the sample $^{230}Th/^{238}U$. Hence, for the purpose of U-series dating, it is sufficient to measure thorium ratios relative to an in-house standard, even if the isotopic composition of that standard is not known absolutely.

3. Results

3.1. Bracketing standard

The results for repeat measurements of the $^{230}Th/^{229}Th$ in the bracketing standard over several measurement sessions are given in Fig. 2A. On average, the within-run measurement precision of $^{230}Th/^{229}Th$ for the in-house standard with a ^{230}Th signal size of 50–60 mV is 0.26‰ (2σ, 2 standard deviations), which is identical to the average within-session reproducibil-

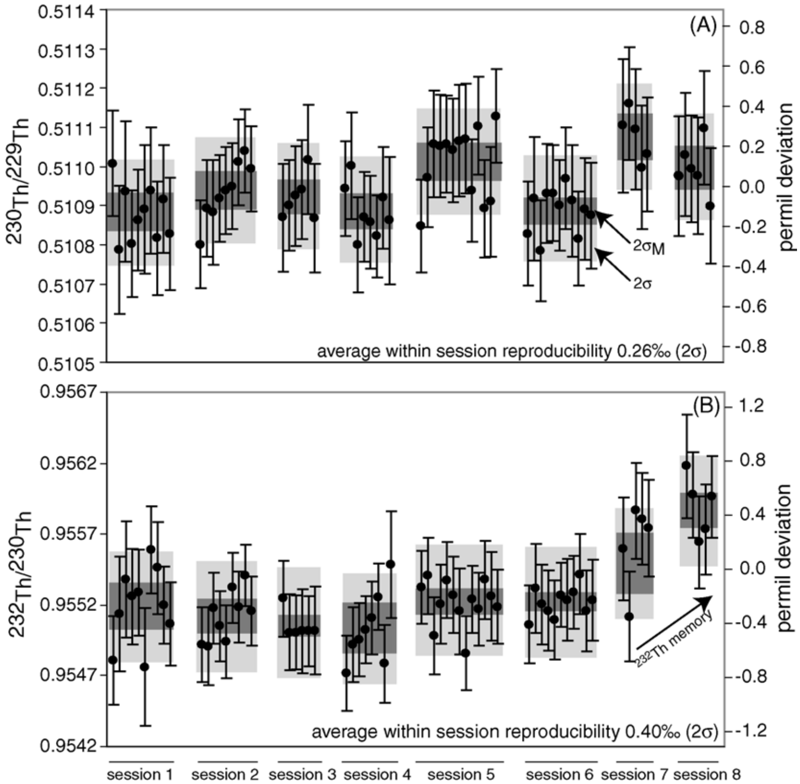


Fig. 2. Repeat measurements of: (A) $^{230}Th/^{229}Th$ and (B) $^{232}Th/^{230}Th$ over eight measurement sessions for the bracketing standard used in the analysis protocol described in this paper. The light-shaded and dark-shaded bands represent the 2σ uncertainty and the $2\sigma_M$ (error of the mean) of the standard analyses for each measurement session respectively. For display purposes, the right axis shows the permil deviation from the mean of all measurement sessions. The 0.26‰ (2σ) average within-session reproducibility of $^{230}Th/^{229}Th$ measurement for a sample size of 25–30 pg of ^{230}Th is superior to any other currently used TIMS or MC-ICPMS technique. The mean value of the standard for each session is used to normalise the samples measurements for each session. The error of the mean ($2\sigma_M$) of the standard's analyses for each session is incorporated statistically into the normalised sample isotope ratios. There is no significant difference in performance (based on the within-session reproducibility) between the Aridus (sessions 1–6) and the MCN desolvators (sessions 7 and 8). The small shift in $^{232}Th/^{230}Th$ in sessions 7 and 8 probably reflects small but significant memory effects on the ^{232}Th signal.

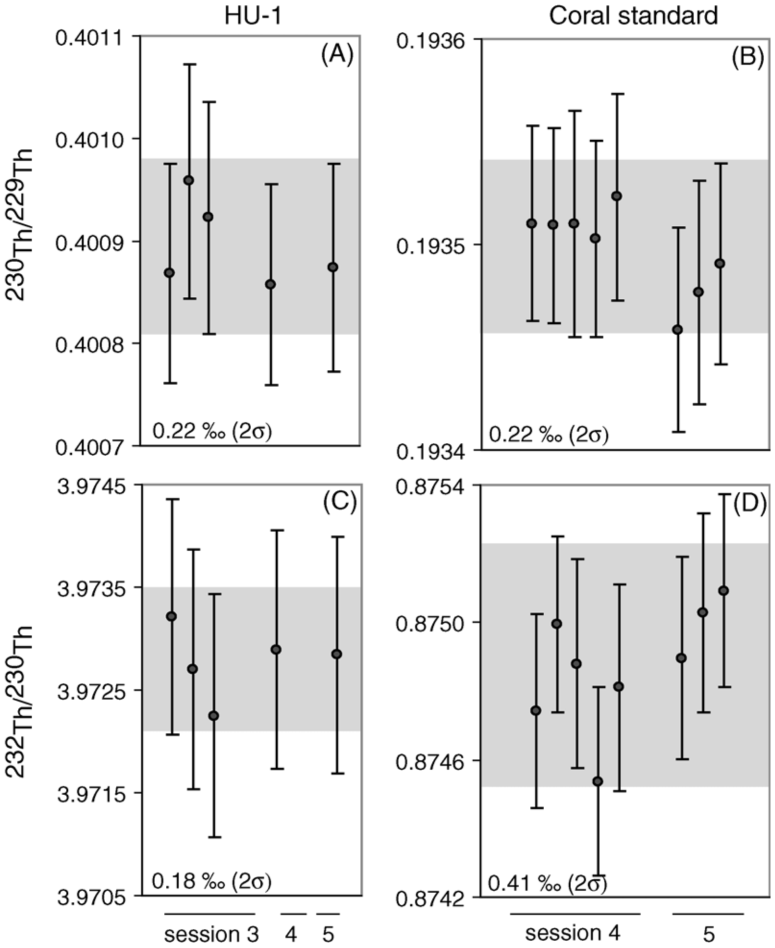


Fig. 3. Repeat measurements of thorium isotopic ratios (A and B) ^{230}Th/^{229}Th and (C and D) ^{232}Th/^{230}Th for an aliquot of spiked HU-1 and a spiked coral standard over three measurement sessions. The ^{230}Th/^{229}Th and ^{232}Th/^{230}Th are normalised to the mean value measured for the in-house standard for each session. Both solutions have a comparable reproducibility to the in-house standard.

ity. Fig. 2A shows that there is some variability in the mean ^{230}Th/^{229}Th between sessions. This may be due to the external normalisation of thorium using uranium. Therefore, all samples are normalised to the mean value of the standard for each session.

The ^{232}Th/^{230}Th values for the standard are shown in Fig. 2B. The within-run 2σ reproducibility on these measurements is 0.4‰. However, the session-to-session reproducibility is slightly poorer, most likely due to more significant memory effects on ^{232}Th. In most geological samples ^{232}Th is by far the most abundant thorium isotope (99.99%) and is likely to dominate any memory introduced to the desolvating nebuliser system by other MC-ICPMS users. However, the ^{232}Th/^{230}Th measurements are used only for monitoring detrital contamination and high accuracy measurement of this ratio is not required for the purposes of U-series dating.

3.2. Samples

To test the reproducibility of the thorium analyses for natural samples separated from matrix, repeat measurements were conducted on a number of solutions, including the HU-1 Harwell uraninite (Fig. 3A and C), an in-house coral standard (Fig. 3B and D), and six Barbados coral samples (Fig. 4, samples 1–6). In all cases the measurements have been carried out over two or three independent sessions and the ^{230}Th/^{229}Th reproducibility is of the same order as the standard (better than 0.3‰).

To demonstrate that matrix effects in natural samples are not dependent on chemical processing, splits of two coral samples were processed independently (Fig. 4, samples 7 and 8). Although the internal precision for these particular measurements are larger due to the slightly lower intensity beams during that session, the splits agree very well within their respective 0.4–0.6‰ uncertainties.

4. Implications for the precision of U-series dating

An improvement in precision of ^{230}Th/^{229}Th has important consequences for the uncertainties attained for U-series ages. The ^{230}Th/^{238}U of a sample can be determined by combining the measured sample-spike uranium and thorium ratios (^{230}Th/^{229}Th and ^{238}U/^{233}U) and the known ^{229}Th/^{233}U value of the mixed spike. This ^{230}Th/^{238}U is then used in conjunction with the measured uranium isotopic composition of the sample (^{234}U/^{238}U) to calculate its U-series age (see Figs. 5 and 6).

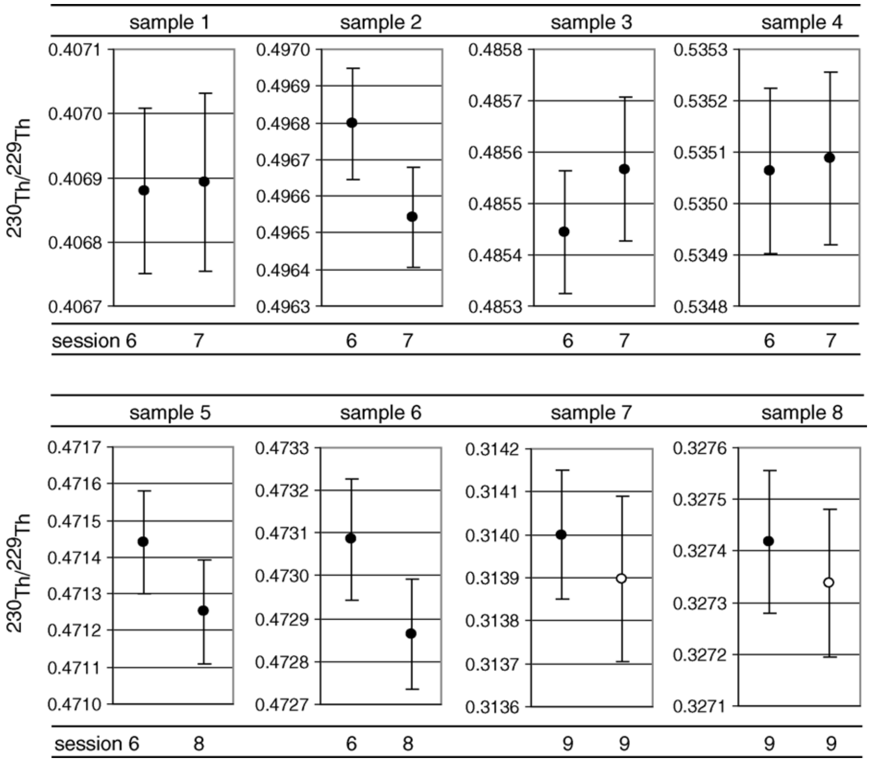
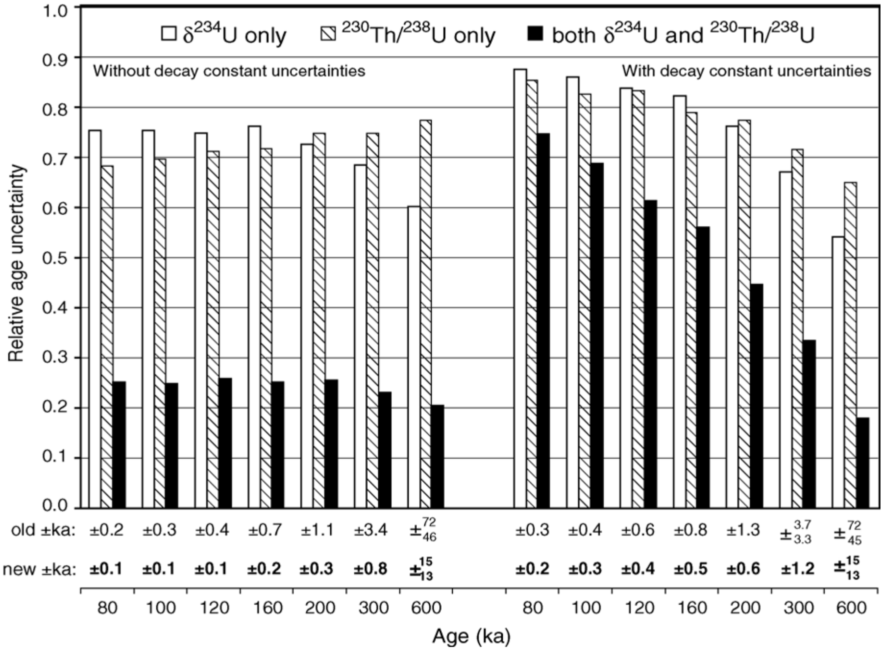


Fig. 4. Repeat $^{230}Th/^{229}Th$ measurements for a suite of eight coral samples spiked with ^{229}Th. For samples 1–6 (with internal errors of around 0.3‰), the measurements represent repeat analyses on single solutions. Samples 7 and 8 (with slightly higher errors of 0.4–0.6‰ because of lower bean intensities in session 9) were spiked and then split for separate chemical processing (the two splits are shown with the closed and open circles). The normalised $^{230}Th/^{229}Th$ values measured in different analysis sessions are in excellent agreement and show that the chemical processing does not introduce additional matrix effects. It is important to note that using the mass bias factor determined for U to correct the measured Th isotope ratios appears to work well, even at the high levels of precision attained with this technique.



Age (ka)	80	100	120	160	200	300	600	80	100	120	160	200	300	600
old ±ka:	±0.2	±0.3	±0.4	±0.7	±1.1	±3.4	$\pm^{72}_{46}$	±0.3	±0.4	±0.6	±0.8	±1.3	$\pm^{3.7}_{3.3}$	$\pm^{72}_{45}$
new ±ka:	**±0.1**	**±0.1**	**±0.1**	**±0.2**	**±0.3**	**±0.8**	$\pm^{15}_{13}$	**±0.2**	**±0.3**	**±0.4**	**±0.5**	**±0.6**	**±1.2**	$\pm^{15}_{13}$

Fig. 5. Graphical representation of improvements in U-series age uncertainties for ages ranging between 80 ka and 600 ka as a result of improving either the $\delta^{234}U$ analytical precision from 1.3‰ to 0.3‰ or improving the $^{230}Th/^{238}U$ precision from 1.5‰ to 0.4‰ or both. The age uncertainties are calculated using a Monte Carlo method, with and without the inclusion of decay constant uncertainties [3]. By improving the analytical precision of either $\delta^{234}U$ or $^{230}Th/^{238}U$ by the amounts quoted above, the age uncertainty is reduced by up to a factor of 1.5 (excluding the decay constant uncertainties). If both $\delta^{234}U$ and $^{230}Th/^{238}U$ are improved by the stated amount, the age uncertainties are decreased by up to a factor of five. When decay constant uncertainties are taken into account, the relative improvement for old ages is particularly profound for very old samples, for which the improvement is almost a factor of six at 600 ka. The absolute value of the "old" and "new" (both $\delta^{234}U$ or $^{230}Th/^{238}U$ improvements) age uncertainties are given in the table beneath the plot.

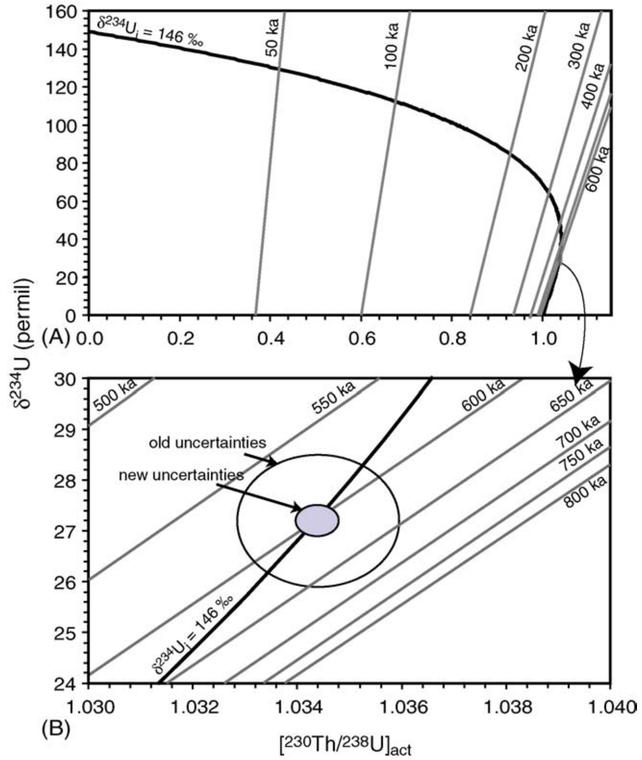


Fig. 6. A diagrammatic representation of the improvement in measurement precision for a 600 ka coral. (A) The "evolution" curve of a coral that was deposited with an initial $\delta^{234}U$ equal to that of modern seawater. (B) A zoom-in on the evolution curve at a sample age of 600 ka. The large ellipse represents the uncertainties representative of some currently used measurement protocols. The smaller, shaded ellipse represents the precision achievable with our new thorium (this study) and uranium [1] techniques.

The $^{230}Th/^{238}U$ precision of better than 0.4‰ achieved with our new thorium ($^{230}Th/^{229}Th$) and uranium ($^{238}U/^{233}U$) [15] isotopic methods represents up to an order of magnitude improvement over currently used TIMS and MC-ICPMS techniques, most of which report U–Th analytical precision ranging between 1‰ and 7‰ [9,10,16–18].

Fig. 5 shows the effect of improving $^{230}Th/^{238}U$ and/or $^{234}U/^{238}U$ errors on U-series age uncertainties for a hypothetical suite of samples with ages between 80 ka and 600 ka. Also included in this comparison is a demonstration of the effect of including decay constant uncertainties in the age-uncertainty calculations. Excluding the decay constant uncertainties (Fig. 5, left panel), the effect of reducing the $^{230}Th/^{238}U$ analytical uncertainty from 1.5‰ to 0.4‰ is a reduction in the U-series age uncertainty of up to a factor of 1.7. Keeping the $^{230}Th/^{238}U$ error constant and reducing the $^{234}U/^{238}U$ analytical uncertainty from 1.3‰ to 0.3‰ [1] leads to a similar improvement in age uncertainty. The implications for the precision of U-series analyses are even more profound when the thorium techniques described here are combined with high precision Faraday uranium isotopic analyses [1]. If both $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ analytical errors are reduced from 1.5‰ and 1.3‰ to 0.4‰ and 0.3‰, respectively, then the U-series age uncertainty is improved by a factor of four, regardless of the sample age.

If decay constant uncertainties are also taken into account (Fig. 5, right panel), the improvement in age precision is particularly striking for old samples (600 ka). If the analytical uncertainties on $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ are both improved by the proportion described in the previous paragraph, then the U-series age uncertainty for a 600 ka sample is reduced dramatically from $\pm^{72}_{45}$ ka to ±14 ka. This represents up to a factor of six improvement compared with previous techniques. Also important to the U-series dating of corals is the back-calculated initial $\delta^{234}U$ value, which provides an indication of the reliability of the sample age. For very old samples the initial $\delta^{234}U$ uncertainty is reduced by a factor of five (excluding decay constant uncertainties) or two (including decay constant uncertainties) (Fig. 5).

5. Conclusions

We have developed a new method that uses Faraday collectors to measure thorium isotope ratios. Measurement precision of better than 0.3‰ for $^{230}Th/^{229}Th$ has been achieved, while consuming only 25 pg of ^{230}Th. To achieve this precision, purified and highly concentrated thorium solutions are run in "time-resolved mode" for very a short duration (1 min on-peak). To minimise the effect of variability in the electronic background noise of the detectors, the thorium beams are maintained above 5×10^{11} A (50 mV across a 10^{11} Ω resistor). The mass bias correction to the thorium isotopic measurement is calculated from normalisation against the $^{238}U/^{235}U$ of admixed uranium. By normalising $^{230}Th/^{229}Th$ measurements to an in-house standard any drift caused by variability in the mass bias of thorium relative to uranium is eliminated in the final calculation of $^{230}Th/^{238}U$.

The thorium Faraday analysis technique presented here complements recent advancements in uranium isotopic analysis by MC-ICPMS [1]. Combined, these developments yield significant improvements in U-series age uncertainties. Examples of the age-precision achievable for corals using these new techniques are <0.1 ka for 100 ka samples, <1 ka for 300 ka samples and ∼14 ka for 600 ka samples. The relative improvements in precision are most profound for older samples that were close to the previous dating limit of U-series analysis (500–600 ka). The combined effect of analytical improvements in thorium and uranium analyses (this study and [1]) together extend the dating limit of U-series analysis from ∼600 ka to 800 ka. These high precision techniques allow, for the first time, a detailed examination of the relationships between climate, sea-level change and climate forcing mechanisms during interglacial–glacial cycles prior to 300 ka.

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