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Uranium-series dating of corals in situ using laser-ablation MC-ICPMS

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Abstract

The in situ U-series dating of corals has been achieved using laser-ablation multiple-collector inductively coupled plasma mass spectrometry (LA MC-ICPMS). Utilising a 193 nm excimer laser coupled to a Nu Instruments Nu Plasma equipped with multiple ion counters, percent-level analytical precision for ^{234}U/^{238}U and ^{230}Th/^{238}U is obtained. Approximately 70 μg of carbonate is consumed during each analysis, containing approximately 0.2 ng of ^{238}U, ∼10 pg of ^{234}U and less than 3 fg of ^{230}Th. A two-cycle, fast magnet jumping procedure is adopted. In the first cycle ^{238}U is measured in a Faraday collector while the low-abundance isotopes ^{234}U, ^{232}Th, and ^{230}Th are measured simultaneously in ion counters. In the second cycle ^{235}U is measured in an ion counter. All samples are bracketed with an isotopically characterised sample to correct for electron multiplier gain and variable elemental fractionation. U-series ages are then calculated from the measured ^{234}U/^{238}U and ^{230}Th/^{238}U. Here, we demonstrate the applicability of this technique by analysing a series of coral samples that have been previously characterised by conventional thermal ionisation mass spectrometry (TIMS) and solution-nebulisation multiple-collector ICP mass spectrometry. Excellent agreement is obtained with independent age estimates. The samples have varying degrees of preservation and ages ranging between <10 and 600 thousand years (ka). The age uncertainties achieved are ±1 ka at 3 ka and ±7 ka at 125 ka. Therefore the technique can be used to distinguish between major climatic sub-stages throughout the last 140,000 years spanning the last glacial-interglacial cycle, as recorded in coral reef terraces. The laser-ablation U-series results are independent of coral species. U-series age uncertainties are comparable to those attained using α-spectrometry but require $\sim 10^4$ times less sample and no chemical preparation.

Keywords: Laser ablation; MC-ICPMS; Coral; U-series dating

1. Introduction

Late Pleistocene carbonates such as corals and speleothems provide an important source of information for paleoclimate studies. For example, they can be used to obtain a record of sea-level changes through glacial-interglacial cycles spanning the Quaternary and to constrain records of continental climate change. The decay half-lives of the uranium-series isotopes ^{234}U and ^{230}Th (∼245 and ∼75 ka, respectively) make this system a uniquely appropriate dating tool for studies of this time period. U-series dating takes advantage of the isotopic disequilibrium at the time of deposition of the carbonate materials [1]. In the case of corals, the isotopic compositions of the uranium (U) and thorium (Th) in the aragonitic skeleton is initially the same as the sea water from which it is precipitated. The carbonate contains virtually no thorium, due to that element's low solubility, and has an excess of ^{234}U relative to secular equilibrium with its parent ^{238}U. With time, the excess ^{234}U decays and its decay product ^{230}Th is produced. The evolution of the isotope system over time can be described in terms of the activity ratios [^{234}U/^{238}U] and [^{230}Th/^{238}U]. With modern, high-precision analytical methods the dating limit of conventional U-series thermal ionisation mass spectrometry (TIMS) and solution-

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aspiration multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) is ∼600 ka (thousand years).

The precision and accuracy of U-series dating have experienced significant advances from the α-spectrometric techniques developed in the 1950s [1–3]. However there are three limitations with current approaches. First, the chemical processing required for the preparation and analysis for conventional TIMS and solution MC-ICPMS is time consuming and labor intensive and remains the limiting factor in sample throughput. Second, despite rigorous physical screening procedures, a large proportion of U-series coral ages tend to be discarded after analysis because of isotopic considerations, i.e. evidence of open system behaviour of the U-series isotopes, which can only be ascertained a posteriori [2,4]. A rapid screening technique would be useful in order to roughly constrain the age of unknown deposits and to identify altered samples prior to further analysis. Third, improving spatial resolution and isolating unaltered portions of carbonate for studies of alteration processes require microscale sampling. Techniques that address these three issues are of great importance for the further development of the field.

The advent of MC-ICPMS and its subsequent coupling with laser-ablation (LA) sample-introduction systems have opened up a range of in situ analysis applications. Laser-ablation techniques are not only valuable for their high spatial resolution, but also for the speed of the measurement and simple preparation procedures [5,6]. Continuing improvements in the sensitivity of second generation MC-ICPMS instruments [7] and the efficiency of ablation and enhanced sample transport from the ablation site [5] enable in situ analyses to be applied to samples with even lower concentrations than could previously be analysed.

To date, in situ uranium-series isotope analyses have focused on high-uranium samples (∼100 ppm) (e.g. [8]) but a lack of suitable matrix-matched standards means that the potential of these techniques as applied to U-series dating of those samples has yet to be fulfilled. In the present study we focus on the application of LA MC-ICPMS to the in situ U-series dating of samples with low uranium (<5 ppm) concentrations such as corals, which are valuable archives of climate and sea level change.

The aim of this study is to evaluate the LA MC-ICPMS technique as a tool for rapid screening. The potential for U-series dating by LA MC-ICPMS was first demonstrated for high-uranium materials such as glass standards, zircon and opal [8]. In that study, which utilised a 266 nm Nd:YAG laser, Stirling et al. noted the effects of elemental fractionation and the cause of this phenomenon has been the subject of much recent investigation [5,9,10]. These investigations have provided evidence that the elemental fractionation is dependent on the particle size distribution of the ablated material [10]. It has been shown that ablation using a 193 nm ArF laser (used in the present study) yields smaller particle sizes, more efficient vaporisation and hence reduced elemental fractionation compared to 266 nm Nd:YAG laser ablation. However, even with the 193 nm laser the elemental fractionation is not completely eliminated and a matrix-matched well-characterised standard is required to monitor and correct for this effect. For the purpose of the following discussion, the term elemental fractionation is used to describe all processes, other than instrumental mass discrimination effects, that lead to a measured U–Th ratio that differs from the true value of the sample.

2. Analytical techniques

2.1. Instrumentation

Analyses in this study were conducted on a 193 nm ArF excimer laser (GeoLas 200 Q of Microlas GmbH, Göttingen) coupled to a Nu Plasma MC-ICPMS (Nu Instruments, Wrexham). The Nu Plasma used in these experiments is equipped with three ion counting detectors and 12 Faraday collectors. The configuration of the ion counters is such that the three low abundance isotopes of interest, ^{234}U, ^{232}Th, and ^{230}Th, can be measured simultaneously (see Table 1), thus reducing the required sample size for a single analysis compared to cycling the isotopes through a single ion counter.

Small pieces of coral were roughly polished (<1 cm^2 surface area) and several pieces were mounted together in the ablation cell. The excimer laser was operated in energy constant mode at 100 ± 2 mJ. A spot size of 120 μm and a repetition rate of 20 Hz was used for ablation. The energy at the sample surface, measured with an externally calibrated energy detector, was 4.3 mJ, which is equivalent to an energy density of ∼38 J cm^{-2} for a 120 μm spot size. The ablation was conducted as a raster along the surface of the sample, thus maintaining a constant signal intensity over several minutes. For thick walled coral species such as *Faviidae* sp. and *Diploria* sp. the dense wall fraction is targeted during laser ablation

Table 1
LA MC-ICPMS data is collected in a two-cycle configuration with background zeros measured at half-mass prior to data acquisition

	Far	Far	Far	Far	IC	Far	IC	Far	IC
Zero 1	238.5	237.5	–	–	234.5	–	232.5	–	230.5
Zero 2	237.5	236.5	–	–	233.5	–	231.5	–	229.5
Cycle 1	^{238}U	–	–	–	^{234}U	–	^{232}Th	–	^{230}Th
Cycle 2	–	^{238}U	–	–	^{235}U	–	–	–	–

In cycle 1, ^{238}U is monitored in a Faraday collector while the three low abundance isotopes ^{234}U, ^{232}Th, and ^{230}Th are monitored simultaneously in ion counters. In the second cycle ^{235}U is measured an ion counter to monitor the instrumental mass bias (based on the known ^{234}U/^{235}U in a characterised standard) and to determine the uranium isotopic composition of the unknown sample. For cycle 1, the mean of two half-mass measurements (mass + 0.5 and mass − 0.5) are subtracted from the on-mass signal. For cycle 2, only a single half-mass measurement is subtracted from the on mass signal (mass − 0.5). The uncertainties introduced by the simple linear interpolation of the baseline measurements and/or the use of a single half-mass measurement are small compared to the total statistical uncertainties of the technique. Drift in the mass bias and the gain of the ion counters is monitored by using a bracketing standard.

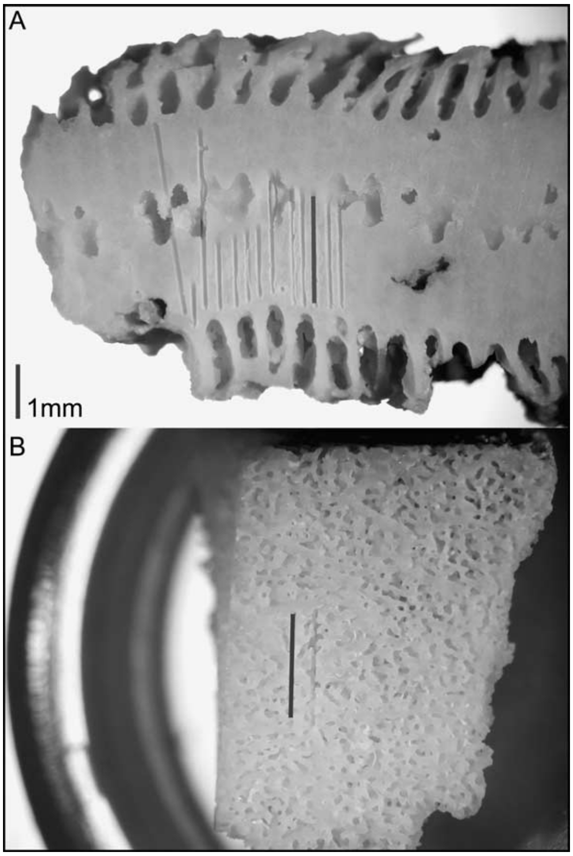

Fig. 1. Ablation traces of corals analysed in this study (each trace represents a single analysis). For thick walled coral species such as *Diploria* sp. (A), the wall section is targeted for ablation because this fraction is free of detrital material and is better preserved than the septa fraction. No specific targeting is made when analysing porous coral types such as *Acropora* sp. (B).

as this portion is less likely to have experienced diagenetic alteration [2] (Fig. 1A). For the more porous coral types such as *Acropora* sp. and *Porites* sp., no specific targeting was made (Fig. 1B). The ablated material is continuously transported from the sample cell with a helium gas flow of 0.06 L min^{-1} that is then mixed with argon before introduction into the plasma [5,8]. Gas flows and other ICPMS parameters are optimised for maximum ^{238}U signal intensity.

2.2. Data collection and processing

Data collection was conducted using a two-step multi-static configuration shown in Table 1. In the first cycle ^{238}U was measured in a Faraday collector while ^{234}U, ^{232}Th, and ^{230}Th were measured simultaneously in each of the three ion counters. In the second cycle, ^{238}U is again measured in a Faraday cup and ^{235}U is measured in an ion counter. The maximum ^{238}U signal achieved is approximately $5–7 \times 10^{-13}$ A, which corresponds to a ^{235}U signal of less than 5×10^{-15} A. A typical analysis has a duration of 5–7 min, depending on the desired precision, which corresponds to around 70 μg of ablated carbonate. This analysis duration includes peak centering and baseline measurement.

The on-mass background signal for the laser introduction system, i.e. sample transport gas with no ablation, is negligible. However, a background correction is required for the baseline noise in the Faraday collectors and to account for the peak tailing contribution from the large ^{238}U ion beam to the smaller beams. Consequently, background measurements are conducted at half-mass prior to the on-mass data collection (Table 1).

The largest isotope, ^{238}U, is measured in a Faraday collector in each of the two cycles and is used as a reference isotope to normalise for instabilities in the beam intensity caused by variations in the amount of ablated material due to density changes. The ^{234}U and ^{235}U signals, which are measured in the same ion counter (IC0), are recorded relative to the ^{238}U beam and are used to calculate ^{234}U/^{235}U. The ratio of ^{230}Th, which is measured in an ion counter, to ^{238}U is also recorded for each sample. The exponential law [11] is applied to all isotope ratios to correct for instrument mass discrimination. Ideally, the instrumental mass bias correction for uranium would be calculated from the measured ^{238}U/^{235}U value compared to its known value of 137.88 [12]. However, in these measurements the ^{238}U/^{235}U cannot be measured precisely because of the small size of the ^{235}U signal in the Faraday cup ($<5 \times 10^{-15}$ A). Instead, the mass bias correction is calculated by comparing the known ^{234}U/^{235}U value of the characterised standard with that measured in the ion counter and the correction then applied to the samples. A scaling factor, calculated by comparing the apparent ^{230}Th/^{238}U of the standard with the true value is used to correct for both “elemental fractionation” between thorium and uranium as well as the gain of the electron multiplier relative to the Faraday collectors. The effects of non linear response of the electron multipliers [13] are considered unimportant relative to the statistical uncertainty of the technique.

2.3. Bracketing standard

Repeat measurements of the chosen in-house coral standard are made at intervals throughout each analysis session. As outlined above, the standard is used to correct for instrumental mass bias, electron multiplier gain and elemental fractionation. In these experiments, the standard was measured once after every three to four sample analyses. The standard used in these experiments was an arbitrarily chosen ∼77 ka (MIS-5a) Barbados *Acropora* sp. coral sample, the composition of which had been determined previously by TIMS [14].

3. Results

3.1. Precision and reproducibility

A typical 5–7 min analysis, with a ^{238}U signal intensity of $5–7 \times 10^{-13}$ A yields a ^{234}U/^{235}U internal precision of 10–12‰ ($2\sigma_m$). The external reproducibility (2σ) of the

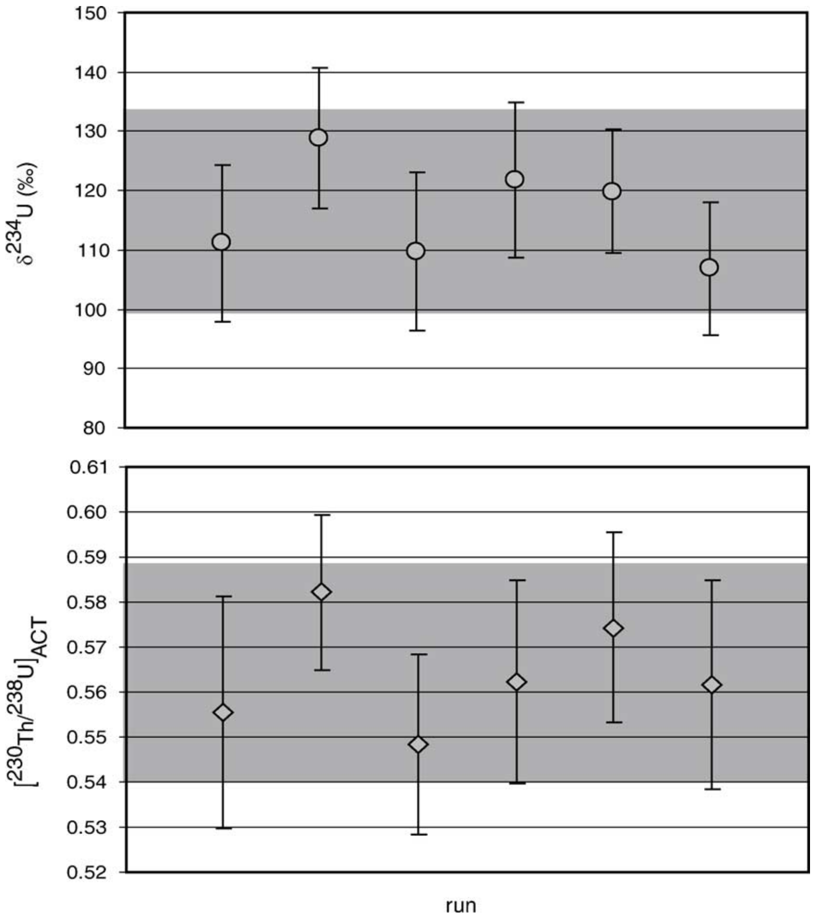

Fig. 2. U–Th isotopic composition of the in-house coral standard during a single measurement session. Values have been normalised to the true isotopic composition of the coral, which was previously determined by conventional U-series analysis techniques. The reproducibility of the standard analyses is marked with the grey bands. The reproducibility of the uranium isotopic composition ($\delta^{234}U$) standard in this session was 17‰ (based on five measurements). However, the long-term $\delta^{234}U$ reproducibility for the same standard over a number of measurement sessions and focussing conditions is 12‰. The within-session reproducibility of $^{230}Th/^{238}U$ is approximately 44‰.

$^{234}U/^{235}U$ is approximately the same as the internal precision (∼12‰) (Fig. 2). The within-session and inter-session reproducibility of the uranium isotopic composition of the standard was found to be comparable to the analytical precision and shows that this ratio is not sensitive to changes in gas flow and focusing conditions. Measured ratios for the "unknown" samples were normalised to the mean value measured for the standard.

The initial thorium content of corals is assumed to be zero, and the ^{230}Th concentration increases with time as the result of the radioactive decay of its parent ^{234}U. Therefore, for very young samples the ^{230}Th count rate is extremely low. For example, the Holocene (3 ka) sample analysed in this study, had a mean ^{230}Th count rate of less than one count per second yielding a $^{230}Th/^{238}U$ uncertainty of ±200–300‰. For the older samples (∼80 to ∼600 ka) the ^{230}Th concentration is higher and $^{230}Th/^{238}U$ uncertainties of ±30–45‰ were achieved. A comparison of the measured $^{230}Th/^{238}U$ of the standard with the known value indicate that the elemental fractionation factor $f_{Th/U} = (Th/U)_{MEAS}/(Th/U)_{TRUE}$ lay in the range between 0.6 and 0.7 (i.e. the thorium signal is between 30% and 40% lower than an unfractionated Th:U ratio). Although this absolute fractionation is large, it is also stable, providing the focussing parameters remain unchanged. The external reproducibility of repeat $^{230}Th/^{238}U$ measurements of the standard within a measurement session is of the same order as the internal precision (∼45‰ for the 77 ka standard).

3.2. Isotopic composition of "unknown" samples

A series of measurement sessions with alternating standard and "unknown" samples was conducted to evaluate the reproducibility of the technique and the reliability of the standard-bracketing normalisation approach. Sites chosen for ablation were recorded in the stage drive controller prior to the start of the session, enabling a rapid transfer between samples. Fig. 3 summarises the data collected during two mea-

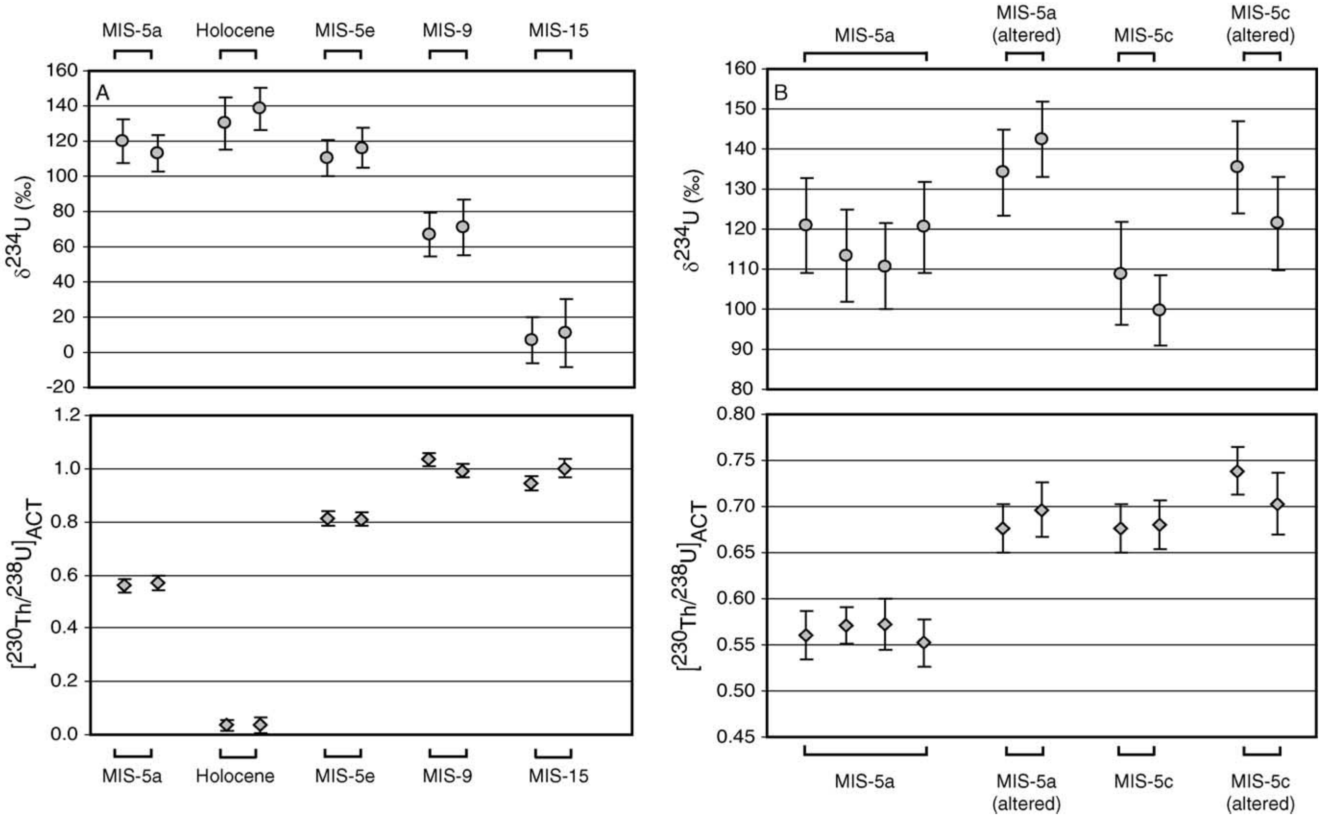

Fig. 3. U–Th isotopic compositions of coral samples determined by LA MC-ICPMS. Values have been normalised to the true isotopic composition of the in-house standard, determined by conventional U-series analysis techniques. (A) $\delta^{234}U$ and $^{230}Th/^{238}U$ for a selection of corals with ages spanning ~600 ka. Repeat measurements of individual samples are separated by a standard measurement and $\delta^{234}U$ and $^{230}Th/^{238}U$ are identical within uncertainty. (B) $\delta^{234}U$ and $^{230}Th/^{238}U$ for a selection of MIS-5 corals with varying degrees of preservation.

surement sessions. All measured $^{234}U/^{235}U$ are converted to $^{234}U/^{238}U$ using the natural uranium $^{238}U/^{235}U$ composition of 137.88. The uranium isotope activity ratio is expressed as $\delta^{234}U$, the permil deviation of $^{234}U/^{238}U$ from its secular equilibrium value:

$$\delta^{234}\mathrm{U} = \left[\left[\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}\right]_{\mathrm{ACT}} - 1\right] \times 1000$$

Repeat analyses on individual samples were separated in time in the order summarised in Table 2. The standard used in these experiments was arbitrarily chosen (MIS-5a) and all measurements were normalised to the isotopic composition of that coral standard. The results shown in Fig. 3 show that repeat measurements of both $\delta^{234}U$ and $^{230}Th/^{238}U$ for all of the samples are identical within the uncertainty of the analysis. This excellent reproducibility means that variations in elemental fractionation on the timescale of the bracketing cycle is negligible compared to the precision of individual measurements. It is also clear that the isotopic composition of samples with the range of ages used in these experiments can be easily distinguished (Fig. 3A).

4. Discussion

4.1. U-series dating applications

A series of coral samples, previously ascertained to be well-preserved based on isotopic considerations, were analysed. Fig. 4 shows a compilation of data for all of these samples in a plot of $[^{230}Th/^{238}U]$ versus $\delta^{234}U$. The curved line in this figure traces the closed-system evolution of the isotopic composition of a coral with an initial $\delta^{234}U$ equal to that of modern corals and seawater. The isotope data for six distinct age groups are shown. These include Holocene (<10 ka), Marine Isotope Stage (MIS)-5a (~77 ka), MIS-5c (~100 ka), MIS-5e (~128 ka), MIS-9 (~330 ka) and MIS-15 (~600 ka) [3,14]. The laser ablation data for each of these samples is clearly distinguishable, demonstrating that the major marine isotope stages, including the sub-stages of MIS-5, with an age separation of ~20 ka, can be easily distinguished from one another using this rapid analysis technique.

Also shown in Fig. 4 is a comparison of the conventional analyses with the multiple laser analyses for each sample. In general, the comparison shows good agreement within the uncertainties of the laser measurement. It is possible that subtle alteration and the associated preferential alteration and

Table 2
Summary of data acquired over three analysis sessions

Sample	$^{234}\mathrm{U}/^{235}\mathrm{U}_\mathrm{m}$	$^{230}\mathrm{Th}/^{238}\mathrm{U}_\mathrm{m}$ ($\times 10^{-6}$)	$\delta\,^{234}\mathrm{U}_\mathrm{s}$	$[^{230}\mathrm{Th}/^{238}\mathrm{U}]_\mathrm{ACT,\,S}$
Analysis session 1				
MIS-5a (std)	0.008363 ± 0.000098	5.87 ± 0.25	111.1 ± 13.3	0.555 ± 0.026
MIS-5a (std)	0.008496 ± 0.000086	6.16 ± 0.15	128.9 ± 11.9	0.582 ± 0.017
MIS-5a (std)	0.008352 ± 0.000098	5.80 ± 0.19	109.7 ± 13.3	0.548 ± 0.020
MIS-5a (std)	0.008442 ± 0.000098	5.95 ± 0.21	121.7 ± 13.1	0.562 ± 0.023
MIS-5a (std)	0.008428 ± 0.000071	6.07 ± 0.20	119.9 ± 10.4	0.574 ± 0.021
MIS-5a (std)	0.008330 ± 0.000077	5.94 ± 0.22	106.8 ± 11.1	0.562 ± 0.023
Mean of standard	0.008402 ± 0.000052	5.97 ± 0.11		
Analysis session 2				
MIS-5a (std)	0.008422 ± 0.000095	4.82 ± 0.21	120.9 ± 11.9	0.560 ± 0.026
MIS-5a (std)	0.008365 ± 0.000091	4.91 ± 0.15	113.4 ± 11.5	0.571 ± 0.020
MIS-5a (altered)	0.008522 ± 0.000086	5.81 ± 0.20	134.2 ± 10.8	0.676 ± 0.026
MIS-5c	0.008331 ± 0.000103	5.81 ± 0.21	108.8 ± 12.9	0.676 ± 0.027
MIS-5c (altered)	0.008532 ± 0.000092	6.35 ± 0.20	135.5 ± 11.4	0.739 ± 0.026
MIS-5a (std)	0.008345 ± 0.000084	4.92 ± 0.22	110.7 ± 10.7	0.572 ± 0.027
MIS-5a (altered)	0.008584 ± 0.000075	5.99 ± 0.24	142.4 ± 9.5	0.697 ± 0.030
MIS-5c	0008263 ± 0.000065	5.84 ± 0.20	99.8 ± 88	0680 ± 0.026
MIS-5c (altered)	0.008426 ± 0.000094	6.04 ± 0.27	121.4 ± 11.7	0.703 ± 0.034
MIS-5a (std)	0.008419 ± 0.000090	4.75 ± 0.20	120.5 ± 11.3	0.552 ± 0.025
Mean of standard	0.008388 ± 0.000039	4.85 ± 0.08		
Analysis session 3				
MIS-5a (std)	0.008451 ± 0.000101	5.27 ± 0.18	119.7 ± 12.4	0.559 ± 0.022
Holocene	0.008528 ± 0.000124	0.33 ± 0.09	130.0 ± 14.9	0.035 ± 0.010
MIS-9	0.008054 ± 0.000096	9.74 ± 0.31	67.1 ± 12.4	1.034 ± 0.037
MIS-15	0.007599 ± 0.000097	8.90 ± 0.33	6.8 ± 13.3	0.945 ± 0.038
MIS-5e	0.008379 ± 0.000083	7.64 ± 0.17	110.2 ± 10.5	0.812 ± 0.023
MIS-5a (std)	0.008400 ± 0.000083	5.36 ± 0.17	113.0 ± 0.5	0.569 ± 0.021
Holocene	0.008591 ± 0.000099	0.33 ± 0.07	1383 ± 12.1	0.035 ± 0.007
MIS-9	0.008085 ± 0.000126	9.34 ± 0.23	71.3 ± 16.0	0.992 ± 0.030
MIS-15	0.007630 ± 0.000145	9.42 ± 0.40	10.9 ± 19.3	1.000 ± 0.046
MIS-5e	0.008424 ± 0.000092	7.61 ± 0.22	116.2 ± 11.5	0.808 ± 0.027
Mean of standard	0.008425 ± 0.000051	5.31 ± 0.09		

The measured ratios $^{234}\mathrm{U}/^{235}\mathrm{U}_\mathrm{m}$ and $^{230}\mathrm{Th}/^{238}\mathrm{U}_\mathrm{m}$ are the mean for each sample run. The $\delta^{234}\mathrm{U}_\mathrm{S}$ and $[^{230}\mathrm{Th}/^{238}\mathrm{U}]_\mathrm{ACT,\,S}$ are the calculated activity ratios for each run and have been normalised to the mean value for the bracketing standard measured for the session and scaled to the known value of the standard. Conventional ^{234}U and ^{230}Th half-lives are used in all calculations [17–19].

mobilisation of U-series isotopes in different parts of the coral could result in small apparent discrepancies between the laser ablation analyses, which consume ~70 μg material, compared to conventional TIMS or ICP-MS analyses, which consume 0.1–1 g. This may be the reason for the small difference between the isotopic composition of the MIS-5e sample determined using conventional and laser ablation analyses (Fig. 4). The variations in bulk structure of the different coral species might lead to differences in the particle size distribution during ablation. If such a species-dependent effect was responsible for the offset observed between the laser and conventional analysis for the MIS-5e sample (*Faviidae* sp.), then a similar offset would be expected for other samples of the same species (MIS-9 and MIS-15), which is not observed. The soundness of the MIS-5a sample for use as a standard is established by the fact that the isotopic compositions, measured by LA MC-ICPMS, of the ‘unknown’ samples are not systematically offset from their corresponding conventionally determined compositions.

The corresponding U-series age and initial δ^{234}U calculations for the well preserved samples are shown in Fig. 5. Typical U-series age uncertainties associated with a single laser analysis are ±1 ka for a sample of Holocene age and ±7 ka for a MIS-5e sample (128 ka). The precision of these analyses is comparable to that of α-spectrometric dating but is achieved by consuming $\sim 10^4$ times less sample material, and acquired with no chemical preparation and with an analysis time of less than 10 min. The MIS-15 sample (~600 ka) is beyond the dating limit of the technique, however its isotopic composition is fully distinct from the MIS-9 sample (~300 ka) (Fig. 4).

4.2. Screening of altered samples

One of the major criteria used to judge the reliability of a coral’s U-series age is the comparison of the calculated initial δ^{234}U of the sample with that of modern corals. If the initial δ^{234}U value is significantly different from the modern value then the sample’s U-series age is considered unreliable.

Fig. 6 shows a plot of $[^{230}\mathrm{Th}/^{238}\mathrm{U}]$ versus δ^{234}U for a selection of four corals (all *Acropora* sp.) collected from MIS-5a and 5c terrace deposits in Barbados. Based on previous

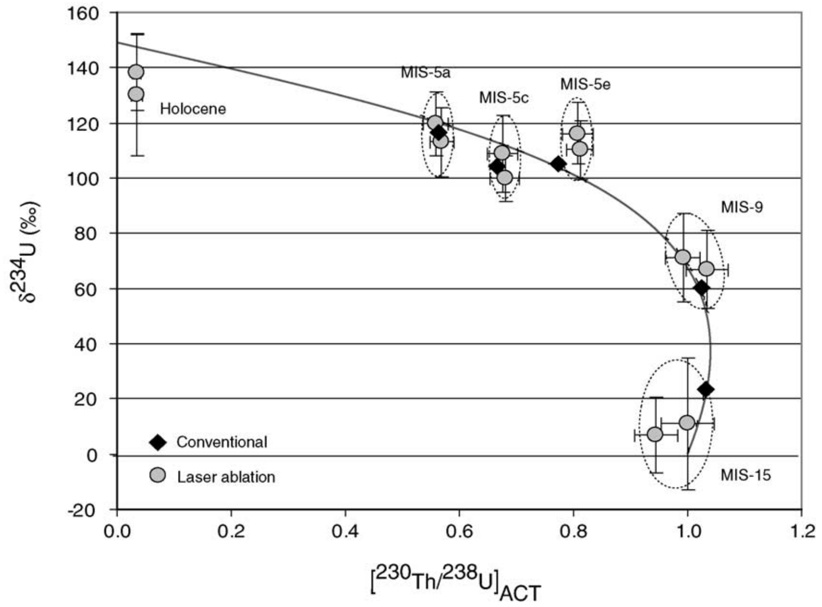

Fig. 4. δ^{234}U vs. ^{230}Th/^{238}U for a selection of corals with ages spanning the last ∼600 ka determined by LA MC-ICPMS (grey circles) compared with conventional analyses (dark diamonds). The solid curve is the isotopic evolution curve for a hypothetical coral that had an initial δ^{234}U equal to that of modern corals (∼149‰). In general the conventionally measured isotopic composition agrees with the LA results, within the uncertainties of the technique. The exception is the MIS-5e sample, for which both ratios are higher than conventional data, however, the offset is small and is likely due to isotopic heterogeneity within the sample.

analyses using conventional techniques, two of these samples (MIS-5a and MIS-5c) have δ^{234}U values which are within error of the modern value and are therefore considered pristine. Two other "altered" samples were collected from the same deposits and are considered to be of the same age as the pristine samples from the corresponding deposits. However, the elevated initial δ^{234}U values of the "altered" samples, determined by conventional TIMS measurements, suggest they have been subject to diagenetic alteration.

A pristine MIS-5a sample was used as the normalising standard in all analyses. The laser-determined δ^{234}U value for the unaltered MIS-5c sample agrees well with its corresponding conventional results. However, in the case of both the "altered" samples the conventionally measured isotopic compositions do not lie within the uncertainties of the laser analyses. The offsets are small and of the same order as observed as for the 'well-preserved' MIS-5e sample in Fig. 4. There are two possible reasons for the observed offsets. The

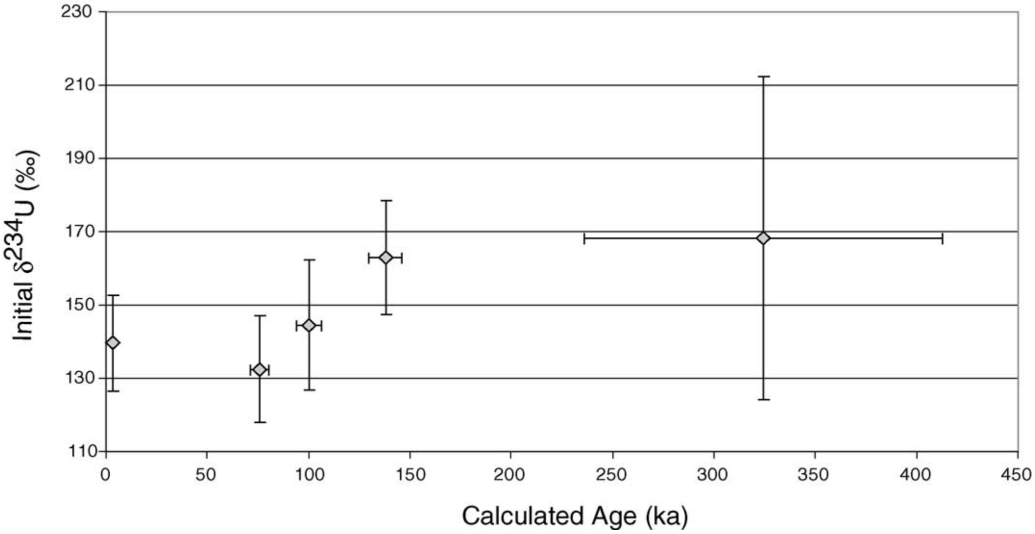

Fig. 5. Calculated age versus initial δ^{234}U for five well-preserved corals analysed in this study (also see Table 2). These age calculations do not include decay constant uncertainties. Typical age uncertainties for these samples are ±1 ka at 3.5 ka (Holocene) and ±7 ka at 125 ka (MIS-5e). U-series age and initial δ^{234}U uncertainties for older samples (MIS-9) are enhanced as the dating limit of the technique is approached.

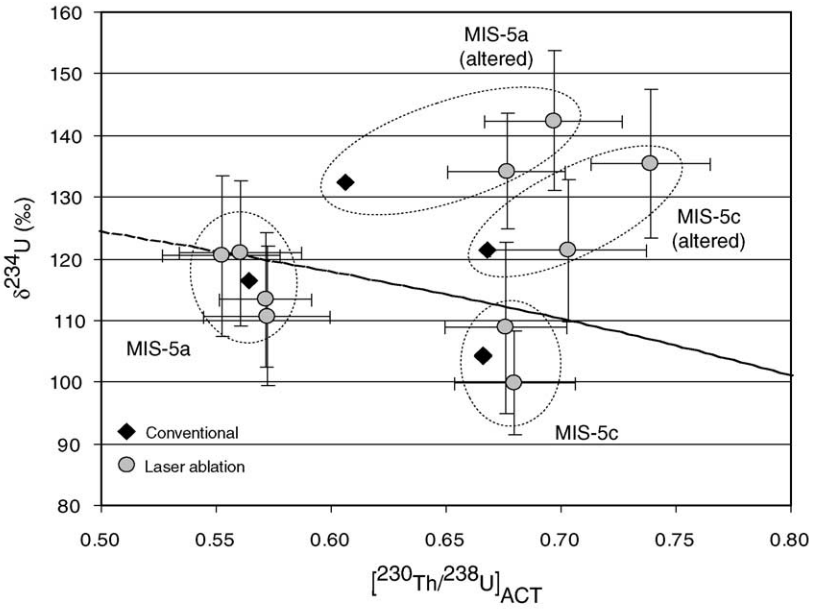

Fig. 6. δ^{234}U versus ^{230}Th/^{238}U for a selection of four MIS-5a and 5c corals with different degrees of preservation (all *Acropora palmata*). Grey circles represent the repeat LA MC-ICPMS analyses, while dark diamonds represent conventional isotope measurements. The solid curve is the isotopic evolution curve for a hypothetical coral that had an initial δ^{234}U equal to that of modern corals (∼149‰). The MIS-5a sample was used as the bracketing standard, therefore its LA measurements are centred on the normalising value defined by the conventional analyses. The LA analysis of the well preserved MIS-5c sample agrees well with the conventionally measured value. The LA results for both altered corals do not agree with the conventional analyses within the stated uncertainty range. These differences may be due to either changes in the matrix structure of altered portions of the coral or heterogeneous isotopic composition caused by alteration.

first possibility is that the alteration process has sufficiently changed the matrix structure so that normalisation using a pristine sample is no longer appropriate. Both of the “altered” samples have more than 98% aragonite, so changes in the matrix would take the form of micron scale calcite structures or secondary aragonite. The observed shift away from the conventionally determined value is larger for the [^{230}Th/^{238}U] than for the δ^{234}U. This is consistent with a matrix effect because it would be expected that this would change the Th/U elemental fractionation but not the uranium isotopic composition.

Alternatively, different sub-samples of the altered corals have experienced different degrees of alteration and the laser ablation measurements reflect microscale heterogeneities in the isotopic composition of those samples. In this context, this technique may provide a useful tool for evaluating such spatial variability. Regardless of the reason for the offset, in the case of both “altered” corals the laser analyses are offset from the evolution curve defined in Fig. 6 and thus the technique can be used to identify altered samples.

The uncertainties associated with our laser ablation technique places a limitation on its use to distinguish samples that are only subtly altered. However, the speed and simplicity of the technique enables the rapid screening of many samples to be conducted, up to 40–50 analyses in a day-long measurement session. In addition, this method has the potential to be used to examine spatial variations in the isotopic composition of samples to aid in the study of diagenetic alteration. These types of studies are required to gain a better understanding of the effects of alteration on U-series dating of corals.

5. Conclusions

The application of LA MC-ICPMS to the in situ U-series dating of corals has been successfully demonstrated in this study. The use of three ion counters to simultaneously measure the three low concentration isotopes of interest (^{234}U, ^{232}Th, and ^{230}Th) minimises analysis time. In this study, a typical 5–7 min analysis consumes 70 μg of carbonate, which corresponds to approximately 0.2 ng of total uranium. The uncertainty of the uranium isotopic measurements (δ^{234}U), using our standard bracketing technique is on the order of 12‰. This can be compared with early U-series LA MC-ICPMS studies which achieved four-fold better uncertainties but consumed up to 20 times more material. Such a comparison highlights the importance of improvements in sensitivity in second generation MC-ICPMS instruments, coupled with multiple ion counters versus single ion counter measurements.

The typical uncertainty of a ^{230}Th/^{238}U measurement on a MIS-5 coral using the techniques described here is around 45‰. The amount of ^{230}Th consumed in the analysis of a 600 ka sample is around 3 fg (3×10^{-15} g). A ^{230}Th/^{238}U uncertainty of 200‰ in a Holocene sample can be achieved by consuming less than 0.1 fg of ^{230}Th. For Holocene-age samples, an age uncertainty of ±1 ka demonstrated that this technique is applicable to even very young samples. The typical age uncertainties for this technique allow the different substages of MIS-5 to be easily distinguished. There is also a clear difference in isotopic composition between 330 ka (MIS-9) and 600 ka (MIS-15). The size of these uncertainties is also comparable to that achieved using α-spectrometry methods, but consumes $\sim 10^4$ times less sample. This technique can therefore be applied to samples with ages spanning the last 600 ka.

This LA MC-ICPMS U-series technique does not require the time consuming and labor intensive chemical preparation used in conventional methods, nor does it require the use of expensive radioactive spikes. The procedure provides an ideal tool for rapid age determination and screening of uncharacterised coral samples. This technique can just as easily be applied to the analysis of other materials. Other applications include the rapid age analysis of speleothems [15], and the dating of fossil remains combined with the modelling of uranium migration in teeth and bone [16].

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