OPEN ACCESS

University of BRISTOL

Publisher's PDF, also known as Final Published Version

Link to published version (if available):
10.1016/j.quageo.2015.10.004

Link to publication record in Explore Bristol Research
PDF-document

Research paper

Rapid uranium-series age screening of carbonates by laser ablation mass spectrometry

Peter T. Spooner[*], Tianyu Chen, Laura F. Robinson, Christopher D. Coath

School of Earth Sciences, University of Bristol, BS8 1RJ, UK

ABSTRACT

Uranium-series dating is a critical tool in quaternary geochronology, including paleoclimate work, archaeology and geomorphology. Laser ablation (LA) methods are not as precise as most isotope dilution methods, but can be used to generate calendar ages rapidly, expanding the range of dating tools that can be applied to late Pleistocene carbonates. Here, existing LA methods are revisited for corals (cold- and warm-water) and speleothems spanning the last 343 thousand years (ka). Measurement of the required isotopes (^{238}U, ^{234}U, ^{230}Th and ^{232}Th) is achieved by coupling a laser system to a multi-collector inductively-coupled-plasma mass spectrometer (MC-ICPMS) using a combination of a single central ion counter and an array of Faraday cups. Each sample analysis lasts for ~4.3 min, and fifty samples can be measured in 12 h with an automated set up, after a day of sample preparation. The use of different standard materials and laser systems had no significant effect on method accuracy. Uncertainty on the measured (^{230}Th/^{238}U) activity ratios ranges from 5.4% to 7.6% for (^{230}Th/^{238}U) ratios equal to 0.7 and 0.1 respectively. Much of this uncertainty can be attributed to the heterogeneity of the standard material (^{230}Th/^{238}U) at the length scale of LA. A homogeneous standard material may therefore improve measurement uncertainty but is not a requirement for age-screening studies. The initial (^{234}U/^{238}U) of coral samples can be determined within ~20‰, making it useful as a first indicator of open-system behaviour. For cold-water corals, success in determination of (^{232}Th/^{238}U) — which can affect final age accuracy — by LA depended strongly on sample heterogeneity. Age uncertainties (2 sigma) ranged from <0.8 ka at 0 —10 ka, ~1.5 ka at 20 ka to ~15 ka at 125 ka. Thus, we have demonstrated that U-series dating by LA-MC-ICPMS can be usefully applied to a range of carbonate materials as a straightforward age-screening technique.

1. Introduction

Carbonate materials such as corals and speleothems are utilised in a wide variety of ways to investigate past ocean and climate states such as sea-level determination through glacial/interglacial cycles (Broecker et al., 1968; Fairbanks, 1989; Gallup, 1997; Potter et al., 2004; Richards et al., 1994; Thompson et al., 2011), tracking changes in Asian monsoon intensity (Cheng et al., 2006; Dykoski et al., 2005; Wang et al., 2001) and assessing ventilation rates of the deep ocean (Adkins et al., 1998; Burke and Robinson, 2012; Mangini et al., 1998; Robinson et al., 2005). Underpinning these

studies is the ability to assign an age to the carbonate material using the decay of uranium-series (U-series) isotopes.

U-series dating is possible because carbonate materials incorporate U and Th isotopes in isotopic disequilibrium (Ivanovich, 1994). By measuring the time-dependent activity ratios (^{230}Th/^{238}U), (^{234}U/^{238}U) and (^{232}Th/^{238}U), sample ages can be calculated by solving the decay equation for t:

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right) - \left(\frac{^{232}\text{Th}}{^{238}\text{U}}\right)\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_i \left(e^{-\lambda_{230}t}\right)$$
$$= 1 - e^{-\lambda_{230}t} + \left(\frac{\delta^{234}\text{U}_m}{1000}\right)\left(\frac{\lambda_{230}}{(\lambda_{230} - \lambda_{234})}\right)\left(1 - e^{(\lambda_{234} - \lambda_{230})t}\right)$$

(1)

where parentheses denote isotope activity ratios, λ_i is the decay constant of isotope i, t is the sample age and (^{230}Th/^{232}Th)$_i$ is the

initial thorium activity ratio in the carbonate, typically estimated in corals by assuming it is equal to modern day seawater at the sample site. It is common practice in U-series dating to use the term $(\delta^{234}U_m)$, defined as:

$$\delta^{234}U_m = ((^{234}U/^{238}U)_{measured} - 1) \times 1000 \qquad (2)$$

It is also common practice to calculate $(\delta^{234}U)$ at the time of carbonate formation $(\delta^{234}U_i)$ where:

$$\delta^{234}U_i = \delta^{234}U_m e^{\lambda_{234}t} \qquad (3)$$

For carbonates formed in the ocean, $\delta^{234}U_i$ is a useful indicator of closed-system behaviour, a requirement for determination of accurate ages. Samples that have remained closed systems are thought to retain a $\delta^{234}U_i$ signal that is within a few per mil of the seawater in which they grew (Henderson, 2002; Stirling et al., 1995). Seawater $\delta^{234}U$ may have varied by up to 15‰ over glacial–interglacial cycles (Henderson, 2002; Henderson et al., 1993; Robinson et al., 2004b; Thompson et al., 2011).

The ratios required for the calculations in Equations (1)–(3) can be measured precisely using isotope dilution (ID) inductively-coupled-plasma mass spectrometry (ICPMS) or thermal ionisation mass spectrometry (TIMS) (Cheng et al., 2000; Edwards et al., 1987, 2003). However, the methods are time consuming (Potter et al., 2005), requiring extensive chemical cleaning of samples, purification of isotope solutions and calibrated uranium and thorium spikes. In addition, open or closed-system behaviour is only indicated after the isotope measurements have been carried out. It is therefore desirable to use methods that: 1) give an initial indication of open-system behaviour and 2) are fast, allowing rapid selection of the most useful samples before more precise methods are employed. Rapid dating techniques also open the door for extensive paleo-biogeographical studies of carbonate-forming marine life (Margolin et al., 2014), for screening ages of many speleothems from caves, or for analysing coral fragments from sediment cores.

Rapid dating methods include reconnaissance radiocarbon dating (Burke et al., 2010; McIntyre et al., 2011), simplified ID techniques (Adkins and Boyle, 1999; Douville et al., 2010) and laser ablation (LA) multi-collector (MC)-ICPMS (Eggins et al., 2005; Hoffmann et al., 2009; McGregor et al., 2011; Potter et al., 2005). Radiocarbon methods have been used to investigate Southern Ocean cold-water coral paleo-biogeography (Margolin et al., 2014; Thiagarajan et al., 2013) but do not provide calendar ages unless the initial marine reservoir carbon isotope ratios are known, and are only useful for dating materials younger than ~35 ka (thousand years old).

Laser ablation MC-ICPMS U-series methods offer the potential for determining calendar ages beyond the limit of radiocarbon dating, as well as providing an initial test of open-system behaviour. Small samples can be cut and analysed with only ~0.05 g of the material used (although cutting samples may be less straightforward than drilling powders for some speleothem samples, because of their slower growth rate and requirement for extensive sectioning to reveal internal stratigraphy). Published precisions on calendar ages for coral specimens obtained using variations of this method range from 7% in corals of ~100 ka to 33% in recent corals of <1 ka (Eggins et al., 2005; McGregor et al., 2011; Potter et al., 2005). Here, rather than attempting to improve upon these precisions, we focussed on developing a simplified, high-throughput LA-MC-ICPMS method applicable for a wide range of cold-water corals, warm-water corals and speleothems, that could be adapted in any laboratory with a laser system and MC-ICPMS.

We employed a standard bracketing procedure (Section 3.2.2) to investigate samples spanning recent corals to speleothems towards the limits of such a technique (~350 ka) (Section 2.1). All samples were also measured using ID-MC-ICPMS to evaluate method accuracy. We investigated the effects of using two different laser systems and two different standard materials on the results, including differences between calcite and aragonite. We examined ^{232}Th incorporation into cold-water corals which has not been previously studied at this scale. We also describe how this method can be adapted for different samples, allowing it to be used to target specific scientific questions.

2. Sample and standard selection and preparation

2.1. Sample selection

Samples in this feasibility study comprised six aragonite cold-water corals (0.5–110 ka), five aragonite warm-water corals (0–119 ka) and three calcite speleothems (36–343 ka) selected for their relatively high (>1μg/g) U concentrations (Table 1). Cold-water corals were collected on two cruises: CE-0806 (2007) to Reykjanes Ridge, Iceland and NBP-0805 (2008) to the Drake Passage. Warm-water coral samples IMI-13 and BRB3-3 were collected from surface exposures and road cuts in Barbados (Potter et al., 2004). GI06-4 was taken from a now exposed last interglacial reef in the Bahamas (Thompson et al., 2011). Two further warm-water corals were collected from shallow water in Florida and Tahiti (Druffel et al., 2008; Robinson et al., 2004a). The speleothem QCW-24-81 was collected from the Mulu region of Borneo. Samples OD-96-06 and 72030 were collected from sub-aerial cave systems in South Wales and Canada respectively (Farrant et al., 2014; Harmon et al., 1977). For all corals and one speleothem, ID-MC-ICPMS age estimates were taken from the literature (Burke, 2012; Burke and Robinson, 2012; Druffel et al., 2008; Potter et al., 2004; Robinson et al., 2004a; Smith, 2014; Thompson et al., 2011). For the two remaining speleothems, we determined ID-MC-ICPMS ages for the layers to be targeted by LA (Section 2.3.2).

2.2. Solid standard selection

Standards should ideally be 1) matrix-matched to the samples, 2) isotopically and chemically homogeneous at the scale of sampling and 3) have relatively high (>1μg/g) concentrations of ^{238}U. In previous LA-MC-ICPMS studies standard materials have included in-house corals (McGregor et al., 2011; Potter et al., 2005), secular equilibrium calcite (Hoffmann et al., 2009) and NIST glass (Eggins et al., 2005). We tested two aragonite standards formed in contrasting natural settings (Table 2).

A cold-water coral (Dr18-1) collected on the cruise CE-0806 (2007) to Reykjanes Ridge, Iceland was used as the first standard, with precise determination of the U-series age from Burke (2012). However, due to variations in the uranium concentration associated with coral growth banding, recoil-assisted movement of ^{234}U (Gutjahr et al., 2013; Robinson et al., 2006) and to variability in ^{232}Th concentration across coral skeletons (this study; Cheng et al., 2000), these corals were not expected to be isotopically homogeneous on the length scales of the laser ablation analyses.

Our second material was an inorganically precipitated aragonite vein sample (VS001/1-A). It was collected from the Salt Wash Graben, Green River, Utah, where it was formed by CO_2-rich fluid leaking upwards through fault zone fractures from a fluid reservoir in the Jurassic Navajo Sandstone (Kampman et al., 2009, 2012). Such veins can be up to 1.5 m thick, so their use as a standard material is not sample limited. We determined the age of the layer to be targeted by LA (~1 cm thick) to be (105.6 ± 1.9 ka) using ID-MC-ICPMS. This age is 5% older than a previous measurement on the same layer (100.16 ± 0.44 ka, pers. comm. Niko Kampman). We

Table 1
Descriptions of the samples used during the study, including references to published isotopic data.

Sample	Sample type	Used for	Sample location	Calendar age
NBP-1103 Big Beauty	Cold-water coral *Desmophyllum*	^{230}Th, ^{234}U, ^{232}Th, ^{238}U	Drake Passage, Southern Ocean	0.468 ± 0.021 ka Burke and Robinson (2012)
CE-0806 Dr31A-1	Cold-water coral *Caryophyllia*	^{230}Th, ^{234}U, ^{232}Th, ^{238}U	Reykjanes Ridge, Iceland	9.676 ± 0.429 ka Burke (2012)
CE-0806 Dr25-7	Cold-water coral *Flabellum?*	^{230}Th, ^{234}U, ^{238}U	Reykjanes Ridge, Iceland	14.424 ± 0.097 ka Burke (2012)
CE-0806 Dr16-5	Cold-water coral *Desmophyllum*	^{230}Th, ^{234}U, ^{238}U	Reykjanes Ridge, Iceland	36.572 ± 0.318 ka Burke (2012)
CE-0806 Dr15-1	Cold-water coral *Desmophyllum*	^{230}Th, ^{234}U, ^{238}U	Reykjanes Ridge, Iceland	69.520 ± 0.499 ka Burke (2012)
CE-0806 Dr19A-3	Cold-water coral *Desmophyllum*	^{230}Th, ^{232}Th, ^{238}U	Reykjanes Ridge, Iceland	72.341 ± 0.872 ka Burke (2012)
Tahiti	Warm-water coral	^{230}Th, ^{238}U	Tahiti	Recent Robinson et al. (2004a)
LA C1 52-56	Warm-water coral *Montastrea*	^{230}Th, ^{238}U	Biscayne National Park, Florida	3.054 ± 0.020 ka Druffel et al. (2008)
IMI-13	Warm-water coral *Acropora*	^{230}Th, ^{238}U	Inch Marlowe Point, Barbados	75.4 ± 0.2 ka Potter et al. (2004)
BRB3-3	Warm-water coral *Acropora*	^{230}Th, ^{238}U	Bats Rock Bay, Barbados	91.2 ± 0.4 ka Potter et al. (2004)
GI06-4	Warm-water coral *Montastrea*	^{230}Th, ^{238}U	Great Inagua Island, Bahamas	118.9 ± 0.6 ka Thompson et al. (2011)
QCW-24-81	Speleothem	^{230}Th, ^{234}U, ^{238}U	Mulu region, Borneo	36.6 ± 0.1 ka (this study)
OD-96-06	Speleothem	^{230}Th, ^{234}U, ^{238}U	Ogof Draenen, Abergavenny, South Wales	186.0 ± 1.1 ka (this study)
72030	Speleothem	^{230}Th, ^{234}U, ^{238}U	Grotte Valerie, Nahanni National Park, Canada	343.1 ± 10.0 ka Smith (2014)

Table 2
Isotopic description of standard materials analysed using ID-MC-ICPMS used throughout the study. Uncertainties throughout are 2 standard errors (S.E.).

Sample	Sample type	[^{238}U] (ppm)	[^{232}Th] (ppt)	$\delta^{234}U_m$ (‰)	(^{230}Th/^{238}U)	Calendar age
CE-0806 Dr18-1	Cold-water coral *Desmophyllum*	5.03 ± 0.02	808 ± 3	107.4 ± 0.5	0.713 ± 0.003	109.8 ± 0.8 ka Burke (2012)
VS001/1-A	Inorganic aragonite vein	4.74 ± 0.05	34.2 ± 2.2	2816.5 ± 2.4	2.61 ± 0.03	105.6 ± 1.9 ka (This study)

measured (^{230}Th/^{238}U) that was 1.7% greater than the previous measurement but was within measurement uncertainties. However, $\delta^{234}U_m$ was ~60‰ lower than the previous measurement, indicating that this part of the vein has a different U-isotope composition, possibly due to diagenesis. The relatively large difference in $\delta^{234}U_m$ meant that the age we obtained was significantly older than the previous measurement. Such inhomogeneity raises difficulties when using this standard material. However, we were able to test the small scale heterogeneity of the vein by LA, using our set of in-house corals (which have known U-isotope compositions) as bracketing standards. Our measurements of $\delta^{234}U_m$ within the aragonite vein piece used for LA (1.5 × 0.5 × 0.5 cm) varied by <12‰, which is within the analytical uncertainty of the technique (Section 4.3). This finding suggests that once an ID-MC-ICPMS measurement has been done, the vein material within ~2 cm can reliably be used as a standard material.

The vein has a similar ^{238}U concentration (~4 ppm) to our coral samples, but the high (^{234}U/^{238}U) combined with the age of the sample means that the ^{230}Th concentration is higher than in our in-house coral standard. Because the material is aragonite, it is a chemical matrix-match to the corals, although it is much more coarsely crystalline and so may differ with regard to optical (and therefore LA) properties.

2.3. Sample preparation

2.3.1. Preparation for LA-MC-ICPMS

Samples were cut with a diamond blade, polished flat using P1200 grade sandpaper and rinsed with 18.2 MΩ cm water. A reusable, pressure-sensitive adhesive (Blu-tac) was used to fix ~50 samples and standards into simple, trough-shaped sample holders (Fig. S1). Depending on the laser sample cell, 50 additional samples could be loaded, eliminating time spent switching samples during analysis.

Samples were cut near to previous ID sub-samples to reduce sampling of systematic isotopic differences across the coral skeleton. Warm-water coral growth rates tend to be high; *Montastrea* grows at 6.6–8.9 mm yr^{-1} (Gladfelter et al., 1978) and *Acropora* grows at 48–99 mm yr^{-1} (Gladfelter et al., 1978; Nakajima et al., 2013). Such growth rates limit the potential for age biases. Growth rates for solitary cold-water corals are lower; of the order 1 mm yr^{-1} (Adkins et al., 2004; Risk et al., 2002). However, sub-sampling within 1 cm should still only result in skeletal age differences of up to 10 years, negligible compared to our expected uncertainties. Of greater concern are variations in the isotopic composition brought about by the incorporation of U and Th during growth and also subsequent diagenetic effects (Robinson et al., 2006).

2.3.2. ID-MC-ICPMS

For each of the samples measured by ID-MC-ICPMS in this study, approximately 0.3 g of carbonate was cut and cleaned by ultra-sonicating in 18.2 MΩ cm water for 15 min, followed by 0.5 M HNO$_3$ for ~2 min and further water washes. Cleaning of the aragonite vein was limited to water washes. Samples were spiked with a mixed ^{229}Th—^{236}U spike calibrated using ID with gravimetrically-prepared standards (Burke and Robinson, 2012). Fractions of U and Th were separated using an iron co-precipitation procedure, followed by

anion exchange columns (Edwards et al., 1987). Thorium fractions were then re-spiked with ^{236}U to provide a normalising isotope for samples with low ^{232}Th (Burke and Robinson, 2012). Samples were analysed using a Thermo Finnigan Neptune MC-ICPMS at the University of Bristol using bracketing standards (CRM-145 and Th-SGS), prepared at Woods Hole Oceanographic Institution (Burke and Robinson, 2012). Fractions of U and Th were analysed using the methods in Burke and Robinson (2012). Aliquots of Harwell Uraninite (HU-1) were run with the analyses to assess measurement accuracy (Burke and Robinson, 2012).

3. Analytical setup

3.1. Laser ablation systems

Laser ablation analyses were carried out in the Bristol Isotope Group (BIG) facilities using either a New Wave Research UP193HE ArF Excimer laser (NW) or a Photon Machines Analyte G2 193 nm laser (PM). We used the NW system for development of the method and its PM successor was used to test our findings and further refine the method. The PM system approach represents current practice in the BIG facilities. For both systems He was used as the carrier gas and was mixed with Ar before injection into the plasma. When using the PM system, N_2 gas was also mixed with the carrier gas prior to plasma injection. A more sophisticated sample chamber design was used with the PM system, involving the use of a static cup within the moving ablation cell to reduce washout times and across-cell fractionation effects.

A limiting factor in the analyses is the signal intensity of the low abundance ^{230}Th isotope. Therefore, we selected LA parameters (spot size, beam energy, repetition rate) to increase our signal intensities as far as possible (Table 3). We chose to ablate along a straight line on the sample surface by moving the LA stage rather than ablating a single spot. This 'line scan' method maintains a steadier signal intensity and inter-element fractionation compared to spot analyses. The depth of the ablated trench was estimated to be 150 μm in the coral samples and 110 μm in the aragonite vein by using a scanning electron microscope (Fig. S2). The trench was 1.3 mm long and 150 μm wide, giving a total ablated mass of ~0.07 mg per measurement in the corals and ~0.05 mg per measurement in the aragonite vein. The typical measurement time was 4.3 min.

3.2. Isotope measurement

3.2.1. Choice of isotope ratios to be measured

An ideal method would seek to measure all of the isotopes ^{230}Th, ^{232}Th, ^{234}U and ^{238}U simultaneously, thus reducing the impacts of sample heterogeneity and reducing the time for analyses. However, during LA analysis, typical signal intensities for ^{230}Th, ^{232}Th and ^{234}U are too low to measure using Faraday cups and must be measured using ion counters. Simultaneous measurements of the low abundance isotopes could be achieved using multiple ion counting (MIC) systems, such as sets of channeltrons (Hoffmann et al., 2009) or compact discrete dinodes (CDDs). The use of these would confer the advantages listed above. However, systems having MICs are less commonly available than systems with a single

central ion counter. Therefore, we focussed on testing a procedure that could be implemented by any laboratory having a laser system and mass spectrometer containing at least one ion counter. The methods presented here could be altered and improved depending on the equipment available to different laboratories. We used a peak-hopping procedure, where the low abundance isotopes are measured in sequence on a single, central ion counter - a secondary electron multiplier (SEM) − with ^{238}U measured simultaneously using Faraday cups. For certain types of sample, measurement of ^{232}Th and/or ^{234}U may not be a requirement for calculating a 'useful' age, reducing measurement time and simplifying the technique. Different users are likely to have different requirements, but we include some suggestions below.

Warm-water corals do not incorporate significant amounts of Th into their skeletons while growing because surface waters contain very low concentrations of Th (Moore, 1981). Therefore, measurements of ^{232}Th to correct for initial Th are not required by our screening technique. However, the (^{234}U/^{238}U) ratio should be measured in order to provide a test for open-system behaviour, which is common in porous warm-water coral skeletons.

Initial (^{234}U/^{238}U) in speleothems cannot be predicted a priori because there is an extremely wide variation within and between cave systems. Therefore, both (^{230}Th/^{238}U) and (^{234}U/^{238}U) must be measured in order to calculate an age. However, ^{232}Th may not be required since initial ^{230}Th is typically low along the central growth axis of pristine calcite samples (Dorale et al., 2004). Alternatively, ^{232}Th could still be monitored using a Faraday cup as a first pass.

For cold-water corals that grew in deep water, it cannot be assumed that initial ^{230}Th is equal to zero (Cheng et al., 2000), because ^{230}Th concentration and the ^{230}Th/^{232}Th ratio generally increase with depth in the ocean (Anderson et al., 1983; Cochran et al., 1987; Guo et al., 1995; Moran et al., 1995; Hayes et al., 2015a). Data from 164 corals (0−200 ka) where age corrections based on ^{232}Th were available (Robinson et al., 2014) indicates that a mean age correction based on initial thorium concentration is 400 years with the most common correction being between 100 and 300 years. These corrections are well within the expected age uncertainties for the majority of corals dated by LA, but there may be cases where assessing initial ^{230}Th concentration is desirable. Data from the same compilation indicate that 89% of cold-water corals studied had $\delta^{234}U_i$ within 10‰ of modern seawater values (Robinson et al., 2014). Therefore, we argue that closed-system behaviour is a reasonable first-order assumption for deep-sea corals. Following this argument, the $\delta^{234}U_i$ could be assumed when calculating ages, thus removing the need for measurement of ^{234}U.

3.2.2. LA-MC-ICPMS

All measurements were carried out using a Thermo Finnigan Neptune MC-ICPMS. We used peak-hopping procedures (Table 4) according to the requirements of the sample being analysed (Section 3.2.1). In order to maximise the signal intensity of the low abundance isotope ^{230}Th, the instrument was tuned for maximum ^{238}U and ^{232}Th intensity using NIST 610 glass and tuning was checked using one of the bracketing carbonate standards. The U/Th elemental fractionation factor, $f_{(Th/U)} = (Th/U)_{meas}/(Th/U)_{true}$, was ~0.5 for both laser systems. Tuning for low fractionation ($f_{(Th/U)}$

Table 3
Laser systems and parameters used throughout the study.*: Value is uncertain due to an old and uncalibrated meter. Gas flows are approximate.

LA system	Spot size (μm)	Repetition rate (Hz)	Energy at sample surface (Jcm^{-2})	Length of line scan (mm)	Line scan speed (μms^{-1})	Ar sample gas flow (Lmin^{-1})	He carrier gas flow (Lmin^{-1})	N add gas flow (Lmin^{-1})
NW UP193E	275 (circle)	20	12.35*	1.3	5	1.0	1.0	−
PM Analyte G2 193	150 (circle)	20	8.47	1.3	5	1.0	0.8	0.005

close to 1) resulted in lower (at least 5 times) signal intensity and was therefore not ideal for measurement of ^{230}Th. We did not use an RPQ energy filter in front of the central ion counter and typical abundance sensitivity for ^{238}U measured at m/z = 237 was 1 ppm. For corals with ~4 ppm ($\mu g/g$) ^{238}U, typical signal intensities were 0.25 V (2.5×10^{-12} A) ^{238}U, 1400 counts per second (cps) ^{234}U and between 1 cps (for recent corals) and 100 cps (for corals 100 ka) ^{230}Th. Secondary electron multiplier darknoise and Faraday cup baselines were measured and corrected online during each measurement session. Background intensities were measured for 25 cycles following every standard measurement, after allowing for instrument washout. Washout time was ~1 min between measurements. Background intensities for ^{230}Th and ^{234}U were typically ~0.5–1.5 cps respectively, and the background intensity for ^{238}U was 10^{-5} V. We also tested the baseline intensities (tailing plus scattered ions) of ^{230}Th and ^{234}U during ablation, by measurement of the signal intensities on the half masses 229.5, 230.5, 233.5 and 234.5. The ablation baselines for ^{230}Th and ^{234}U were ~0.5 cps and 2 cps above the background baselines respectively. We expect our standard bracketing procedure to account for most of this ablation background effect, but simultaneous measurement using additional ion counters would be a beneficial approach.

Measurements consisted of 20–50 cycles, each cycle an integration of signal intensity over 4.192 s. Anomalous spikes in ^{230}Th intensity with means of up to 1000 cps occurred on average once every twenty cycles, and these spikes were removed during data processing (see Section 3.3 for details).

In order to correct for elemental fractionation and fractionation instability, bracketing standards were measured regularly. For initial method development, every sample was bracketed by standard measurements. However, when using the PM system we found that increasing the radio frequency (RF) power to the plasma from 1200 W to 1410 W resulted in elemental fractionation that was stable over longer periods of time (Fig 1). Spot size, repetition rate, energy at the sample surface and the length and speed of each line scan were held constant during tests of different RF powers, suggesting that the change in RF power was the main factor in improving the stability. Under these improved conditions we were able to reduce the number of bracketing standards measured to one for every three samples with no effect on the reproducibility of measured isotope ratios. We also automated the analyses of up to ~25 samples at a time. The automation is achieved by using the laser ablation software, 'Chromium 2', to ablate pre-programmed and auto-focussed line scans, the ablation of which in turn triggers the mass spectrometer's data acquisition. Around 50 samples could be measured in 12 h in this way. After the 12 h period signal intensity had often decreased by ~1/3 due to partial clogging of the skimmer and/or sampler cones due to carbonate build up. Therefore cones were cleaned between each 12 h measurement session.

3.3. Offline data processing

Visual inspection of histograms of ^{230}Th intensity along LA profiles suggested that, whilst the majority of the data fell within a normal distribution, spikes in ^{230}Th occurred that did not fit the distribution of the rest of the data. Cycles with anomalous ^{230}Th intensity (defined here as 1.5 times the interquartile range beyond the upper and lower quartiles) were removed, with on average one in twenty cycles removed in this way. Remaining cycles were used to calculate mean isotope intensities, from which the background intensity was subtracted before calculating isotope ratios. The bracketing standards were used to correct for instrumental, elemental and isotopic fractionation, assuming that mass-loading effects caused by the differences in ablated mass (Section 3.1) were negligible. Further tests of the mass loading effect may be desirable as a refinement of the method. Resulting ratios were then used to determine sample age by iteratively solving the age equation (Equation (1)) (Kaufman and Broecker, 1965) using the Newton–Raphson method. For each isotope ratio, the standard error on the measured ratio (over n cycles) was propagated analytically through each stage of the standard corrections. The standard errors of the background measurements were also analytically propagated into the final error of each isotope ratio, as were the errors on the ID-MC-ICPMS isotope ratios of the standards. Final propagation of errors through the age equation was done using a Monte Carlo technique: measured isotope ratios and their uncertainties were used to generate random distributions of data for each ratio, and these data were then used to calculate a distribution of possible ages, from which the sample age and its errors could be determined. We use the term 'internal precision' throughout the paper to describe these errors on the isotope ratios and ages. The relationship between the internal errors and the external reproducibility of measurements is discussed in Section 5.2.

4. Results

4.1. Speleothems measured by ID-MC-ICPMS

For the two speleothem samples measured by ID-MC-ICPMS in this study, we compared our results with existing data. For the sample OD-96-06, we obtained an age of 186.0 ± 1.1 ka, 21 mm from the base (Table S5). Published ages from Farrant et al. (2014) range from 170.2 ka to 185.3 ka and show significant inversions with distance from the base, indicating diagenetic alteration. Our result is consistent with this pattern.

Preliminary ages for the speleothem QCW-24-81 were 37 ka at the speleothem base and 28 ka at 180 mm above the base (pers. comm. David Richards). Our sample was cut 62 mm above the base and we obtained an age of 36.6 ± 0.1 ka (Table S5), consistent with the ages above.

4.2. Measurement of (^{230}Th/^{238}U) ratios

4.2.1. Reproducibility of isotope analyses on the standards

Repeat (^{230}Th/^{238}U) measurements of the aragonite vein standard with the NW laser ablation system and of the cold-water coral Dr18-1 standard with both the NW and PM systems were made to determine the analytical reproducibility of the method. The aragonite vein analyses were bracketed against themselves and the Dr18-1 analyses were bracketed both against themselves and

Table 4
Description of the different measurement procedures used during the study.

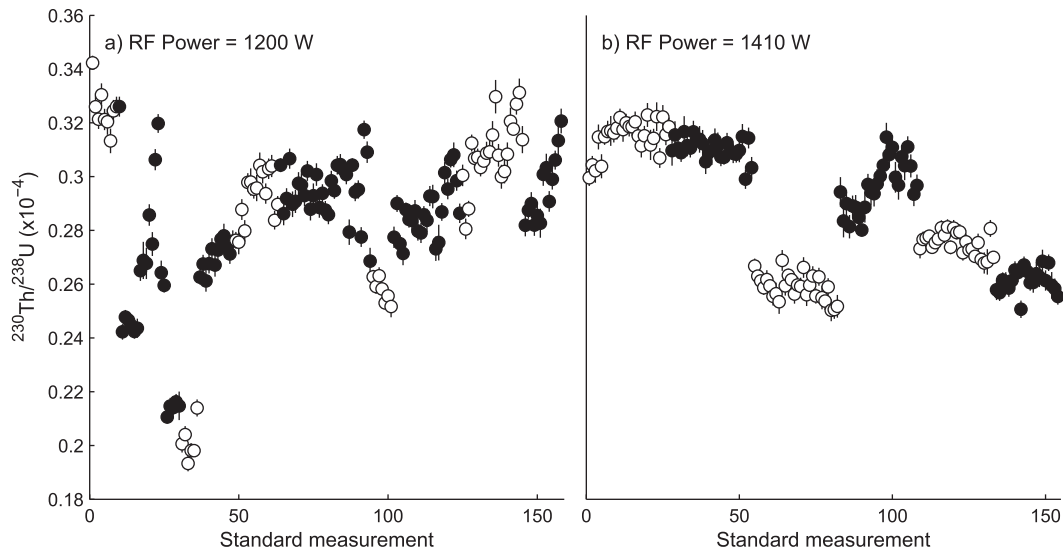| Procedure	Cycles	Integration time per cycle (s)	Collection	Cup configuration				
				SEM	H1	H2	H3	H4
1	50	4.192	Static	^{230}Th				^{238}U
2	25	4.192	Peak Hopping	^{230}Th				^{238}U
				^{234}U		^{238}U		
3	25	4.192	Peak Hopping	^{230}Th				^{238}U
				^{232}Th			^{238}U	

Fig. 1. Multiple measurements on the aragonite vein standard illustrating the effect of using radio frequency (RF) powers of a) 1200 W and b) 1410 W on the stability of the intensity ratio ^{230}Th/^{238}Th. Alternating white/black symbols are used to separate individual analysis sessions lasting 12—24 h. The time between each analysis session was typically several days.

against the aragonite vein analyses (Fig. 2, Tables S1—S3). Bracketing standards were measured both before and after samples, including when self bracketed. Both procedures 1 and 2 (Table 4) were used as shown in Tables S1—S3.

To test the agreement between the ID-MC-ICPMS and LA measurements we calculated the t statistic given by,

$$ t = \frac{x_{ID} - x_{LA}}{\left(s_{ID}^2 + s_{LA}^2/n \right)^{1/2}}, $$

where x_{ID} and x_{LA} are the (^{230}Th/^{238}U) ratios for the ID and mean LA measurements respectively and s_{ID} and s_{LA} are the uncertainty of the ID measurement and sample standard deviation (sample size n) of the LA measurements respectively. The value of t was compared to the critical values of a Monte-Carlo (MC) simulated reference distribution where the population means of the distributions of x_{ID} and x_{LA} are the same, i.e. the null hypothesis. For the MC simulation, 100,000 values of the ID measurement and 100,000 values of each of the n LA measurements were generated. We applied the test at the 99% confidence level. For the coral Dr18-1 measured with the NW system and bracketed by the aragonite vein the mean (^{230}Th/^{238}U) ratio differed from the ID measurement by this test. The difference is 2.5% and could be due to skeletal heterogeneity rather than inaccuracy of the measurement method. All other LA measurements passed the t-test at this level of confidence. We therefore conclude that we can measure (^{230}Th/^{238}U) accurately enough for the purposes of this age-screening application.

4.2.2. Cold-water corals

We measured five further cold-water corals using both the NW and PM laser systems and the two standards (Fig 3a—e, Tables S1—S3) and compared these to the ID measured values. Of the 15 results, only Big Beauty measured using the NW system bracketed by the aragonite standard fell outside the 99% confidence interval, with a difference between the LA and ID measured (^{230}Th/^{238}U) of only 0.003. Therefore we again conclude that the LA methods reproduce the ID measured value accurately enough for this application.

For cold-water corals, the best internal precision on (^{230}Th/^{238}U) was obtained by using the combination of the PM laser system and the aragonite vein as bracketing standard suggesting that, 1) the

aragonite vein may be more homogeneous than the in-house coral at the scale of the laser sampling, resulting in reduced scatter and/or 2) the PM system exhibits greater stability of the (^{230}Th/^{238}U) ratio, possibly due to an improved sample cell design (Section 3.1). However, the external reproducibility of the measurements was similar regardless of methodology and is likely limited by isotopic heterogeneity within the samples and standards (Section 5.2).

As expected, younger corals show greater relative uncertainty due to their lower ^{230}Th content. External reproducibility (2 S.D.) ranged from 7.6% to 5.4% for samples with (^{230}Th/^{238}U) of 0.1 and 0.7 respectively.

4.2.3. Warm-water corals and speleothems

We also measured a number of warm-water coral skeletons and speleothems (Fig. 3f—m, Table S1). The warm-water corals (Fig. 3f—j) are structurally distinct from the cold-water corals, their skeletons containing numerous pores compared to the high skeletal density of cold-water corals. This difference means that LA tracks often pass over pores. However, the accuracy (the offset of our LA measurements from the ID measurement) in these corals was typically the same as in cold-water corals for comparable ages. More measurements would be needed in order to fully assess the reproducibility of our method in these corals.

Calcite speleothems are made of the same chemical matrix as the inorganic aragonite standard. However, it is possible that differences in mineralogy between calcite and aragonite could result in different optical properties and ablation yield. The mean (^{230}Th/^{238}U) ratios measured by LA-ICPMS for OD-96-06 and GB-89-25-3 and 72030 were not statistically different to the ID values at the 99% confidence level. Therefore, we find no evidence that differences between calcite and aragonite significantly affect our results, demonstrating that our inorganic aragonite standard can be used for measurement of either aragonite or calcite materials.

4.3. Measurement of (^{234}U/^{238}U)

We used procedure 2 (Table 4) with the NW laser system to determine $\delta^{234}U_m$ (Equation (2)). The inorganic aragonite was used as the bracketing standard in all cases. The $\delta^{234}U_m$ was then used with the calculated sample age to estimate $\delta^{234}U_i$ (Equation (3)).
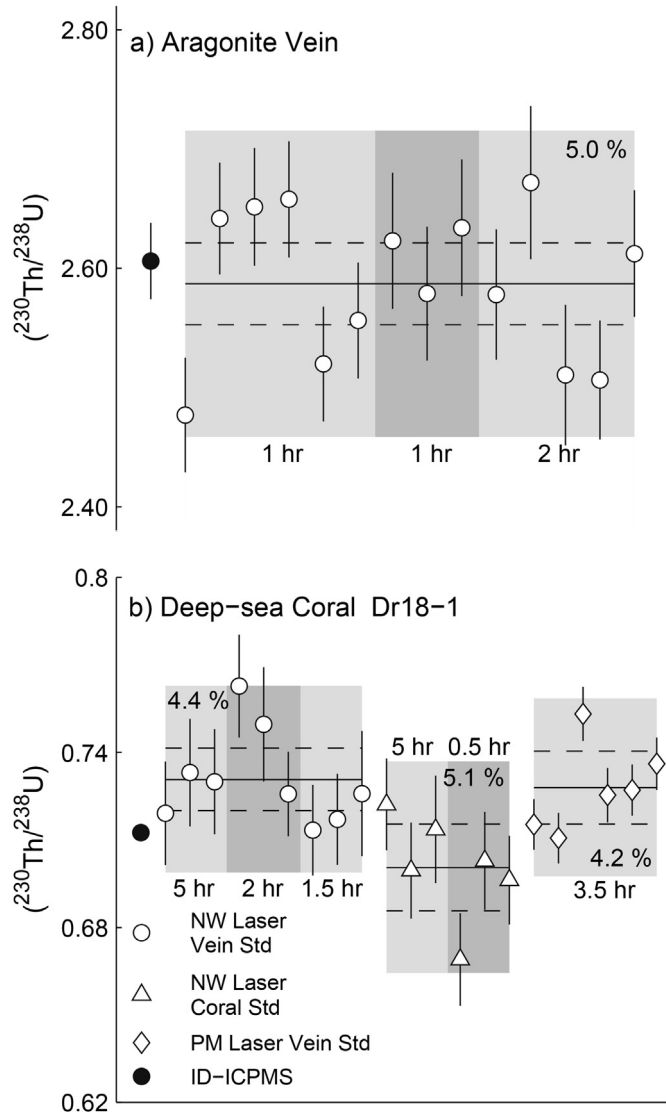
Fig. 2. (^{230}Th/^{238}U) measured for a) the inorganic aragonite vein standard and b) the in-house deep-sea coral standard Dr18-1 ordered by date and time. Filled black circles indicate values obtained by ID-MC-ICPMS. Error bars represent the internal ±2 S.E. for each measurement. Where error bars are absent, errors are less than the size of the plotted symbols. The mean, ±2 S.D. and ±2 S.E. for each set of measurements are indicated by the black line, grey bars and dashed lines respectively. The percentage uncertainty represented by the grey bars is shown. Alternating shades of grey indicate different days of measurement, and the length of time spanned by the measurements is indicated.

4.3.1. Cold-water corals

Out of 18 individual LA measurements of $\delta^{234}U_m$ in six cold-water corals, 16 analyses agreed with the corresponding ID-MC-ICPMS values within the internal precision (6–10‰) of the LA-MC-ICPMS measurements (Fig. 4, Table S1). The two coral measurements that were outside internal precision were within 12‰. After accounting for the uncertainty of the ^{230}Th/^{238}U-derived ages, internal precision on $\delta^{234}U_i$ was typically ~20‰ and all LA measurements were within internal precision of ID-MC-ICPMS values. Therefore, we can determine $\delta^{234}U_i$ accurately to within ~20‰. The internal precision on a single measurement appears to be an appropriate estimate of the error on (^{234}U/^{238}U) ratios for these corals. This level of uncertainty would allow screening of corals that have U isotope compositions more than 20‰ from the seawater value, around 3% of cold-water corals (Robinson et al., 2014). Since

it is such a low proportion of cold-water corals that could be screened for diagenesis using this technique, measurement of (^{234}U/^{238}U) may not be essential when rapidly dating these corals (section 3.2.1). However, for researchers measuring warm-water corals our method would be useful in pre-screening for corals with $\delta^{234}U_i$ far from the expected seawater composition at the time of formation, since these corals are more susceptible to diagenesis.

4.3.2. Speleothems and inorganic aragonite

Measurements of $\delta^{234}U_m$ and $\delta^{234}U_i$ in speleothems and inorganic aragonite samples were all within internal precision of ID-MC-ICPMS values, showing that the internal precision of $\delta^{234}U$ measurements is appropriate to use as an error estimate (Table S1). Precision of $\delta^{234}U_m$ ranged from 6‰ for $\delta^{234}U_m = -305$‰ to 21‰ for $\delta^{234}U_m = 2800$‰. Precision of $\delta^{234}U_i$ ranged from 14‰ for $\delta^{234}U_i = -340$‰ and age = 36 ka, to 9‰ for $\delta^{234}U_i = 1800$‰ and age = 343 ka.

4.4. ^{232}Th Analysis and implications

Procedure 3 (Table 4) was used to determine (^{232}Th/^{238}U) ratios on five cold-water corals (Table S4). Measurements were carried out using the coral standard Dr18-1, because the aragonite vein has a far lower ^{232}Th concentration (Table 2).

For three out of five corals, the LA (^{232}Th/^{238}U) ratio agreed with the ID ratio within the internal precision, which was around 5% (2s). For the remaining two corals (Dr31A-1 and Dr19A-3), analytical uncertainty was larger (30%) and the LA (^{232}Th/^{238}U) ratios were 1.5 and 1.9 times greater than the ID ratio respectively. ID estimates of isotopic concentrations indicate that these two corals had the lowest ^{238}U and highest ^{232}Th concentrations of the five corals (Table S4).

The first three corals also had approximately constant ^{232}Th/^{238}U atom ratios along a single LA track, with standard deviations of 9–13%. By contrast DR31A-1 and DR19A-3 displayed clear spatial structure in their ^{232}Th/^{238}U ratios (e.g. Fig. 5), with standard deviations of 69% and 76% respectively. The variability in the ^{232}Th/^{238}U ratios was dominated by within-coral ^{232}Th heterogeneity. This heterogeneity, combined with high ^{232}Th concentration, was likely the cause of the difference between the LA and ID measured ^{232}Th/^{238}U ratios. It appears that a high standard deviation of ^{232}Th/^{238}U is a good indicator of ^{232}Th/^{238}U ratios that do not agree with the bulk value for that coral. However, because the correction for initial ^{230}Th based on ^{232}Th results in an age correction which is generally smaller than the LA age uncertainty (400 yrs compared to >1000 yrs in most cases, see Section 3.2.1), using the uncorrected age would be acceptable in most LA screening surveys or reconnaissance work.

4.5. Sample ages

Given that we can measure both ^{230}Th/^{238}U and ^{234}U/^{238}U accurately using our methods, we can also determine accurate ages. Uncorrected ages from six cold-water corals (36 measurements on each laser system) were calculated using the assumption that $\delta^{234}U_i = 146 \pm 10$‰ (Fig. 6, Tables S1 and S3). For the NW and PM systems, the data fit the 1:1 line shown with R^2 values of 0.991 and 0.995 respectively, based on residuals for the fit y = x. Another 18 uncorrected ages were calculated for the same six corals using $\delta^{234}U_m$ and using the NW system (Fig. 6, Table S1). These data fit the same line with an R^2 of 0.998. Warm-water coral samples in this study had previously been analysed with ID techniques and shown to satisfy the closed-system criteria. Therefore in this case we assumed $\delta^{234}U_i = 146 \pm 10$‰ and calculated uncorrected ages based solely on the measured (^{230}Th/^{238}U) ratio (Fig. 6, Table S1). Ages fit

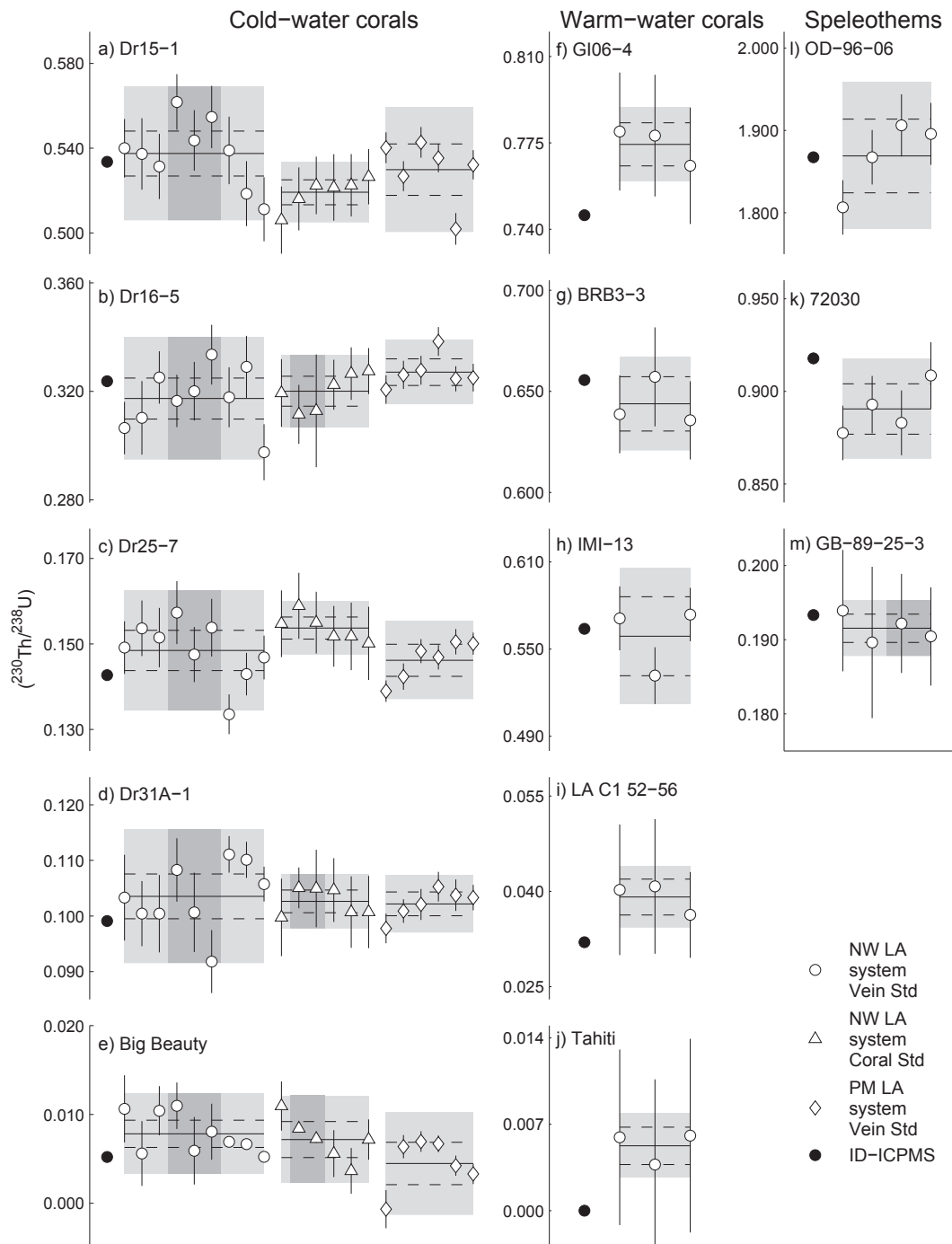**Fig. 3.** $(^{230}Th/^{238}U)$, measured for the left column: a) Dr15-1, b) Dr16-5, c) Dr25-7, d) Dr31A-1, e) Big Beauty; the middle column: f) GI06-4, g) BRB3-3, h) IMI-13, i) LA C1 52-56, j) Tahiti and the right column: k) 72030, l) OD-96-06 and m) GB-89-25-3. Error bars represent the internal ± 2 S.E. for each measurement. Where error bars are absent, errors are less than the size of the plotted symbols. The mean, ± 2 S.D. and ± 2 S.E. for each set of measurements are indicated by the black line, grey bars and dashed lines respectively. Alternating shades of grey indicate different measurement sessions.

on the 1:1 curve with an R^2 of 0.991. Uncorrected speleothem ages include measurement of $\delta^{234}U_m$ as well as $(^{230}Th/^{238}U)$ (Fig. 6, Table S1). The ages fit the 1:1 curve with an R^2 of 0.995.

5. Discussion

5.1. ^{232}Th: further considerations and suggestions

It seems likely that the offset between the ID and LA determined

$^{232}Th/^{238}U$ in some samples is due to the extensive chemical cleaning applied to ID samples that is designed to remove organic materials and the metal-rich crusts that form on coral skeletons in the deep ocean (Cheng et al., 2000). We have shown that LA measured $^{232}Th/^{238}U$ can be up to twice the bulk coral ID value, apparently due to heterogeneous ^{232}Th distribution within coral skeletons.

For the two corals with the most heterogeneous ^{232}Th, peaks in ^{232}Th intensity appeared to correlate closely with peaks in ^{238}U
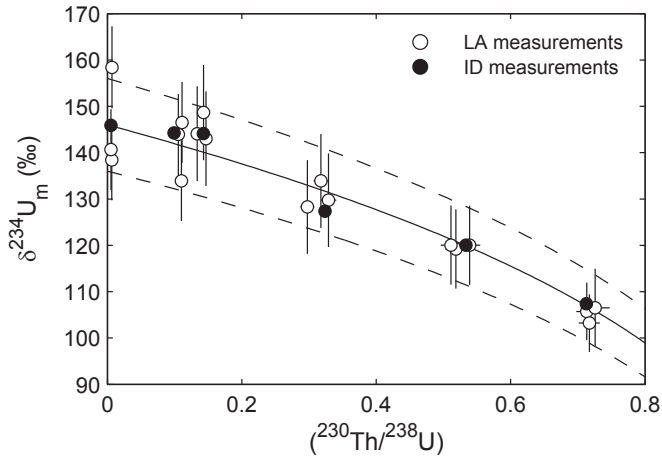
Fig. 4. $\delta^{234}U_m$ versus $(^{230}Th/^{238}U)$ measured in six cold-water corals. The solid curve represents the evolution of these ratios over time assuming an initial $\delta^{234}U$ of modern-day seawater, an initial $(^{230}Th/^{238}U)$ of zero and a closed system. The dashed lines indicate starting compositions of 136‰ and 156‰. Where error bars are absent, errors are less than the size of the plotted symbols.

intensity (Fig. 5). The intensity (which we take as a proxy for concentration) of ^{232}Th varied by a factor of ~20, much larger than the factor of ~2 seen for ^{238}U. This correlation suggests that there may be a common mechanism influencing incorporation of uranium and thorium into the skeleton. This inference is rather surprising given the different chemical properties of the two elements. Uranium is thought to be incorporated into the aragonite lattice as the tetravalent uranyl carbonate ion (Reeder et al., 2000). Thorium, however, is insoluble in seawater, and is thought to scavenge out onto surfaces (Bacon and Anderson, 1982; Hayes et al., 2015b). Chemical cleaning is designed to remove much of this scavenged thorium before ID analyses, whereas LA analyses have not been subject to cleaning and so may ablate scavenged Th which would then be analysed giving a higher ^{232}Th concentration. Adkins et al. (2003) showed that the central growth bands of the coral *Desmophyllum dianthus* are isotopically depleted with respect to $\delta^{18}O$ and $\delta^{13}C$, and used this as evidence that the central bands consist of rapidly deposited carbonate. Modelling of physiochemical calcification suggests that U concentration is inversely related to calcification rate (Sinclair et al., 2006). Indeed, it is these rapidly deposited central bands that have been shown to have low U (Anagnostou et al., 2011; Robinson et al., 2006). The rapid growth of such bands may mean that less thorium is scavenged onto their surfaces during growth, leading to the covariance in uranium and thorium that we observe (Fig. 5). This observation warrants further investigation by studies seeking to determine the vital effects in scleractinian corals.

5.2. Estimation of uncertainties in $(^{230}Th/^{238}U)$ and sample age

We have shown that we achieve the best internal errors on the $(^{230}Th/^{238}U)$ when using the PM system and the aragonite vein standard. These internal errors are close to what we would expect from counting statistics, which are dominated by the counts of ^{230}Th in the samples (Fig. 7a). Unfortunately LA analyses do not allow measurement of the same fragment of carbonate twice. Therefore, the external reproducibility ($\pm$ 2 S.D.) of measurements is dependent on factors that include counting statistics, sample heterogeneity, standard heterogeneity and short-term instrumental drift and is therefore greater than the internal errors. One way to reduce the uncertainty would be to make repeat
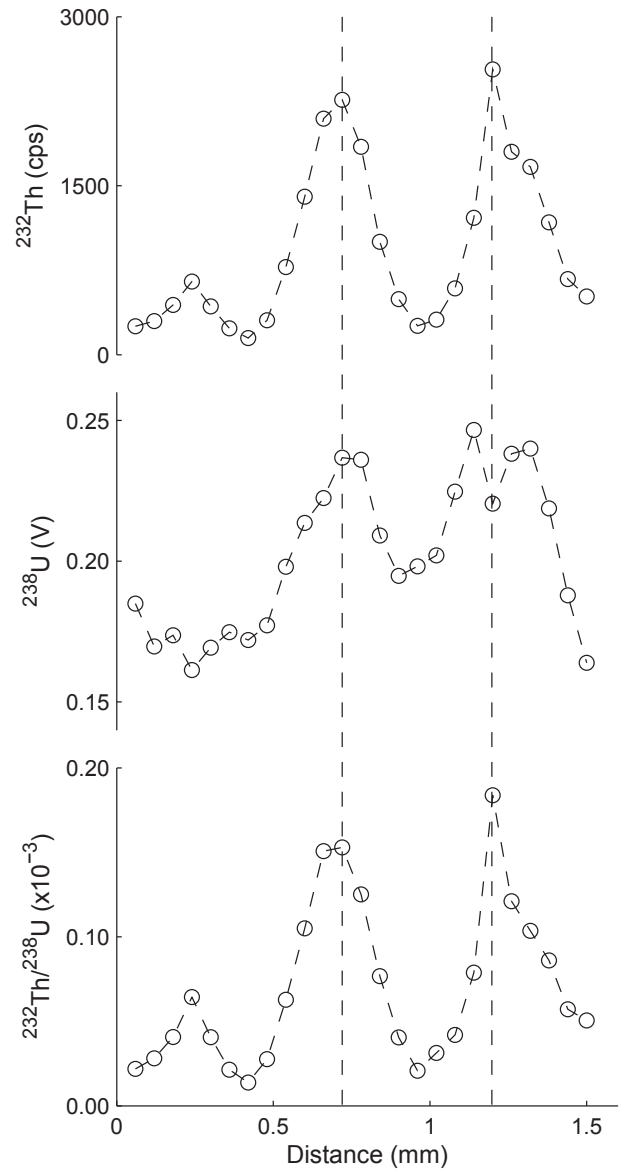

Fig. 5. A 25-cycle LA profile for cold-water coral Dr31A-1. Panels from top to bottom show the ^{232}Th signal intensity, the ^{238}U signal intensity and the signal intensity ratio $^{232}Th/^{238}U$ versus the distance along the LA profile. Vertical dashed lines go through the peak in $^{232}Th/^{238}U$ and are closely aligned to peaks in ^{232}Th and ^{238}U.

measurements of each sample. However, repeats would increase the analysis time.

We were able to reproduce our observed external reproducibility using a model that included counting statistics, sample heterogeneity and standard heterogeneity. Cold-water coral skeletons have been shown to be isotopically heterogeneous for U-series isotopes at similar length scales to our LA analyses (Robinson et al., 2006). The available data suggest that $\delta^{234}U$ heterogeneity may increase as a function of age due to recoil-assisted movement of ^{234}U away from regions of high U concentration. For the purposes of our model we assumed that this function is smooth and linear, which results in $(^{230}Th/^{238}U)$ heterogeneity that increases over time, with 2 S.D.s about the bulk mean coral ratio that range from 1% in recent corals to 3.5% in older corals (120 ka). The aragonite vein standard may be heterogeneous for similar reasons, and short term instrumental drift may also play a role in increasing our uncertainty. We do not separate these two factors for the purposes of
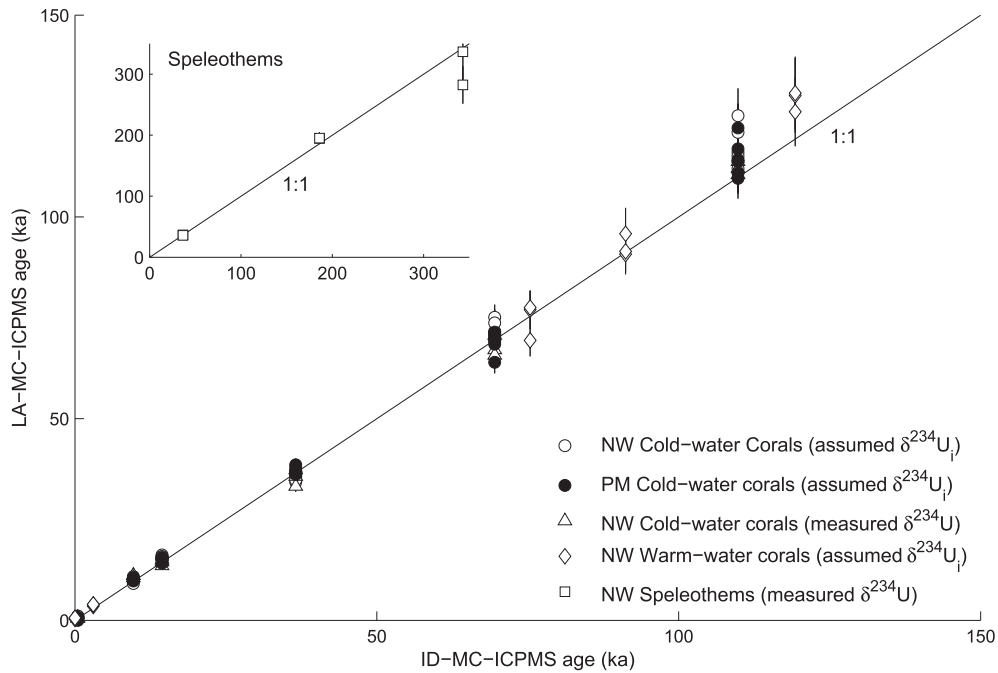
Fig. 6. Uncorrected LA-ICPMS age (ka) versus corrected IDS-ICPMS age (ka) for 14 samples including 6 cold-water corals, 5 warm-water corals and 3 speleothems, measured using the NW and PM laser systems. Coral ages were either calculated by assuming an initial $\delta^{234}U_i$ (circles) or by measuring the $\delta^{234}U_m$ (triangles). The solid lines indicate a 1:1 relationship. Where error bars are absent, errors are less than the size of the plotted symbols.

this model, instead combining them into the parameter 'apparent standard heterogeneity', which we were able to estimate for the vein material from 14 measurements (Fig. 2) made using the NW laser system (5%, 2s). Given the expected uncertainties, we were able to estimate the reproducibility we could expect using our LA dating technique for any cold-water coral given its ($^{230}Th/^{238}U$) ratio, obtaining good agreement with our analyses (Fig. 7a). At very young ages the uncertainty is dominated by counting statistics. The effect of apparent standard heterogeneity is important at all ages, with the effect of sample heterogeneity becoming as important as standard heterogeneity for older samples (~70 ka).

For the PM system currently in use at the University of Bristol, uncertainties range from <0.8 ka during the Holocene (0−10 ka) and ~1.5 ka during the Last Glacial Maximum (~ 20 ka) to ~15 ka during the last interglacial (~125 ka). These uncertainties make the current method very useful for the purposes of age-screening. However, to improve the final age uncertainty, a homogeneous standard and/or replicate analyses would be needed.
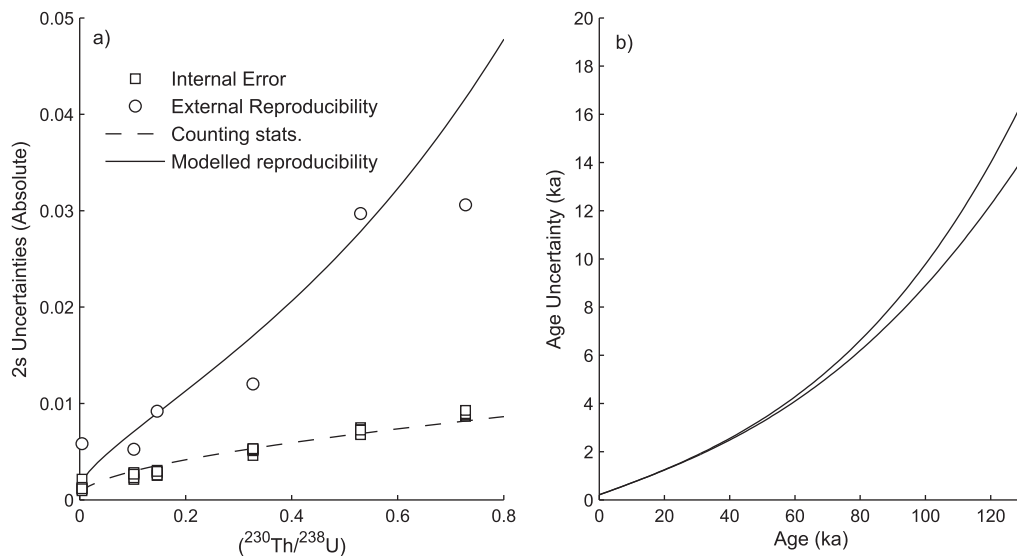

Fig. 7. Estimates of the errors on LA-MC-ICPMS U-series analyses. a) Estimates of the expected errors from 1) counting statistics on the samples, standards and blanks (dashed line) and 2) from a combination of counting statistics, sample heterogeneity and apparent standard heterogeneity (solid line). These lines are plotted with the measured internal precision (squares, see Section 3.3) and the external reproducibility of LA analyses on cold-water corals (circles). b) Positive and negative age uncertainties derived from the solid line in (a). The difference arises due to the non-linear evolution of the ($^{230}Th/^{238}U$) ratio with time.

6. Conclusions

We have developed and refined a simple laser ablation (LA) technique for rapidly obtaining U—Th ages for both aragonite and calcite materials. This technique could be adapted in any laboratory having identified a matrix matched, high uranium concentration (~4 ppm) standard material and having an appropriate laser system and MC-ICPMS with at least one ion counter. Small samples must be cut prior to measurement, which may be more difficult than drilling powders for some sample types, such as speleothems. Measurement of a single sample took ~4.3 min and, with the stable signal achieved using an RF power of 1410 W, we can routinely measure 50 samples in 12 h in an automated run, with an additional day required for sample preparation. The method can be adapted depending on the isotope ratios needed and time constraints. We found no evidence of differences between aragonite and calcite having a significant effect on our results.

Accuracy was assessed in a suite of corals and speleothems by comparison with precise ID analyses. The uncertainties of $(^{230}Th/^{238}U)$ and age were controlled by a combination of counting statistics and isotopic heterogeneity of samples and standards, and can therefore be modelled for any sample without having to do replicate analyses. The $(^{230}Th/^{238}U)$ external precision ranged from 5.4% to 7.6% for samples with $(^{230}Th/^{238}U)$ ratios of 0.7 and 0.1 respectively. A homogeneous standard material could improve these precisions but is not a requirement for age-screening studies. The $\delta^{234}U_i$ could be determined within ~20‰ making it useful as an initial indicator of open-system behaviour. The $^{232}Th/^{238}U$ ratio can generally be determined by LA to within analytical uncertainty (5%) of ID measurements unless the ratio is strongly heterogeneous in the sample. However, in order to avoid potential issues with the correction for initial thorium concentration, we report uncorrected ages even though ages may be ~400 years older than the calendar ages (depending on the $^{230}Th/^{232}Th$ ratio).

Uncertainties on cold-water coral ages generated by assuming $\delta^{234}U_i$ ranged from <0.8 ka in Holocene specimens to ~1.5 ka for samples from the Last Glacial Maximum to ~15 ka for samples with ages of 125 ka. These uncertainties may be improved with the use of an isotopically homogeneous standard material. These findings, combined with the simple and high throughput set up we have used, should benefit the wider paleoclimate community.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quageo.2015.10.004.

References

Adkins, J.F., Boyle, E.A., 1999. Age screening of deep-sea corals and the record of deep North Atlantic circulation change at 15.4 ka. Reconstructing ocean history: a window into the future. In: 6th International Conference on Paleoceanography Aug 23-28, 1998 Lisbon, Portugal, pp. 103—120.

Adkins, J.F., Boyle, E.A., Curry, W.B., Lutringer, A., 2003. Stable isotopes in deep-sea corals and a new mechanism for "vital effects". Geochim. Cosmochim. Acta 67, 1129—1143. http://dx.doi.org/10.1016/s0016-7037(00)01203-6.

Adkins, J.F., Cheng, H., Boyle, E.A., Druffel, E.R.M., Edwards, R.L., 1998. Deep-sea coral evidence for rapid change in ventilation of the deep North Atlantic 15,400 years ago. Science 280, 725—728. http://dx.doi.org/10.1126/science.280.5364.725.

Adkins, J.F., Henderson, G.M., Wang, S.L., O'Shea, S., Mokadem, F., 2004. Growth rates of the deep-sea scleractinia Desmophyllum cristagalli and Enallopsammia rostrata. Earth Planet. Sci. Lett. 227, 481—490. http://dx.doi.org/10.1016/j.epsl.2004.08.022.

Anagnostou, E., Sherrell, R.M., Gagnon, A., LaVigne, M., Field, M.P., McDonough, W.F., 2011. Seawater nutrient and carbonate ion concentrations recorded as P/Ca, Ba/Ca, and U/Ca in the deep-sea coral Desmophyllum dianthus. Geochim. Cosmochim. Acta 75, 2529—2543. http://dx.doi.org/10.1016/j.gca.2011.02.019.

Anderson, R.F., Bacon, M.P., Brewer, P.G., 1983. Removal of Th-230 and Pa-231 from the open ocean. Earth Planet. Sci. Lett. 62, 7—23. http://dx.doi.org/10.1016/0012-821x(83)90067-5.

Bacon, M.P., Anderson, R.F., 1982. Distribution of thorium isotopes between dissolved and particulate forms in the deep-sea. J. Geophys. Res. Oceans Atmos. 87, 2045—2056. http://dx.doi.org/10.1029/JC087iC03p02045.

Broecker, W.S., Thurber, D.L., Goddard, J., Ku, T.L., Matthews, R.K., Mesolell, Kj, 1968. Milankovitch hypothesis supported by precise dating of coral reefs and deep-sea sediments. Science 159, 297—300. http://dx.doi.org/10.1126/science.159.3812.297.

Burke, A., 2012. Constraining Circulation Changes through the Last Deglaciation with Dynamic Tracers: Insights from Deep-sea Coral Radiocarbon and Sedimentary 231Pa/230Th. Ph.d. thesis. Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, USA.

Burke, A., Robinson, L.F., 2012. The Southern Ocean's role in carbon exchange during the last deglaciation. Science 335, 557—561. http://dx.doi.org/10.1126/science.1208163.

Burke, A., Robinson, L.F., McNichol, A.P., Jenkins, W.J., Scanlon, K.M., Gerlach, D.S., 2010. Reconnaissance dating: a new radiocarbon method applied to assessing the temporal distribution of Southern Ocean deep-sea corals. Deep-Sea Res. Part Oceanogr. Res. Pap. 57, 1510—1520. http://dx.doi.org/10.1016/j.dsr.2010.07.010.

Cheng, H., Adkins, J., Edwards, R.L., Boyle, E.A., 2000. U-Th dating of deep-sea corals. Geochimica Cosmochim. Acta 64, 2401—2416. http://dx.doi.org/10.1016/s0016-7037(99)00422-6.

Cheng, H., Edwards, R.L., Wan, Y.J., Ko, X.G., Ming, Y.F., Kelly, M.J., Wang, X.F., Gallup, C.D., Liu, W.G., 2006. A penultimate glacial monsoon record from Hulu Cave and two-phase glacial terminations. Geology 34, 217—220. http://dx.doi.org/10.1130/g22289.1.

Cochran, J.K., Livingston, H.D., Hirschberg, D.J., Surprenant, L.D., 1987. Natural and anthropogenic radionuclide distributions in the northwest Atlantic-ocean. Earth Planet. Sci. Lett. 84, 135—152. http://dx.doi.org/10.1016/0012-821x(87)90081-1.

Dorale, J., Edwards, L., Alexander Jr., C., Shen, C.C., Richards, D., Cheng, H., 2004. Studies of cave sediments. Book section: uranium-series dating of speleothems: current techniques. Limits Appl. 177—197.

Douville, E., Sall, E., Frank, N., Eisele, M., Pons-Branchu, E., Ayrault, S., 2010. Rapid and accurate U-Th dating of ancient carbonates using inductively coupled plasma-quadrupole mass spectrometry. Chem. Geol. 272, 1—11. http://dx.doi.org/10.1016/j.chemgeo.2010.01.007.

Druffel, E.R.M., Robinson, L.F., Griffin, S., Halley, R.B., Southon, J.R., Adkins, J.F., 2008. Low reservoir ages for the surface ocean from mid-Holocene Florida corals. Paleoceanography 23, PA2209. http://dx.doi.org/10.1029/2007pa001527.

Dykoski, C.A., Edwards, R.L., Cheng, H., Yuan, D.X., Cai, Y.J., Zhang, M.L., Lin, Y.S., Qing, J.M., An, Z.S., Revenaugh, J., 2005. A high-resolution, absolute-dated holocene and deglacial Asian monsoon record from Dongge Cave, China. Earth Planet. Sci. Lett. 233, 71—86. http://dx.doi.org/10.1016/j.epsl.2005.01.036.

Edwards, R.L., Chen, J.H., Ku, T.L., Wasserburg, G.J., 1987. Precise timing of the last interglacial period from mass-spectrometric determination of Th-230 in corals. Science 236, 1547—1553. http://dx.doi.org/10.1126/science.236.4808.1547.

Edwards, R.L., Gallup, C.D., Cheng, H., 2003. Uranium-series dating of marine and lacustrine carbonates. Uranium-Series Geochem. 52, 363—405. http://dx.doi.org/10.2113/0520363.

Eggins, S.M., Grun, R., McCulloch, M.T., Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer, G., Shelley, M., Murray-Wallace, C.V., Spotl, C., Taylor, L., 2005. In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology. Quat. Sci. Rev. 24, 2523—2538. http://dx.doi.org/10.1016/j.quascirev.2005.07.006.

Fairbanks, R.G., 1989. A 17,000-year glacio-eustatic sea-level record - influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. Nature 342, 637—642. http://dx.doi.org/10.1038/342637a0.

Farrant, A.R., Smith, C.J.M., Noble, S.R., Simms, M.J., Richards, D.A., 2014. Speleogenetic evidence from Ogof Draenen for a pre-Devensian glaciation in the Brecon Beacons, South Wales, UK. J. Quat. Sci. 29, 815—826. http://dx.doi.org/10.1002/jqs.2751.

Gallup, C.D., 1997. High-precision Uranium-series Analyses of Fossil Corals and Nicaragua Rise Sediments: the Timing of High Sea Levels and the Marine Delta U-234 Value during the Past 20,000 Years. Ph.D. thesis. University of Minnesota, USA.

Gladfelter, E.H., Monahan, R.K., Gladfelter, W.B., 1978. Growth-rates of 5 reef-

building corals in the northeastern Caribbean. Bull. Mar. Sci. 28, 728–734.

Guo, L.D., Santschi, P.H., Baskaran, M., Zindler, A., 1995. Distribution of dissolved and particulate Th-230 and Th-232 in seawater from the Gulf-of-Mexico and off Cape-Hatteras as measured by SIMS. Earth Planet. Sci. Lett. 133, 117–128. http://dx.doi.org/10.1016/0012-821x(95)00063-i.

Gutjahr, M., Vance, D., Hoffmann, D.L., Hillenbrand, C.D., Foster, G.L., Rae, J.W.B., Kuhn, G., 2013. Structural limitations in deriving accurate U-series ages from calcitic cold-water corals contrast with robust coral radiocarbon and Mg/Ca systematics. Chem. Geol. 355, 69–87. http://dx.doi.org/10.1016/j.chemgeo.2013.07.002.

Harmon, R.S., Ford, D.C., Schwarcz, H.P., 1977. Interglacial chronology of Rocky and Mackenzie mountains based upon Th-230-U-234 dating of calcite speleothems. Can. J. Earth Sci. 14, 2543–2552. http://dx.doi.org/10.1139/e77-220.

Hayes, C.T., Anderson, R.F., Fleisher, M.Q., Huang, K.F., Robinson, L.F., Lu, Y., Cheng, H., Edwards, R.L., Moran, S.B., 2015a. Th-230 and Pa-231 on GEOTRACES GA03, the US GEOTRACES North Atlantic transect, and implications for modern and paleoceanographic chemical fluxes. Deep-Sea Res. Part II-Top. Stud. Oceanogr. 116, 29–41. http://dx.doi.org/10.1016/j.dsr2.2014.07.007.

Hayes, C.T., Anderson, R.F., Fleisher, M.Q., Vivancos, S.M., Lam, P.J., Ohnemus, D.C., Huang, K.F., Robinson, L.F., Lu, Y., Cheng, H., Edwards, R.L., Moran, S.B., 2015b. Intensity of Th and Pa scavenging partitioned by particle chemistry in the North Atlantic Ocean. Mar. Chem. 170, 49–60. http://dx.doi.org/10.1016/j.marchem.2015.01.006.

Henderson, G.M., 2002. Seawater (U-234/U-238) during the last 800 thousand years. Earth Planet. Sci. Lett. 199, 97–110. http://dx.doi.org/10.1016/s0012-821x(02)00556-3.

Henderson, G.M., Cohen, A.S., Onions, R.K., 1993. U-234/U-238 ratios and Th-230 ages for Hateruma Atoll corals — implications for coral diagenesis and seawater U-234/U-238 ratios. Earth Planet. Sci. Lett. 115, 65–73. http://dx.doi.org/10.1016/0012-821x(93)90213-s.

Hoffmann, D.L., Spoetl, C., Mangini, A., 2009. Micromill and in-situ laser ablation sampling techniques for high spatial resolution MC-ICPMS U-Th dating of carbonates. Chem. Geol. 259, 253–261. http://dx.doi.org/10.1016/j.chemgeo.2008.11.015.

Ivanovich, M., 1994. Uranium series disequilibrium — concepts and applications. Radiochim. Acta 64, 81–94.

Kampman, N., Bickle, M., Becker, J., Assayag, N., Chapman, H., 2009. Feldspar dissolution kinetics and Gibbs free energy dependence in a CO2-enriched groundwater system, Green River, Utah. Earth Planet. Sci. Lett. 284, 473–488. http://dx.doi.org/10.1016/j.epsl.2009.05.013.

Kampman, N., Burnside, N.M., Shipton, Z.K., Chapman, H.J., Nicholl, J.A., Ellam, R.M., Bickle, M.J., 2012. Pulses of carbon dioxide emissions from intracrustal faults following climatic warming. Nat. Geosci. 5, 352–358. http://dx.doi.org/10.1038/ngeo1451.

Kaufman, A., Broecker, W., 1965. Comparison of 230Th and 14C ages for carbonate materials from lakes Lahontan and Bonneville. J. Geophys. Res. 70, 4039–4054. http://dx.doi.org/10.1029/JZ070i016p04039 times Cited: 199 200.

Mangini, A., Lomitschka, M., Eichstadter, R., Frank, N., Vogler, S., Bonani, G., Hajdas, I., Patzold, J., 1998. Coral provides way to age deep water. Nature 392, 347–348. http://dx.doi.org/10.1038/32804.

Margolin, A., Robinson, L.F., Burke, A., Waller, R.G., Scanlon, K.M., Roberts, M.L., Auro, M.E., van de Flierdt, T., 2014. Temporal and spatial distributions of cold-water corals in the Drake passage: insights from the last 35,000 years. Deep Sea Res. Part II Top. Stud. Oceanogr. 99, 237–248.

McGregor, H.V., Hellstrom, J., Fink, D., Hua, Q., Woodroffe, C.D., 2011. Rapid U-series dating of young fossil corals by laser ablation MC-ICPMS. Quat. Geochronol. 6, 195–206. http://dx.doi.org/10.1016/j.quageo.2010.10.002.

McIntyre, C.P., Roberts, M.L., Burton, J.R., McNichol, A.P., Burke, A., Robinson, L.F., von Reden, K.F., Jenkins, W.J., 2011. Rapid radiocarbon (C-14) analysis of coral and carbonate samples using a continuous-flow accelerator mass spectrometry (CFAMS) system. Paleoceanography 26, PA4212. http://dx.doi.org/10.1029/2011pa002174.

Moore, W.S., 1981. The thorium isotope content of ocean water. Earth Planet. Sci. Lett. 53, 419–426. http://dx.doi.org/10.1016/0012-821x(81)90046-7.

Moran, S.B., Hoff, J.A., Buesseler, K.O., Edwards, R.L., 1995. High-precision Th-230 and Th-232 in the Norwegian Sea and Denmark by thermal ionization mass-spectrometry. Geophys. Res. Lett. 22, 2589–2592. http://dx.doi.org/10.1029/95gl02652.

Nakajima, R., Yoshida, T., Fuchinoue, Y., Okashita, T., Maekawa, T., Kushairi, M.R.M., Othman, B.H.R., Toda, T., 2013. Sedimentation impacts on the growth rates of the scleractinian coral Acropora formosa from fringing reefs of Tioman Island, Malaysia. Sains Malays. 42, 1201–1205.

Potter, E.K., Esat, T.A., Schellmann, G., Radtke, U., Lambeck, K., McCulloch, M.T., 2004. Suborbital-period sea-level oscillations during marine isotope substages 5a and 5c. Earth Planet. Sci. Lett. 225, 191–204. http://dx.doi.org/10.1016/j.espl.2004.05.034.

Potter, E.K., Stirling, C.H., Wiechert, U.H., Halliday, A.N., Spotl, C., 2005. Uranium-series dating of corals in situ using laser-ablation MC-ICPMS. Int. J. Mass Spectrom. 240, 27–35. http://dx.doi.org/10.1016/j.ijms.2004.10.007.

Reeder, R.J., Nugent, M., Lamble, G.M., Tait, C.D., Morris, D.E., 2000. Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. Environ. Sci. Technol. 34, 638–644. http://dx.doi.org/10.1021/es990981j.

Richards, D.A., Smart, P.L., Edwards, R.L., 1994. Maximum sea levels for the last glacial period from U-series ages of submerged speleothems. Nature 367, 357–360. http://dx.doi.org/10.1038/367357a0.

Risk, M.J., Heikoop, J.M., Snow, M.G., Beukens, R., 2002. Lifespans and growth patterns of two deep-sea corals: Primnoa resedaeformis and Desmophyllum cristagalli. Hydrobiologia 471, 125–131. http://dx.doi.org/10.1023/a:1016557405185.

Robinson, L.F., Adkins, J.F., Fernandez, D.P., Burnett, D.S., Wang, S.L., Gagnon, A.C., Krakauer, N., 2006. Primary U distribution in scleractinian corals and its implications for U series dating. Geochem. Geophys. Geosyst. 7, Q05022. http://dx.doi.org/10.1029/2005gc001138.

Robinson, L.F., Adkins, J.F., Frank, N., Gagnon, A.C., Prouty, N.G., Roark, E.B., van de Flierdt, T., 2014. The geochemistry of deep-sea coral skeletons: a review of vital effects and applications for palaeoceanography. Deep-Sea Res. Part II-Top. Stud. Oceanogr. 99, 184–198. http://dx.doi.org/10.1016/j.dsr2.2013.06.005.

Robinson, L.F., Adkins, J.F., Keigwin, L.D., Southon, J., Fernandez, D.P., Wang, S.L., Scheirer, D.S., 2005. Radiocarbon variability in the western north Atlantic during the last deglaciation. Science 310, 1469–1473. http://dx.doi.org/10.1126/science.1114832.

Robinson, L.F., Belshaw, N.S., Henderson, G.M., 2004a. U and Th concentrations and isotope ratios in modern carbonates and waters from the Bahamas. Geochim. Cosmochim. Acta 68, 1777–1789. http://dx.doi.org/10.1016/j.gca.2003.10.005.

Robinson, L.F., Henderson, G.M., Hall, L., Matthews, I., 2004b. Climatic control of riverine and seawater uranium-isotope ratios. Science 305, 851–854. http://dx.doi.org/10.1126/science.1099670.

Sinclair, D.J., Williams, B., Risk, M., 2006. A biological origin for climate signals in corals — Trace element "vital effects" are ubiquitous in Scleractinian coral skeletons. Geophys. Res. Lett. 33, L17707. http://dx.doi.org/10.1029/2006gl027183.

Smith, C.J., 2014. Laser ablation: A new approach to U-Pb speleothem dating. In: Conference Paper: British Cave Research Association (BCRA): Cave Science Symposium, University of Birmingham. URL: https://www.researchgate.net/publication/270580199_Laser_ablation_A_new_approach_to_UPb_speleothem_dating.

Stirling, C.H., Esat, T.M., McCulloch, M.T., Lambeck, K., 1995. High-precision U-series dating of corals from western-Australia and implications for the timing and duration of the last interglacial. Earth Planet. Sci. Lett. 135, 115–130. http://dx.doi.org/10.1016/0012-821x(95)00152-3.

Thiagarajan, N., Gerlach, D., Roberts, M.L., Burke, A., McNichol, A., Jenkins, W.J., Subhas, A.V., Thresher, R.E., Adkins, J.F., 2013. Movement of deep-sea coral populations on climatic timescales. Paleoceanography 28, 227–236. http://dx.doi.org/10.1002/palo.20023.

Thompson, W.G., Curran, H.A., Wilson, M.A., White, B., 2011. Sea-level oscillations during the last interglacial highstand recorded by Bahamas corals. Nat. Geosci. 4, 684–687. http://dx.doi.org/10.1038/ngeo1253.

Wang, Y.J., Cheng, H., Edwards, R.L., An, Z.S., Wu, J.Y., Shen, C.C., Dorale, J.A., 2001. A high-resolution absolute-dated late Pleistocene monsoon record from Hulu cave, China. Science 294, 2345–2348. http://dx.doi.org/10.1126/science.1064618.