Research Paper

U-series dating of carbonates using inductively coupled plasma-quadrupole mass spectrometry

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ABSTRACT

We describe an analytical methodology to quantify ^{238}U – ^{234}U and ^{230}Th using isotope-dilution systematics and inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS) for geochronological purposes. This required characterization of the mass spectrometer detector performance over a large dynamic range, including a careful calibration between pulse and analogue ion-counting modes. Our methodology gives an analytical precision for $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ of 4‰ and 7‰ ($2 \times$ standard error), respectively, and yields ^{230}Th -ages with 4–5% uncertainty from 500 ng of ^{238}U . We tested our methodology by analyzing carbonate samples (corals and speleothems) which were previously dated using MC-ICPMS; excellent agreement between both techniques was obtained. Our results indicate that ICP-QMS is suitable to obtain valuable meaningful geochronological data, but it is limited to dating samples older than 1 ka, and younger than 400 ka. Our methodology thus represents an attractive alternative to obtain geochronological data to select the most interesting samples prior to high-precision analysis. Moreover, such data would also be valuable to build preliminary age-models, which can be further complemented with high-precision analyses.

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1. Introduction

U–Th geochronology is one of the most powerful tools for unraveling the complex geological and climatic history of the Earth during the late Quaternary; the use of U and Th-isotope composition as proxies for a wide range of geological and environmental processes also makes them an essential tool for modern geochemical studies (Bourdon et al., 2003). Despite this, only a few laboratories worldwide have this capability, primarily because of the extremely low $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios, the inherent difficulty of detecting the low-abundance isotopes ^{234}U and ^{230}Th in the presence of high-abundance ^{238}U , and the scarcity of high-purity spikes, particularly ^{229}Th , required for the precise and accurate determination of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ by isotope-dilution.

Because of the low activity of ^{234}U and ^{230}Th , uncertainties of several % are typically obtained during the U–Th dating of carbonates by α -spectrometry (Goldstein and Stirling, 2003). Such uncertainties, along with the large amount of sample required, were significantly diminished after the introduction of magnetic-sector mass-spectrometric methods in the 1980's (Chen et al., 1986; Edwards et al., 1987); since then, further advances in mass-spectrometry technology have improved detection limits and precision by enhancing ion-production (Houk et al., 1980), increasing detector sensitivity, reducing or controlling the sources of background (Hunter, 1994), and increasing signal stability (Bradshaw, 1989). These, along with improvements in U and Th purification methods, make possible sub-permil precision and fg/g or pg/g detection limits (Andersen et al., 2004; Potter et al., 2005a), allowing the detection of small deviations from secular equilibrium in very old samples (Andersen et al., 2008), or quantification of extremely small amounts of ^{230}Th in very young samples (McCulloch and Mortimer, 2008; Shen et al., 2008; Zhao et al., 2009). Moreover, the ability to measure instrumental mass bias for Th isotopes has also enhanced the accuracy of U-series dating (Hoffmann et al., 2007; Hoffmann, 2008). Unfortunately, the high-

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precision instrumentation required for such measurements is not always available. Here we explore the feasibility of using the widely available inductively coupled plasma-quadrupole mass spectrometry (ICPM-QMS) coupled with a high-efficiency sample introduction system (APEX-Q). We show that this provides an alternative to high-precision instrumentation to quantify ^{234}U and ^{230}Th in carbonates by isotope-dilution for ^{234}U – ^{230}Th geochronological purposes.

Modern ICP-QMS is an attractive, low-cost, and widely available alternative to high-precision instrumentation. It is characterized by detection limits of only few pg/g, which can be improved $\sim 10\times$ by using an efficient sample introduction system, such as a desolvators. Moreover, isotope-ratio measurements with sub-permil precision can be achieved in the most ideal cases (Bandura et al., 2000; De Muynck et al., 2008). In conjunction with laser ablation, ICP-QMS is commonly used for U–Pb dating of zircons and other accessory igneous mineral phases, with age uncertainties of only 2–4% (Horn et al., 2000; Kosler et al., 2002; Black et al., 2004; Solari et al., 2010). ICP-QMS has also been demonstrated to be useful for Rb–Sr geochronology (Vanhaecke et al., 2003), although few applications have followed suit. Moreover, most ICP-QMS are equipped with long-dynamic range electron multipliers suitable for measuring very low isotope ratios ($<10^{-4}$), such as $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$.

The feasibility of measuring U-isotopic compositions using ICP-QMS, including $^{234}\text{U}/^{238}\text{U}$, has been previously demonstrated (Shaw and Francois, 1991; Mas et al., 2006) and per-mil precision can be achieved (Shen et al., 2006). Recently, deviations from secular equilibrium have been successfully measured in ancient carbonates with the aim of age-scan samples prior to high-precision U-series dating (Douville et al., 2010). Alternative methodologies for age-scanning have been proposed earlier (Potter et al., 2005b; McGregor et al., 2011). These are based on laser-ablation micro-sampling and, in addition to the requirement of very specialized instrumentation, significant method optimization prior to sample analysis is required. Moreover, the lack of a geological certified standards for microanalysis with known $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ is a significant conundrum that needs to be solved, usually via extensive spatial and isotopic characterization (e.g. Bernal et al., 2005), prior to routine age-scan analysis, otherwise, complex and uncharacterized matrix effects can potentially lead to incorrect geochronological conclusions. The methodology presented here is based on the same principles as the most precise methods (Luo et al., 1997; Hellstrom, 2003; Fietzke et al., 2005; McCulloch and Mortimer, 2008; Shen et al., 2008), and full implementation is possible after some instrumental characterization.

The methodology presented here required us to carefully characterize the response of the detector over its dynamic range, and developed a methodology to fully correct for the small differences in detector efficiencies between the different sections (pulse-counting and analogue). This has allowed us to determine $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ with uncertainties of 4‰ and 7‰ ($2 \times$ standard error, 2E), respectively, from ~ 500 ng U aliquots, which translates into 3–5% age uncertainties for samples older than 1 ka. We assess the accuracy of our methodology by analyzing secular equilibrium standards, as well as coral and speleothem samples previously dated by MC-ICPMS.

2. Experimental

2.1. Standards, reagents and ^{229}Th and ^{233}U tracers

All samples and solutions were prepared and stored in PTFE vessels in a Class 100 laboratory under laminar-flow hoods, using triple-distilled acids diluted in Milli-Q water (18.2 M Ω). Procedural

blanks were always ≤ 12 pg/g of ^{238}U and <1 pg/g for ^{232}Th and ^{230}Th , thus corrections by blank contributions were not necessary. A solution of the U isotopic standard NIST SRM 960 was prepared from U metal. This was previously cleaned in Milli-Q water, 1:1 HNO₃, 1:3 HCl, thoroughly rinsed in Milli-Q water, and vacuum dried in a desiccator at room temperature (Cali, 1972). Once cleaned and dried, the material was dissolved in 1:1 HNO₃ and gravimetrically diluted to obtain a 10 mg/g U stock solution, from which further dilutions were prepared as required. This standard is certified for a $^{238}\text{U}/^{235}\text{U}$ composition of 137.88 (Cali, 1972), but recent and more precise measurements have concluded that such value is between 0.03% (Richter et al., 2010) and 0.08% (Condon et al., 2010) lower than the certified composition. Although this material is not certified for its $^{234}\text{U}/^{238}\text{U}$ composition, analysis by several laboratories using MC-ICPMS and TIMS yield a $^{234}\text{U}/^{238}\text{U} = (52.86 \pm 0.021) \times 10^{-6}$ (robust mean from Andersen et al., 2004), equivalent to $\delta^{234}\text{U} = -36.87 \pm 0.40\text{‰}$ ($n = 17$, MSWD 0.54, probability 0.93), which is in agreement with the recently published value by Richter et al. (2010).

The U and Th isotopes were quantified using normal isotope-dilution systematics. Samples were spiked with known amounts of ^{233}U and ^{229}Th acquired from Isotrak (AEA Technology QSA Inc, UK). The spikes were calibrated for their isotopic composition by measuring three different aliquots bracketed by SRM 960 to correct for mass bias using $^{238}\text{U}/^{235}\text{U} = 137.88$. The resulting isotopic composition for each spike is summarized in Table 2, and shows good agreement with the available data from the certificate provided by AEA Technology. We note that use of the recently published improved values of $^{238}\text{U}/^{235}\text{U}$ for SRM 960 (Condon et al., 2010; Richter et al., 2010) represent only a small change ($<0.1\text{‰}$) in the calculated isotopic compositions and ages presented here, and well within the uncertainty of our measurements. Because of the relatively low-purity of our ^{229}Th tracer ($^{229}\text{Th}/^{230}\text{Th} = 650 \pm 21$, see below), its concentration in the spiked sample was kept as low as possible to minimize its contribution upon the total ^{230}Th ; resulting in $^{239}\text{Th}_{\text{spike}}/^{230}\text{Th}_{\text{sample}}$ lower than 250.

To assess the precision and accuracy of our measurements, we prepared solutions from Harwell uraninite (HU-1), which is known to be in secular equilibrium with respect to $^{234}\text{U}/^{238}\text{U} = (54.875 \pm 0.003) \times 10^{-6}$ (robust mean from data summarized in Andersen

Table 1
Summary of relevant instrumental parameters used in this work.

Forward power	1450 W
Carrier gas	0.7 l min ⁻¹
Make-up gas	0.3 l min ⁻¹
Sample uptake	400 $\mu\text{l min}^{-1}$
Extraction voltage 1	2.1 V
Extraction voltage 2	143 V
Omega-bias	-18 V
Omega lens	2.4 V
Detector voltages	
Pulse counting	1660 V
Analogue	1300 V
Discriminator (factory setting)	4 mV
Dwell time (s):	
^{238}U	0.7
^{235}U	0.85
^{234}U	1.1
^{233}U	0.3
^{232}Th	0.2
^{230}Th	1.0
^{229}Th	0.85
Settling time	0.001
APEX	
Heating	120 °C
Cooling	2 °C
No N ₂ added.	

Table 2

Isotopic compositions of the U-3 and T-9 spikes used in this work. For all cases the error weighted mean is the result from 3 independent analyses of U-3 and 4 independent analysis of T-9. Uncertainties correspond to ± 1 SE. Expected values correspond to specifications from Isotrak product UBP 10010 certificate obtained by alpha spectrometry.

	^{233}U	^{234}U	^{235}U	^{238}U
% w/w	99.658 ± 0.008	0.240 ± 0.005	$0.020 \pm 0.001\%$	$0.090 \pm 0.004\%$
Expected	99.7	0.24	0.02	0.07
$^{233}\text{U}/^{238}\text{U}$	—	418 ± 6	6038 ± 46	1092 ± 43
	^{229}Th	^{230}Th	^{232}Th	
% w/w	99.01 ± 0.02	0.150 ± 0.005	0.84 ± 0.02	
$^{229}\text{Th}/^{232}\text{Th}$	—	650 ± 21	117 ± 2	

et al., 2004) and very close to secular equilibrium with respect to $^{230}\text{Th}/^{238}\text{U} = (16.995 \pm 0.0028) \times 10^{-6}$ (Cheng et al., 2000). These solutions allowed us to verify the concentration of our ^{229}Th spike.

2.2. Samples and sample preparation

Six coral samples were analyzed with our methodology; these correspond to exposed fossil coral reef specimens of *Acropora palmata* from the Yucatán Peninsula, which have been interpreted to reflect a marine high-stand during the last interglacial (Blanchon et al., 2009). Their U-concentration ranges between 2.5 and 3.5 $\mu\text{g/g}$, with measured $\delta^{234}\text{U}$ ranging between 144 and 172‰; ^{232}Th is below 0.5 ng/g, thus corrections for the detrital contributions are negligible. The samples were previously dated by MC-ICPMS at the Leibniz Institute of Marine Sciences (GEOMAR), using multi-static, multi-ion counting methodologies detailed in Fietzke et al. (2005).

The samples were dissolved with concentrated HNO_3 in PTFE vessels and spiked with ^{233}U and ^{229}Th . The dissolved coral samples were treated with H_2O_2 to decompose organic matter. U and Th were separated by extraction chromatography using the TRU resin (Eichrom Technologies, Inc) following the procedures by Luo et al. (1997); however, Th was eluted using HCl 0.5 M in order to attain a better separation between U and Th (Howritz et al., 1993). Under this conditions, >97% of total Th is consistently leached from the resin, whilst >99% U remains in the column, which is then eluted with a 0.1 M HCl/HF mixture; U and Th recoveries were always >95%. In order to reduce any potential spectral interference by non-digested organic material eluted from the resin (Pietruszka et al., 2002; McCulloch and Mortimer, 2008), a pre-filter material consisting on non-functionalized resin support (also supplied by Eichrom) was introduced to the column underneath the resin, to adsorb such organic material.

In addition to the coral samples, two stalagmites previously dated by MC-ICPMS at the Australian National University (ANU) were analyzed to compare the performance of our methodology. A detailed description of the methodology used at the ANU is described in McCulloch and Mortimer (2008). The stalagmites, COYO-01 and COYO-04 were collected from Coyozochico Cave in Cuetzalan, México, and are characterized for their relatively high U-content ($\sim 8 \mu\text{g/g}$), and very low detrital contamination, with $[^{230}\text{Th}/^{232}\text{Th}] > 1000$, hence corrections for the presence of $^{230}\text{Th}_{\text{detrital}}$ are negligible (Hernández-Mendiola et al., 2007). For each stalagmite, a basic age-model was constructed based upon the MC-ICPMS ages by linearly interpolating between each dated site.

Sub-samples collected in the vicinity of the dated sites were extracted and dated by ICP-QMS; the resulting ages are compared with that expected from the MC-ICPMS age-model.

2.3. Instrumental

All measurements were done with an Agilent 7500ce ICP-QMS coupled with an Elemental Scientific APEX-Q high-efficiency sample introduction system, using a PFA microflow nebulizer with a sample uptake of 400 $\mu\text{l/min}$ force-feed by a peristaltic pump. This configuration yields $\sim 10^6$ cps per ppb (ng/g) for ^{238}U . Most instrumental variables are summarized in Table 1. In our system the formation of oxide (UO^+/U^+) and hydride (UH^+/U^+) were always below 0.1% and 0.01%, respectively. Contributions from high intensity peaks onto lower masses were not significant, and always lower than 10 ppm at m/z 237, and less than 1 ppm at m/z 236, thus corrections for these potential contributions are negligible. No attempts to measure isotope compositions with the collision cell pressurized were made.

The ICP-QMS is equipped with an ETP electron multiplier which can measure ion beams in pulse-counting (PC), and analogue (A) modes for count-rates lower and higher than 5×10^6 cps, respectively. Because of the differences in the efficiencies between both amplifying sections (Hunter and Stresau, 2005), a detailed cross-calibration procedure between both was developed and is presented below.

Detector dead-time (τ) was calibrated at 40 ns following the methods recommended by Agilent (2004); an alternative method to calculate τ (Held and Taylor, 1999) resulted in $\tau = 39.7 \pm 1.2$ ns. Moreover, $^{234}\text{U}/^{238}\text{U}$ measured at ^{238}U countrates between 2×10^5 and 6×10^8 are essentially identical and do not show any systematic bias, even after correction for efficiencies differences between different amplifying sections of the detector (see below), indicating that τ is accurate within the attained precision of our measurements.

Because very low-intensity ion-beams (< 3000 cps) are expected for the measurement of ^{230}Th , it is essential to reduce detector background as much as possible. We achieved this by adjusting the detector discriminator voltage in order to obtain the best signal-to-noise ratio. The voltage is factory-set at 4 mV to produce the highest possible count-rates for routine quantitative analysis; however, a 20–40 (± 15) cps background was observed under these conditions (Fig. 1). By increasing the discriminator voltage, the U count-rate decreases linearly, but the background in the m/z^+ region 228–233 decreases exponentially (Fig. 1), thus the signal-to-noise ratio increases accordingly until it reaches a maximum at 16 mV.

Fig. 1. Effect of the detector discriminator voltage on the ^{234}U signal and background measured as the average signal in the m/z^+ range 228–233 (left axes) and signal-to-noise ratio (right) from a 5 ng/g U solution.

² Where $\delta^{234}\text{U} = ((^{234}\text{U}/^{238}\text{U})_{\text{sample}}/(^{234}\text{U}/^{238}\text{U})_{\text{SE}} - 1) \times 1000$ and $^{234}\text{U}/^{238}\text{U}_{\text{SE}} = (54.891 \pm 0.094) \times 10^{-6}$ (Cheng et al., 2000).

Under such conditions, a background of 8 ± 4 cps was usually obtained, which typically corresponds to a signal-to-noise ratio >200 and >30 for ^{234}U and ^{230}Th , respectively, for a ~ 20 ka sample. Further reductions in background were not possible since the detector was reaching the end of its lifetime, and high acceleration voltages applied to the dynodes are required, resulting in such background values.

An additional source of high-background during Th and U analysis is the inefficient removal of residual Th and/or U from the sample introduction system once the sample has been analyzed, leading to potential cross-contamination between samples (Shen et al., 2002; McCulloch and Mortimer, 2008). This is particularly delicate during the analysis of low-intensity ion-beams, such as those from Th, because even a small contamination might increase the ^{230}Th , ^{232}Th and ^{229}Th signals leading to incorrect Th-isotope compositions. Consequently the sample introduction system must be thoroughly cleaned after each sample or standard is analyzed until the normal background of 8 ± 4 cps is reached for all U and Th isotopes. A cleaning routine consisting in four different rinse steps was implemented (McCulloch and Mortimer, 2008), and its effects on the Th and U signals are shown in Fig. 2. The first step consists on rinsing the sample probe tip with de-ionized water; removing any remaining droplet from the previously analyzed sample, and helping to maintain the cleanliness of the forthcoming solutions. Then, a 10% HNO_3 solution, followed by 10% $\text{HNO}_3 + 1\%$ Triton (a surfactant) $+ 0.05\%$ HF are aspirated; this mixture removes most of the residual Th and U. Finally, the last traces of U and Th are removed from the system by aspirating a 2% HNO_3 for few minutes, until normal background levels are reached. Total cleaning time between samples is ~ 15 min for U, and ~ 10 min for Th.

2.4. Cross calibration between pulse-counting and analogue detection modes

As mentioned above, the instrument is equipped with an electron multiplier which is divided in two amplifying sections, providing the capability to measure ion-beams up to 10^9 cps. This detection technology is specially attractive for the measurements of very low isotope ratios such as $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. However,

in order to achieve the large dynamic range, it is necessary to correct for the difference in electronic yield between the pulse-count (PC) and analogue (A) modes. This is done in the Agilent 7500ce by calculating a “P/A factor” for each isotope to be analyzed, which cross calibrates the analogue signal to its equivalent in PC-mode (Agilent, 2004). P/A factors are calculated by comparing simultaneously the electric response of both amplifying sections to an incident ion beam within a 4×10^5 cps to 4×10^6 cps count-rate. In principle, this measurement provides an instrumentally correct figure for the actual difference on the electrical response between both sections of the detector and, thus, provides the spectrometer software with the information required to cross calibrate the signal and extend the linear range. However, initial appraisal on the performance of such correction revealed significant deviations from the expected isotope ratio when the two isotopes are measured in different amplifying sections of the detector (Fig. 3A and C). Note, however, that even in those cases when ^{238}U is measured in A-mode, $^{234}\text{U}/^{235}\text{U}$ does not show any bias (Fig. 3B), since both isotopes are always measured in PC-mode.

The differences in detector efficiencies represent a significant source of inaccuracy if uncorrected because, in the absence of a ^{233}U – ^{236}U double spike, we are limited to monitor instrumental mass bias with $^{238}\text{U}/^{235}\text{U}$, and correct assuming a constant composition (137.88) for natural U.

To overcome the bias introduced by the differences in detector efficiencies, two options were considered: a) measure ^{229}Th – ^{230}Th – ^{232}Th and ^{233}U – ^{234}U – ^{235}U – ^{238}U in PC-mode, or b) independently measure the detector efficiencies and correct off-line. Option A implies that all count-rates should remain below 10^6 cps during the course of the analysis; which can be achieved by analyzing solutions with <1 ng/g of ^{238}U , with the subsequent loss of precision for the low-abundance isotopes. Alternatively, one could increase the countrate for the low-abundance isotopes by increasing the amount of U introduced, and reference their abundances to ^{235}U instead of ^{238}U . This would imply that mass-bias cannot be internally measured and corrected for each sample (since we do not have access to a ^{233}U – ^{236}U double-spike), thus external standardization would be required with a low-concentration U standard, so as to be able to measure $^{238}\text{U}/^{235}\text{U}$

Fig. 2. U and Th washout routine after each sample. The washout profile time are not comparable, but in both cases correspond to actual samples.

Fig. 3. $^{238}\text{U}/^{235}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{234}\text{U}/^{235}\text{U}$ from SRM 960 at different ^{238}U count rates. (A) $^{238}\text{U}/^{235}\text{U}$, and (C) $^{234}\text{U}/^{238}\text{U}$ shift when ^{238}U signal reaches analogue mode ($>5 \times 10^6$ cps); the same sample does not show any shift in $^{234}\text{U}/^{235}\text{U}$ (B) since both isotopes are measured in PC mode. (C) Also shows that $^{234}\text{U}/^{238}\text{U}_A$, after correction by “F” (open symbols), are identical to those measured in PC mode, but the precision is slightly lower due to the quadratic expansion of uncertainties. Shaded squares highlight datapoints used to calculate corresponding average. For some points, uncertainties are smaller than symbol size.

in PC-mode. The latter approach, however, is prone to introduce significant uncertainties as mass-bias might be influenced by the matrix, concentration of the isotopes, and instrumental drift over the course of the analytical session.

In contrast, method B (calibration for differences in detector efficiencies followed by off-line correction), is less prone to uncontrolled bias, and offers the most precise measurement of ^{234}U and ^{230}Th due to their higher count rate. Moreover, whilst the assumption of constant $^{238}\text{U}/^{235}\text{U}$ in nature has been shown to be incorrect (Stirling et al., 2007), the bias introduced by the small deviations in $^{238}\text{U}/^{235}\text{U}$ from the nominal 137.88 are expected to be small ($<0.1\%$).

In order to cross calibrate between the two amplifying sections, we analyzed a series of solutions of NIST SRM 960 in a range of concentrations between 0.1 and 100 ng/g; this allowed us to measure ^{238}U in both sections of the detector (low-U concentration in PC-mode, and high-U concentration in A-mode), whilst ^{235}U was always measured in PC-mode. We then averaged the $^{238}\text{U}/^{235}\text{U}$ obtained when both isotopes were measured in PC-mode ($^{238}\text{U}/^{235}\text{U}_{\text{PC/PC}}$), and compared it to the average $^{238}\text{U}/^{235}\text{U}$ when ^{238}U was measured in A-mode, ($^{238}\text{U}/^{235}\text{U}_{\text{A/PC}}$). The difference between both is a measure of the bias introduced by the differences in detector efficiency. A correction factor, F, was then calculated as:

$$F = \left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{A/PC}} / \left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{PC/PC}}, \quad (1)$$

which can then be used to correct all isotope ratios referenced to ^{238}U measured in A-mode. Fig. 3C shows that multiplying $^{234}\text{U}/^{238}\text{U}$ isotope ratios where ^{238}U was measured in A-mode by F, effectively

removes any bias introduced by the differences between PC and A modes, as the corrected isotope ratios are statistically identical to those obtained when both isotopes are measured in PC-mode.

In practical terms, the procedure described above for cross-calibration is equivalent to the cross-calibration between electron multipliers and Faraday cups routinely carried out with multi-collector spectrometers (TIMS and MC-ICPMS) equipped with one or more SEMs. However, in contrast to the latter, it was not possible for us to obtain the actual count-rates when an ion-beam was measured in both modes during the calculation of P/A factors. Moreover, while F could be measured by simply analyzing only two standards (one for each detection mode), our approach to use three or more solutions for each detection mode decreases significantly the uncertainty associated with F, which is expanded to the corrected $^{234}\text{U}/^{238}\text{U}$. This is particularly important for our methodology because it allows to maintain an acceptable level of precision for $^{234}\text{U}/^{238}\text{U}$ ($<5\%$) after the quadratic expansion of uncertainties. We note that F does not vary more than 1‰ within an analytical session, and less than 1% between different sessions, as long as the detector acceleration and discriminator voltages are kept constant.

2.5. Measurement protocol

When measuring ^{230}Th – ^{234}U – ^{238}U , it is important to achieve the highest possible precision, while keeping sample requirements as low as possible. Thus a compromise between sample consumption and precision must be made. Hence, U and Th were measured separately to maximize the counting efficiency and reduce the sample requirements. Counting times were selected giving preference to the low-abundance isotopes (^{234}U and ^{230}Th), then the tracers (^{233}U and ^{229}Th) and, finally ^{232}Th , ^{235}U and ^{238}U (Table 1). In the case of our ICP-QMS configuration, per-mil level uncertainties for $^{234}\text{U}/^{238}\text{U}$ can be attained from solutions producing an ion-beam of 10^7 cps for ^{238}U (Fig. 4), equivalent to ~ 10 ng/g of ^{238}U . However, in order to produce more precise geochronological data with this configuration (low per-mil), while maintaining reasonable sample requirements, we analyzed solutions of ~ 50 ng/g of ^{238}U , producing $\sim 5 \times 10^7$ cps, and resulting in uncertainties of 3–4‰ for $^{234}\text{U}/^{238}\text{U}$. This implies that ~ 500 ng of

Fig. 4. $^{234}\text{U}/^{238}\text{U}$ uncertainty for 47 analysis of un-spiked NIST SRM 960, showing that using our configuration, per-mil precision can only be attained from solutions producing a ^{238}U ion-beam $>10^7$ cps. Dashed line indicates the expected uncertainty from counting statistics (taken as $2 \times \sqrt{n}$). Highlighted square indicates the “working area”, where low-permil precision is typically obtained.

U are required for each analysis if precision in the low per-mil level is to be achieved. Such levels of uncertainty are approximately $2 \times$ higher than the theoretical precision expected from such countrates (taken as $2 \times \sqrt{n}$).

2.6. Data reduction

Isotope ratios were calculated from background-corrected intensities and, when applicable, corrected for differences in detector efficiencies using Equation (1). The correction factor F was measured at the beginning of each analytical session and remained essentially constant throughout it (see above). Mass fractionation corrections for $^{233}\text{U}/^{234}\text{U}$, $^{234}\text{U}/^{235}\text{U}$, $^{233}\text{U}/^{238}\text{U}$, $^{229}\text{Th}/^{230}\text{Th}$ and $^{229}\text{Th}/^{232}\text{Th}$ ratios were made following the exponential law (Russell et al., 1978), assuming a constant $^{238}\text{U}/^{235}\text{U}$ value for natural U of 137.88 ± 0.01 (Cowan and Adler, 1976) after subtraction of tracer contributions. As discussed above, variability in $^{238}\text{U}/^{235}\text{U}$ (Stirling et al., 2007; Richter et al., 2010) yield $^{234}\text{U}/^{238}\text{U}$ isotope ratios that are not significantly different, and well within the uncertainty of the measurement. Activity ratios were calculated using the generally accepted half-lives for ^{238}U (Jaffey et al., 1971), ^{234}U and ^{230}Th (Cheng et al., 2000) and are denoted by square brackets. All uncertainties reported here correspond to $2 \times$ standard error ($2 \times \text{SE}$) and were expanded quadratically, with the exception of the ^{230}Th -age calculation, since Isoplot 2.49 t (Ludwig, 2001) was used for this purpose.

3. Results and discussion

3.1. Analysis of standards

The accuracy, precision and reproducibility of our methodology was first assessed by analyzing a series of non-spiked

aliquots of SRM 960 and HU-1 for $^{234}\text{U}/^{238}\text{U}$, followed by analysis of spiked aliquots for $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. The results from different analytical sessions are summarized in Fig. 5, where good agreement between measured and expected $^{234}\text{U}/^{238}\text{U}$ compositions is generally observed. The average for our $^{234}\text{U}/^{238}\text{U}$ measurements in NIST SRM 960, $(52.87 \pm 0.072) \times 10^{-6}$, equivalent to $\delta^{234}\text{U} = -36.0 \pm 1.3\text{‰}$ (2SE, $n = 18$) agrees well with the robust mean calculated from the compilation made by Andersen et al. (2004), $(52.86 \pm 0.021) \times 10^{-6}$, $\delta^{234}\text{U} = -36.87 \pm 0.40\text{‰}$, and also within error of the average of Cheng et al. (2000), $(52.860 \pm 0.025) \times 10^{-6}$, $\delta^{234}\text{U} = -36.94 \pm 0.45\text{‰}$. For Harwell Uraninite, an average for $^{234}\text{U}/^{238}\text{U} = (54.8 \pm 0.11) \times 10^{-6}$ (2SE, $n = 18$) is also in good agreement with the expected secular equilibrium value of $(54.891 \pm 0.094) \times 10^{-6}$ from Cheng et al. (2000), as well as the robust mean, $(54.875 \pm 0.003) \times 10^{-6}$, calculated from the compilation made by Andersen et al. (2004). In both cases, the average uncertainty of our $^{234}\text{U}/^{238}\text{U}$ measurements is 3–4‰, but uncertainties as low as 2‰ can be achieved.

Measurements of $^{230}\text{Th}/^{238}\text{U}$ in HU-1 by isotope-dilution are also in good agreement with accepted values. Replicate analysis by isotope-dilution resulted in an average $^{230}\text{Th}/^{238}\text{U} = (16.95 \pm 0.05) \times 10^{-6}$ (2SD, $n = 4$), within the uncertainty reported by Cheng et al. (2000). The average uncertainty observed is $\sim 6\text{‰}$, which is about twice the reproducibility of our HU-1 analyses. We note that, under the current analytical conditions, this level of precision is probably the best attainable for ^{230}Th measurements, considering that the precision is mostly limited by its low count-rate, and significantly larger ion beams for ^{230}Th are not expected, since datable samples have $^{230}\text{Th}/^{238}\text{U}$ values that are considerable lower than HU-1. This result implies that, in terms of age calculation, the upper-age limit of our method is ~ 400 ka (as discussed below).

Fig. 5. Repeat measurements of Harwell Uraninite (HU-1 –top) and NIST SRM 960 (middle) for $^{234}\text{U}/^{238}\text{U}$ of spiked and non-spiked samples, and $^{230}\text{Th}/^{238}\text{U}$ (spiked) for HU-1. Along with their external reproducibility. Error-bars and uncertainties correspond to $2 \times \text{SE}$. Dashed lines indicate expected value. Continuous line in $^{230}\text{Th}/^{238}\text{U}$ plot indicates secular equilibrium. The first set of four HU-1 analysis are slightly bias toward lower values because APEX rinse was not carefully monitored, and U from the previous analysis (SRM 960) was not properly removed from the system.

3.2. Analysis of coral fossils

U–Th isotopic data and dates for six coral samples previously dated by MC-ICPMS (Blanchon et al., 2009) are presented in Table 3 and Fig. 6. Good agreement between the MC-ICPMS and ICP-QMS ages is observed. In terms of accuracy, both methods yield undistinguishable data, however, the MC-ICPMS ages are, as expected, significantly more precise than ICP-QMS. The uncertainty of the measured activity ratios for these samples (Table 3) is $\sim 3\%$ and $\sim 15\%$ for $[^{234}\text{U}/^{238}\text{U}]$ and $[^{230}\text{Th}/^{238}\text{U}]$, respectively; which translates into $\sim 3\%$ uncertainties on a ~ 125 ka ^{230}Th -age.

The ability to measure accurately the initial $\delta^{234}\text{U}$, $\delta^{234}\text{U}_0$, is essential for the U-series dating of corals, as $\delta^{234}\text{U}_0$ is commonly used a tracer for diagenetic alteration (Edwards et al., 2003). Deviations larger than $\pm 15\%$ from the modern-day $\delta^{234}\text{U}$ in seawater ($146.8 \pm 0.1\%$, Andersen et al., 2010) in coral fossils as old as 370 ka, strongly suggest that the isotopic composition of the sample has been altered, thus the ^{230}Th -age is not reliable (Gallup et al., 1994; Stirling et al., 1995, 1998, 2001; Henderson, 2002). Due to the lack of geological reference materials certified for their $\delta^{234}\text{U}$ composition, these samples are particularly relevant to assess the accuracy of our $\delta^{234}\text{U}$ measurements in real samples, since our ^{233}U tracer contains traces of ^{234}U (Table 2), which has to be taken into account during data reduction.

Fig. 6 shows the $\delta^{234}\text{U}_0$ values for the six corals analyzed by isotope-dilution. Good agreement between the MC-ICPMS and ICP-QMS results is obtained; as expected, the latter yields lower precision (3% vs. 4.5%). The accuracy and precision of our method appears to be sufficient to correctly discriminate between those samples that have suffered diagenetic alteration from those that have pristine isotopic composition. Small differences between the $\delta^{234}\text{U}_0$ from MC-ICPMS and ICP-QMS are discernable for some aliquots of samples XA4-2 and XE2-2, ($\Delta\delta^{234}\text{U} \sim 5\%$), however, these do not lead to different conclusions regarding the reliability of the corresponding ^{230}Th -ages.

3.3. Analysis of stalagmites

Fig. 7 shows the age models for the two different stalagmites previously dated by MC-ICPMS at the ANU. Three MC-ICPMS ages constrain the growth of stalagmite COYO-04 between 72.30 ± 0.86 and 55.84 ± 1.24 ka at a rate of 5.3 ± 0.27 mm/ka (from a linear

Fig. 6. Comparison of $\delta^{234}\text{U}$ (top) and ^{230}Th -age (bottom) for six last-interglacial samples of *A. Palmata* previously dated by MC-ICPMS (Blanchon et al., 2009) with ICP-QMS data from. Open symbols correspond to ICP-QMS, filled symbols different replicates obtained by MC-ICPMS. In both cases error bars correspond to $2 \times \text{SE}$. Shaded area correspond to isotopic compositions indicating “strictly reliable” data ($\delta^{234}\text{U}_0 = 146.6\text{--}149.6\%$), while dashed lines limit the “reliable” isotope composition; both criteria established in Blanchon et al. (2009).

error-weighted regression, Fig. 7A). For this study, four samples from stalagmite COYO-04, including replicates, were analyzed. All the ICP-QMS dated samples from this stalagmite fall within the age model previously established, and allow to refine it. A slightly slower growth rate (5.2 ± 0.3 mm/ka) is obtained once the ICP-QMS dated samples are incorporated into the age-model. By linearly extrapolating the MC-ICPMS age-model, we estimate the age for the tip at 50.1 ka, which is slightly biased from the ^{230}Th -age of 51.1 ± 0.8 ka obtained by ICP-QMS. However, a refined age-model based upon the MC-ICPMS and ICP-QMS ages, produces a second-degree equation which estimates the age of the tip at 51.12 ka, in excellent agreement with the ^{230}Th -age obtained here.

The age-model for stalagmite COYO-01 is based on five MC-ICPMS samples. The stalagmite grew between ~ 25.5 and 22.5 ka; however, in contrast to COYO-04, the growth-history of COYO-01 is

Table 3
 $[^{230}\text{Th}/^{238}\text{U}]$, $[^{234}\text{U}/^{238}\text{U}]$, ^{230}Th -ages and $\delta^{234}\text{U}_0$ for six coral samples from Xcaret, Mexico, previously dated by MC-ICPMS. a,b,c correspond to replicate analysis reported in Blanchon et al. (2009). Square brackets indicate activity ratio. Uncertainties expressed are absolute and correspond to $2 \times \text{SE}$. Numbers in italics are uncertainties expressed in per-cent or per-mil as indicated. $\delta^{234}\text{U}$ calculated using the secular equilibrium $^{234}\text{U}/^{238}\text{U}$ from Cheng et al. (2000). Ratios between square brackets correspond to activity ratios.

Sample	[²³⁰ Th/ ²³⁸ U]	± (%)	[²³⁴ U/ ²³⁸ U]	± (‰)	²³⁰ Th-ages (ka)	± (%)	δ ²³⁴ U ₀ (‰)	±	²³⁰ Th-age (expected)	±	δ ²³⁴ U ₀ (expected)	±	
XA4-2	0.803	0.0118 (1.5)	1.1084 (3.1)	0.0034 (3.1)	135	4.3 (3.2)	155	3	a	138.1	1.8	154	3
				b		132.6			1.6	148	3		
				c		134.3			1.4	149	3		
XC7-5	0.726	0.0097 (1.33)	1.1318 (2.5)	0.0029 (2.5)	108	2.7 (2.5)	175	3	a	110.7	1	172	3
				b		107.7			1	172	3		
				c		110.2			1.2	169	3		
XD4-2	0.763	0.015 (1.9)	1.1046 (6.3)	0.0069 (6.3)	124	4.9 (3.9)	145	7	a	117	1	147	3
				b		122.8			1.1	144	3		
				c		137.7			1.1	146	3		
XD4-3	0.762	0.015 (1.9)	1.1056 (3.9)	0.0043 (3.9)	123	4.7 (3.8)	146	4	a	119.5	1.1	148	3
				b		126.2			1.1	145	3		
				c		123.5			1	145	3		
XE2-2	0.752	0.016 (2.1)	1.1151 (3.3)	0.0037 (3.3)	118	4.7 (4.0)	157	4	a	117.7	1.1	156	3
				b		121.9			1.2	162	3		
				c		118.4			1	172	3		
XE3-1	0.768	0.0086 (1.13)	1.1053 (5.1)	0.0056 (5.1)	128	3.3 (2.6)	146	5	a	123.8	1.4	148	3
				b		123.5			1	147	3		
				c		126.4			1.1	145	3

Fig. 7. ^{230}Th -ages for the stalagmite sub-samples and their correspondence with their respective age-model (continuous line) based only on the MC-ICPMS ages. Dashed lines indicate age model considering the ages obtained by ICP-QMS. A) data for stalagmite COYO-04, MC-ICPMS age model is $\text{Age} = 72.13 - 0.18699 \times D$, MC-ICPMS + ICP-QMS age model: $\text{Age} = 72.36 - 0.22012 \times D + 3.7913 \times 10^{-4} \times D^2$, where D is the distance from the base in mm and age in ka. B) data for stalagmite COYO-01, MC-ICPMS age model is: $\text{Age} = 25.04 - 0.0162 \times D$ (for $D < 114$) and $\text{Age} = 23.42 - 0.00261 \times D$ (for $D > 114$). MC-ICPMS + ICP-QMS age models are: $\text{Age} = 25.03 - 0.01628 \times D$ (for $D < 114$, and $\text{Age} = 23.53 - 0.0029 \times D$ (For $D > 114$), where D is the distance from the base in mm, and age in ka.

slightly more complex (Fig. 7B): a growth rate of ~ 60 mm/ka is estimated between 24.1 and 23.1 ka, and abruptly increases to 340 ± 37 mm/ka between 23.1 and 22.5 ka. Four samples dated by ICP-QMS agree well with this model and allow to refine it; two samples with expected ages of 24.5 and 24.7 ka, yield ^{230}Th -ages of 24.73 ± 0.64 and 25.08 ± 0.66 ka, respectively; an error-weighted age-model indicates that the growth rate for this stalagmite is 58 ± 12 mm/ka, in excellent agreement with the estimation made from the MC-ICPMS ages. Two additional samples ran as replicates produced identical ^{230}Th -ages (22.87 ± 0.33 and 22.86 ± 0.39 ka), which are also in perfect agreement with their stratigraphic position, and provide additional robustness to the corresponding section of the age-model (Fig. 7).

3.4. Analytical constraints and their geochronological implications

We have demonstrated that ICP-QMS coupled with a high-efficiency sample introduction system, provides the required sensitivity to accurately measure ^{234}U and ^{230}Th , resulting in $\delta^{234}\text{U}$ values and ^{230}Th -ages which are consistent with independent measurements from two different laboratories and methodologies. However, the sequential nature of the measurement, along with the inherent characteristics of quadrupoles producing Gaussian-peaks for each isotope result in ^{230}Th -ages with $\sim 5\%$ uncertainties. This, combined with the isotopic composition of our ^{229}Th tracer, represents a limitation for analyzing samples with ages near or at the upper and lower dating-limits by U-series geochronology.

A good analogue for the analysis of very old samples is HU-1 which, in practical terms, is in secular equilibrium with respect to $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. Our isotope-dilution results for HU-1 have average uncertainties of $\pm 4\%$ and $\pm 6\%$ for $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$, respectively. This implies that samples with U activity ratios $[^{234}\text{U}/^{238}\text{U}] < 1.004$ (assuming most specimens have $^{234}\text{U}/^{238}\text{U}$ higher than secular equilibrium) and $[^{230}\text{Th}/^{238}\text{U}] > 0.994$, cannot be dated with our methodology and instrumentation. Consequently, an

age upper-limit of 407 ± 36 ka can be assumed, which is also ultimately dependant on the $[^{234}\text{U}/^{238}\text{U}]_{\text{initial}}$ of the sample.

Dating of very young samples is limited not only by the precision of the measurement, but also by the composition of the ^{229}Th tracer, and the detector background. Considering the latter at 8 ± 4 cps, and $^{229}\text{Th}/^{230}\text{Th} = 650 \pm 21$ for our ^{229}Th tracer (Table 2), along with a ^{229}Th count-rate of ~ 5000 cps, we estimate that the lowest $[^{230}\text{Th}/^{238}\text{U}]$ activity ratio measurable with our methodology and instrumentation is $\sim 0.017 \pm 0.004$, which corresponds to a ^{230}Th -age of 0.83 ± 0.48 ka for a $[^{234}\text{U}/^{238}\text{U}] = 1.000 \pm 0.004$. This dating limit, and its absolute uncertainty, decreases exponentially for $[^{234}\text{U}/^{238}\text{U}] > 1.000$; however, in practical terms, samples younger than 1000 years cannot be dated reliably by our methodology and instrumentation.

The assumption that natural U has a constant $^{238}\text{U}/^{235}\text{U}$ has been recently demonstrated to be incorrect (Stirling et al., 2007; Weyer et al., 2008; Bopp et al., 2009; Brennecka et al., 2010). A shift as large as 1% in $^{238}\text{U}/^{235}\text{U}$ has been observed in stalagmite calcite (Stirling et al., 2007), which can result in 30–100-year shifts in the calculated ^{230}Th -age, for 30 ka and 100 ka old samples, respectively. Such age-displacements are well within the uncertainty of our measurements and calculated ages. However, larger $^{238}\text{U}/^{235}\text{U}$ fractionations cannot be ruled out in low-temperature environments where adsorption appears to be a significant fractionation factor, which would impinge a more noticeable bias in calculated ^{230}Th -ages, if un-accounted. The use of gravimetric ^{233}U – ^{236}U double spikes eliminates the potential of such bias.

4. Conclusions

We are able to accurately measure large isotope ratios, such as $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ with reasonable good precision and sample requirement using an ICP-QMS. This required a careful characterization of the detector performance for measuring low and high count-rates, and minimizing any bias introduced by the differences in detector efficiency between the different amplifying sections. This has allowed us to demonstrate the feasibility of using

ICP-QMS coupled with a high efficiency sample introduction system to produce accurate ^{230}Th -ages and $\delta^{234}\text{U}$ values, comparable to those obtained by MC-ICPMS over a wide range of ages, from secular equilibrium to ~ 20 ka, but with slightly lower precision than multicollector methodologies.

The precision attained is, however, sufficient to produce isotopic and geochronological meaningful data, and provides a low-cost option for laboratories lacking access to high-precision instrumentation. Moreover, our methodology can also be used to obtain reconnaissance geochronological information in order to build preliminary age-models and time-series, thus the user is able to select samples for detailed high-precision dating using multicollector ICPMS instrumentation as required.

Improvements in precision can be achieved by the use of a ^{233}U – ^{236}U double spike, to monitor and correct for instrumental mass-bias. Furthermore, the use of such a double spike will eliminate any potential bias introduced by the fractionation in $^{238}\text{U}/^{235}\text{U}$, and enhance even more the accuracy of the methodology. Additionally, the use of a ^{229}Th spike of higher purity than the one used in this paper, is essential to improve the dating of very young samples. Moreover, further improvements in detection technology, ion production, extraction and transmission in for ICP-QMS will also reflect in lower sample requirements and improved precision.

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