



^{230}Th isotope measurements of femtogram quantities for U-series dating using multi ion counting (MIC) MC-ICPMS

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ABSTRACT

Results of Th isotope measurements on Harwell Uraninite (HU) solution aliquots and carbonates such as corals and speleothems using multi ion counter (MIC) procedures are presented. A multi ion counter array available for the ThermoFinnigan Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) is used for simultaneous measurements of ^{230}Th and ^{229}Th ion beams. A static collection of low-level ion beams improves the efficiency of isotope measurements which in turn reduces the required sample size and measurement time. The static measurement also circumvents problems with ion beam intensity fluctuations often observed with a plasma source. Instrumental bias corrections are based on a sample bracketing in-house Th standard solution. The accuracy and precision of the MIC array procedures for $^{230}\text{Th}/^{229}\text{Th}$ measurements are investigated by comparison to a MC-ICPMS peak jump procedure using just a single ion counting channel. The results show that similar precisions for $^{230}\text{Th}/^{229}\text{Th}$ measurements can be achieved using the MIC procedure with less than half total ^{230}Th consumed compared to a peak jump routine. Thus, the MIC setup allows to use less than half the sample sizes for $^{230}\text{Th}/\text{U}$ dating of carbonates compared to peak jump methods enabling higher spatial resolution sampling.

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1. Introduction

Multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) has become an important technique for isotope geochemistry in general and in particular for U-series isotopes measurements [1]. Technical advances in the last decade led to increasingly high precisions for isotope measurements using MC-ICPMS which enables precise and accurate $^{230}\text{Th}/\text{U}$ dating, for example for palaeoclimate reconstruction using speleothems [2]. However, there is demand for even higher spatial resolution dating and therefore using very small sample sizes to investigate timing of climate events or rates of climate changes in more detail. There are two main limitations for the minimum sample size needed for $^{230}\text{Th}/\text{U}$ dating of carbonates. Firstly, the U concentration and secondly, the ^{230}Th concentration in a given sample which in turn depends on the U concentration and the age of the sample. Of the two, ^{230}Th is usually the ultimate limiting factor and defines the sample size required for $^{230}\text{Th}/\text{U}$ dating. It is therefore desirable to further optimise Th isotope measurements, e.g., by using one static ^{229}Th – ^{230}Th isotope measurement instead of a peak jump procedure.

In this study the application of a multi ion counter (MIC) array available for the Neptune MC-ICPMS [3] for static Th isotope measurements is investigated. The potential use of multiple ion counting techniques for U-series measurements has been proposed by Goldstein and Stirling [1] as future development. Fietzke et al. [4] apply a set of three ion counters for U-series measurements, but they use a U double spike for multiplier yield and mass fractionation correction for both U and Th isotope measurements. This procedure is problematic for Th isotope measurements because differences between U and Th in mass fractionation and yield are shown to be significant [5,6]. Here, procedures employing an in-house Th isotope standard solution [5] for precise and accurate Th measurements using a multi ion counting array are presented.

2. Methods

2.1. Instrumentation

The measurements presented in this study were performed in the Bristol Isotope Group (BIG) laboratory using a ThermoFinnigan Neptune MC-ICPMS. The sample introduction system on the Neptune incorporates a Cetac Aridus nebuliser with a PFA spray-chamber and a nebuliser tip with a nominal uptake rate of

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Table 1
Cup and MIC configuration for Th isotope measurements. For this study, samples are measured statically using MIC1

	IC2	IC3	IC4	IC5	L4	L3
MIC1		(228)	²²⁹ Th	²³⁰ Th		²³² Th
MIC2	(228)	²²⁹ Th	²³⁰ Th	(231)	²³² Th	
MIC half		228.5	229.5	230.5		

MIC2 and MIChalf are used to assess the ²³²Th peak tailing.

50 µl/min. The ion collection efficiency of the Neptune is in the range of 1% with a typical ²³⁸U intensity of about 100 pA using a 30 ppb NBL-112a U-solution. The Neptune collector system consists of eight moveable Faraday cups and a fixed centre cup. The axial beam can also be deflected into a single ion counting channel with a secondary electron multiplier (SEM) which is located behind an energy and angular filtering device (Retarding Potential Quadrupole, RPQ). A multi ion counting (MIC) array has been recently installed in the Neptune. The MIC array consists of four miniaturised channeltron type multiplier identical in size with the standard Faraday cups and setup with fixed spacing corresponding to 1 amu set for U–Th isotope analysis. The array is installed on the low mass side, attached to Faraday cup L4. Table 1 shows the cup configuration for Th isotope measurements using the MIC array. More details about MIC arrays can be found in Wieser and Schwieters [3].

2.2. Multi ion counter (MIC) MC-ICPMS measurement

Basic analytical MC-ICPMS procedures are reported in detail in Hoffmann et al. [5]. Here, the application of a MIC array for Th isotope measurements of samples with high ²³⁰Th/²³²Th concentration ratios (>10⁻³) is presented. The abundance sensitivity at 2 amu without RPQ is in the range of 10⁻⁷ to 10⁻⁶, thus a tailing contribution of the ²³²Th beam on the ²³⁰Th measurement is negligible for ²³⁰Th/²³²Th > 10⁻³. The BIG in-house ²²⁹Th–²³⁰Th–²³²Th standard (TEDDi) [5] is used for sample–standard bracketing of Th isotope measurements (²³⁰Th/²²⁹Th ratio of 1.519 ± 0.002 and ²³⁰Th/²³²Th = (4.444 ± 0.007) × 10⁻³). The TEDDi solution is used for static ²²⁹Th and ²³⁰Th measurements on two ion counters together with ²³²Th on a Faraday cup. The intensity of ²²⁹Th applied to a channeltron ion counter is in the range of 5000 cps. All Th solution samples in this study were measured with cup configuration MIC1 (Table 1). Optimised peak alignment of the ²²⁹Th and ²³⁰Th peaks on two ion counters with fixed spacing is achieved using the ion optics device. The ion counter pair IC4–IC5 is used because the position of the Faraday cup L3 can be varied relative to the MIC array to achieve optimised ion counter–Faraday cup peak alignment. The extend of ²³²Th tailing is monitored at 1 amu (²³¹/²³²Th) using TEDDi solution and cup configuration MIC2. All samples analysed in this study have ²³⁰Th/²³²Th > 10⁻³ and in no case a tail correction was needed. The Th isotope ratios of sample measurements are corrected for both mass fractionation and ion counter yield using the measured and known ratio of the bracketing TEDDi solution.

U isotope ratios are all measured following Hoffmann et al. [5] because the application of MIC does not have advantages for U isotope measurements. MIC measurements do not incorporate the RPQ for ²³⁶U and ²³⁴U. Since ²³⁸U has a tailing contribution to ²³⁶U which is significantly reduced by the RPQ, procedures described in Hoffmann et al. [5] are advantageous. Therefore, for this study all U isotope ratios are measured in two separate static measurements (²³⁴U–²³⁸U and ²³⁶U–²³⁵U–²³⁸U) using the centre SEM located behind an RPQ for the minor isotope measurements (²³⁴U and ²³⁶U, respectively). U isotope measurements are bracketed and corrected using an NBL-112a solution. The procedures are described in full in Hoffmann et al. [5].

2.3. Samples and sample preparation

For this study a Harwell Uraninite (HU) solution (URAN 84.5, provided by UKAEA Harwell in 1990), the coral powder AC1 and flowstone SPA59 were analysed. The HU solution has a ²³⁴U/²³⁸U unity activity ratio and is shown to be slightly elevated from secular equilibrium in the ²³⁰Th/²³⁸U activity ratio [5]. AC-1 is a 124 ka old coral powder taken from a large porites coral in Aladdin's cave on the Huon Peninsula (Papua New Guinea) with a ²³⁸U concentration of 3.22 ± 0.01 µg/g [7,5]. SPA59 is an alpine flowstone from Spannagel Cave (Austria) that formed between 260 and 55 ka with hiatuses during cold phases [8]. It has exceptionally high U concentrations between 10 and 168 µg/g and allows the use of sample sizes smaller than 1 mg for ²³⁰Th/U dating.

Six carbonate pieces of 0.5–1 mg were cut from SPA59 at a spatial resolution of 0.8 mm using a diamond coated wire saw. The pieces were cleaned in an ultrasound MQ bath to remove potential surface contamination or residuals from the cutting process and then dried. Three sub-samples of about 60 mg of the powdered sample AC-1 were taken from a stock. This is sufficient material for at least 10–15 MC-ICPMS measurements. After weighing, the carbonate samples were placed in a clean Teflon beaker, MQ was added and the carbonate sample carefully dissolved by stepwise addition of 7N HNO₃. A defined quantity of a mixed ²²⁹Th/²³⁶U spike was added and the solution evaporated to dryness for sample–spike equilibration. Organic components are attacked by dissolving the residual in a combination of concentrated HNO₃, HCl and H₂O₂. The solutions were refluxed for 30 min and again evaporated to dryness. The dry residues were taken up in 6N HCl and processed through pre-cleaned ion exchange resin (AG 1 × 8) to separate Th and U fractions. Th passes through the resin in 6N HCl and U is then eluted with 1N HBr followed by MQ. After drying down, the two fractions were taken up in 7N HNO₃ and separately passed through the ion exchange resin for purification. Th is eluted from the resin with 6N HCl, U is eluted with 1N HBr and MQ. The final U- and Th-sample solutions were dried down and both U and Th taken up in 0.6N HCl for MC-ICPMS measurements. U and Th of the spiked HU aliquots were also separated and purified.

3. Results

3.1. Stability of MIC response

Stability of the detection system response is important for a sample–standard bracketing procedure and therefore investigated for the channeltron type ion counters used for Th isotope measurements. Two examples for the response stability of ion counter pair IC4–IC5 for different applied beam intensities are shown in Fig. 1a and b. Fig. 1b shows the change of the ion counter to Faraday cup gain and Fig. 1a the relative ion counter gain of IC4 and IC5. Seven sample solutions were measured bracketed by the in-house Th standard solution. For the first example, the ²³⁰Th and ²²⁹Th intensities of the bracketing standard were 12,000 and 8000 cps, respectively, and the sample intensities varied between 3000 and 9000 cps for ²³⁰Th and 13,000–20,000 cps for ²²⁹Th. The ion beams were collected on the ion counters for about 5–6 min. Over the course of this sequence including eight standard and seven sample measurements, i.e., 1.5 h effective use of the channeltrons spread over a total sequence time of 8 h, the ion counter to Faraday cup yield decreases by about 1.5%. The stability of the channeltron ion counter at 10 kcps is specified to be ±0.2% per hour, thus within specification a maximum drift of 0.4% can be expected. The result shown here potentially also includes drifts in plasma conditions over the 8 h sequence time. However, in most cases the difference

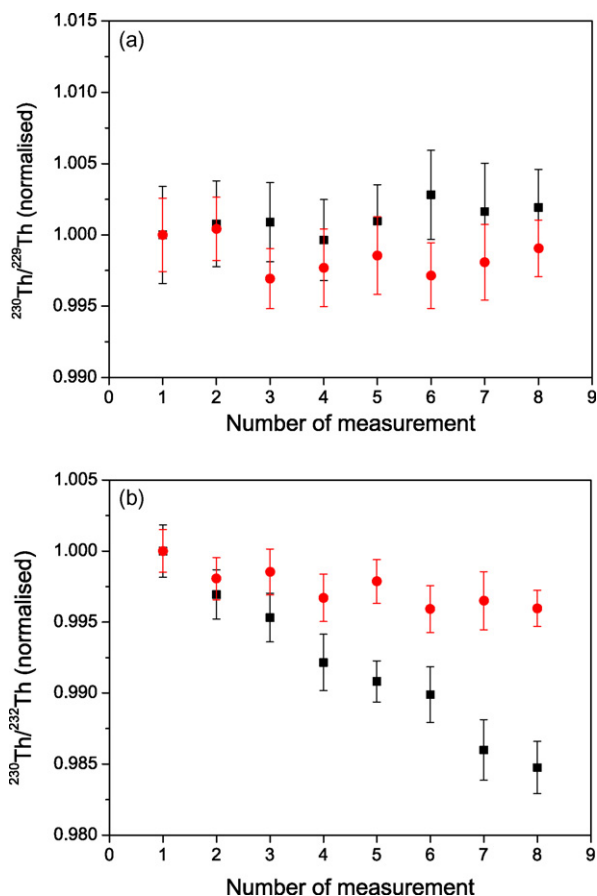


Fig. 1. Change of the measured $^{230}\text{Th}/^{229}\text{Th}$ (a) and $^{230}\text{Th}/^{232}\text{Th}$ (b) ratios of the Th standard TEDDi over the course of two sequences. The ^{229}Th and ^{230}Th are measured on a pair of ion counters, ^{232}Th is measured on a Faraday cup. All ratios are shown relative to the ratio of measurement number 1. Sequence 1 (squares) shows the ion counter response change for applied intensities exceeding 10,000 cps. Here, the TEDDi intensity was 12,000 (^{230}Th) and 8000 (^{229}Th), respectively, and the sample intensities varied between 3000 and 20,000 cps. The ion counter–Faraday cup gain drifted by 1.5% whereas the relative ion counter gain remains stable within uncertainty. Sequence 2 (circles) shows the ion counter response change for all intensities smaller than 10,000 cps. The ion counter–Faraday cup gain is more stable with a drift of 0.4%, the relative ion counter gain is again stable (see text for details).

between two subsequent bracketing standards is smaller than 0.2% and can be reliably corrected. More important, the relative yield of the two ion counters IC4–IC5 is stable within analytical error showing only gradual increase of 0.2% from start to end. The second example shown in Fig. 1 demonstrates the ion counter response stability with all beam intensities smaller than 10 kcps. Here, the ^{230}Th intensity of TEDDi solution was kept at about 5000 cps, the ^{230}Th intensity of the samples was between 50 and 5000 cps and the ^{229}Th intensity was between 3000 and 5000 cps for samples and standard. In this case the ion counter–Faraday cup gain changes by 0.4% in total and the relative yield of IC4–IC5 is again stable within uncertainties. Although the MIC are specified for an ion beam intensity of 10 kcps the results of the response stability tests, which were performed after a sufficient “burn-in” phase, indicate that the best performance is achieved if this intensity is not exceeded. Hence, for high precision analyses the miniaturised channeltron ion counter should ideally not be loaded with intensities higher than 10 kcps.

3.2. MIC linearity assessment

The linearity of an ion counter needs to be considered for accurate measurements and thus has to be characterised [9,10]. One

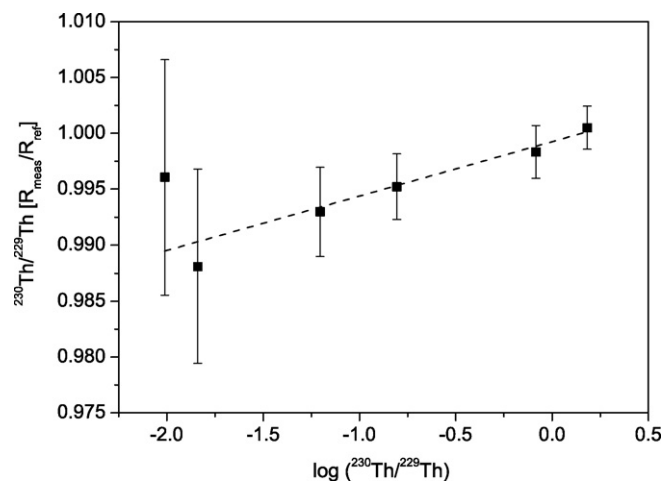


Fig. 2. Linearity assessment for a pair of ion counters. Five Th isotope solutions with $^{230}\text{Th}/^{229}\text{Th}$ ratios ranging between 0.001 and 1 are measured using MIC pair IC4–IC5. The ^{229}Th intensity is always run at 5000 cps, the ^{230}Th intensity varied between 50 and 5000 cps. The measurements were bracketed and corrected using the TEDDi Th standard solution with a $^{230}\text{Th}/^{229}\text{Th}$ ratio of 1.519. The results are shown relative to the “known” ratios characterised using methods outlined in Hoffmann et al. [5] in log-linear space (see text for details).

nonlinearity effect of the channeltrons, namely the ion counter deadtime, is electronically set to 70 ns and corrected accordingly [10]. The additional nonlinear response to different beam intensities needs to be characterised experimentally [10]. The nonlinearity of the miniaturised channeltrons is more difficult to assess than that of a discrete dynode type SEM as outlined in Hoffmann et al. [10] because of the response change described above. The linearity of ion counters used in this study is determined using Th solutions with different well-characterised isotope ratios. The Th isotope solutions with $^{230}\text{Th}/^{229}\text{Th}$ concentration ratios between 0.001 and 1 were prepared for the linearity assessment and characterised following the procedures outlined in Hoffmann et al. [5]. The solutions were then measured using the MIC array, bracketed and corrected with the TEDDi standard which has a $^{230}\text{Th}/^{229}\text{Th}$ ratio of 1.519. The ^{229}Th intensity of the solutions was always run at about 5000 cps, thus the ^{230}Th intensity varied between 50 and 5000 cps. The bracketing TEDDi standard solution was run with a ^{230}Th intensity of about 5000 cps. Fig. 2 shows the measured ratios relative to the “known” ratios determined using methods outlined in Hoffmann et al. [5]. The resulting $^{230}\text{Th}/^{229}\text{Th}$ ratios are accurate for ^{229}Th and ^{230}Th intensities similar to the bracketing TEDDi solution. For ^{230}Th intensities smaller than TEDDi the $^{230}\text{Th}/^{229}\text{Th}$ ratio is systematically underestimated. The general form of the relationship between the nominal $^{230}\text{Th}/^{229}\text{Th}$ and thus the ^{230}Th intensity and the measured $^{230}\text{Th}/^{229}\text{Th}$ ratio is exponential and the data in Fig. 2 can be conveniently described by a linear function in log-linear space. Since only the ^{230}Th intensity measured on IC5 is varied the nonlinear response shown in Fig. 2 can be ascribed to IC5. The MIC pair IC4–IC5 which is used for Th isotope measurements has a relative nonlinearity of $(0.55 \pm 0.04)\%$ per order of magnitude difference in the $^{230}\text{Th}/^{229}\text{Th}$ ratio relative to the bracketing standard with ^{230}Th and ^{229}Th at similar intensities. All MIC results presented in this study are measured on IC4–IC5 and corrected for the nonlinearity effect with a factor of $(0.55 \pm 0.04)\%$ per order of magnitude difference in the $^{230}\text{Th}/^{229}\text{Th}$ ratio. It is important to note that the nonlinear response found for IC5 is relatively large and probably not representative for the miniaturised channeltrons available for the Neptune. Similar tests on the ion counter pair IC3–IC4 indicate smaller relative nonlinearity with a factor of 0.2% per order of magnitude difference of the $^{230}\text{Th}/^{229}\text{Th}$ ratio. Further

Table 2
 $^{230}\text{Th}/^{229}\text{Th}$ results on Th fractions of Uraninite samples using MC-ICPMS and SEM peak jump [5], MIC (this study), static Faraday cup MC-ICPMS [5] and TIMS [5] procedures

Sample	$^{230}\text{Th}/^{229}\text{Th}$ peak jump	$^{230}\text{Th}/^{229}\text{Th}$ MIC	$^{230}\text{Th}/^{229}\text{Th}$ FAR	$^{230}\text{Th}/^{229}\text{Th}$ TIMS
BIG-UTh-A94	0.4955 ± 0.0009 ($n=1$)	0.4951 ± 0.001 ($n=3$)	–	–
BIG-UTh-A181	0.2621 ± 0.00014 ($n=48$)	0.2622 ± 0.00013 ($n=26$)	–	0.2612 ± 0.0007 ($n=1$)
BIG-UTh-A182	0.5397 ± 0.00044 ($n=8$)	0.5402 ± 0.00042 ($n=6$)	0.5393 ± 0.001 ($n=1$)	0.5393 ± 0.0014 ($n=1$)
BIG-UTh-A183	2.7928 ± 0.0062 ($n=2$)	2.7952 ± 0.0033 ($n=7$)	–	–
BIG-UTh-A184	0.1638 ± 0.00021 ($n=8$)	0.1637 ± 0.0002 ($n=3$)	0.1637 ± 0.0005 ($n=1$)	0.1641 ± 0.00045 ($n=1$)
BIG-UTh-A185	0.5806 ± 0.00077 ($n=4$)	0.5799 ± 0.0010 ($n=3$)	0.5790 ± 0.001 ($n=1$)	0.5795 ± 0.0026 ($n=1$)

work is planned to investigate the linearity of the MIC arrays in more detail.

3.3. Results on Harwell Uraninite

In order to assess the accuracy and precision of the MIC application, Th isotope ratio measurements are compared to previously collected results following methods outlined in Hoffmann et al. [5]. Six HU aliquots with different sample–spike ratios and thus different $^{230}\text{Th}/^{229}\text{Th}$ ratios were used. Three of the aliquots were also analysed using MC-ICPMS procedures with all Th isotopes measured statically on Faraday cups. Additionally, parts of four Th aliquots were loaded on Re filaments and analysed by TIMS as described in Hoffmann et al. [5]. Table 2 shows the $^{230}\text{Th}/^{229}\text{Th}$ ratios obtained using the different procedures. All the results agree well within the uncertainties. The main difference between the results is the total sample solution consumed for a single analysis. On average, the amount of ^{230}Th used for a measurement of HU Th solution employing the SEM peak jump procedure (Hoffmann et al. [5]) is 200 fg. For a TIMS measurement about 5 pg were loaded on the filament and a static Faraday cup MC-ICPMS measurement, which requires ion beam intensities of more than 20 mV, consumed about 20 pg ^{230}Th . In contrast, for a single MIC measurement only about 80 fg ^{230}Th were used.

3.4. Results on carbonate samples AC1 and SPA59

For MIC measurements of Th isotopes in carbonate samples three aliquots of the coral powder AC1 were used that have been previously analysed with a MC-ICPMS SEM peak jump procedure [5]. Eleven analysis of the AC1 U and Th solutions using MIC for the Th isotope measurements yield identical results as published in Hoffmann et al. [5]. The $^{230}\text{Th}/\text{U}$ age derived using MIC is 124.0 ± 0.4 ka with $^{230}\text{Th}/^{238}\text{U} = 0.759 \pm 0.001$, and $^{234}\text{U}/^{238}\text{U} = 1.102 \pm 0.001$. This compares very well with the previous MC-ICPMS (age of 124.3 ± 0.3 ka, $^{230}\text{Th}/^{238}\text{U} = 0.760 \pm 0.001$, and $^{234}\text{U}/^{238}\text{U} = 1.102 \pm 0.001$) and TIMS (age of 123.98 ± 0.82 ka, $^{230}\text{Th}/^{238}\text{U} = 0.759 \pm 0.003$, and $^{234}\text{U}/^{238}\text{U} = 1.102 \pm 0.001$) results [5] and demonstrates the reliability of the MIC application. Again, an advantage of MIC measurements is the reduction in sample size needed for one measurement. This also results in reduced measurement time for Th isotopes and therefore allows faster sample throughput.

Table 3
 Comparison of MIC and SEM peak jump MC-ICPMS results of flowstone SPA59

Sample ID	Sample size (mg)	^{238}U ($\mu\text{g/g}$)	^{230}Th (ng/g)	^{230}Th intensity (cps)	MIC ^{230}Th consumed (fg)	SEM ^{230}Th consumed (fg)	U–Th age MIC (ka)	U–Th age SEM (ka)
BIG-UTh-A346	0.55	63.9 ± 0.3	0.958 ± 0.005	3500	58	145	191.9 ± 2.0	191.3 ± 1.8
BIG-UTh-A347	0.75	39.0 ± 0.2	0.607 ± 0.003	3300	50	125	212.5 ± 2.5	212.1 ± 2.4
BIG-UTh-A348	0.48	13.6 ± 0.1	0.258 ± 0.002	740	14	35	Out of range	Out of range
BIG-UTh-A349	0.44	134.3 ± 0.6	1.691 ± 0.009	4900	82	205	134.2 ± 1.0	134.2 ± 1.0
BIG-UTh-A350	0.46	97.0 ± 0.4	1.232 ± 0.005	4300	63	158	133.6 ± 1.1	133.2 ± 0.9
BIG-UTh-A351	0.81	63.8 ± 0.3	0.813 ± 0.004	4600	74	185	133.6 ± 1.1	133.1 ± 1.0

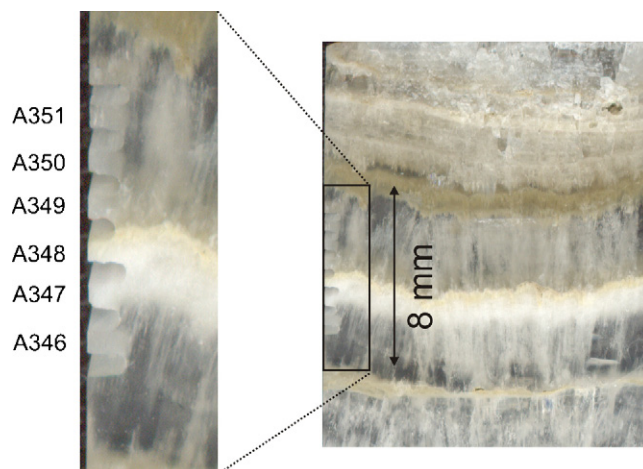


Fig. 3. A thin slice taken from the middle part of SPA59 [8] showing horizontal growth layers of the flowstone. The white band marks the hiatus between 192 and 137 ka. Enlarged on the left-hand side are the wire saw cuts for the samples BIG-UTh-A346–351 (Table 3) prior to be taken off the slice. The sample sizes of the small carbonate pieces were between 0.5 and 1 mg.

An application to high spatial resolution $^{230}\text{Th}/\text{U}$ dating is demonstrated using the alpine flowstone SPA59 [8]. Fig. 3 shows a 2 mm thin slice cut from SPA59 which was sub-sampled at a spatial resolution of 0.8 mm across a hiatus between 192 and 137 ka [8]. Due to exceptionally high U concentrations in this flowstone [8] less than 1 mg carbonate can be used. The low ^{232}Th concentrations in SPA59 [8] result in high $^{230}\text{Th}/^{232}\text{Th}$ ratios ($>10^{-3}$) and allow Th measurements using the MIC procedure outlined above. The sample sizes of 0.5–1 mg were big enough to analyse the Th solutions using both MIC procedures and MC-ICPMS SEM peak jump methods. The results listed in Table 3 show excellent agreement between the two measurement procedures.

4. Discussion

The HU, AC1, and SPA59 results demonstrate that samples which are suitable for MIC procedures can be accurately measured at high precision with less sample consumption, e.g., compared to procedures outlined in Hoffmann et al. [5]. With a MIC array it is possible to increase Th isotope measurement efficiency by at least a factor of 2 compared to a SEM peak jump routine. Thus,

for $^{230}\text{Th}/\text{U}$ dating at a given precision less than half the sample size is required. SPA59 results presented in Table 3 indicate that it is possible to derive high precision Th isotope measurements with a total ^{230}Th consumption of 10 fg. The MIC procedures can also be used to measure ^{230}Th samples as small as 1 fg with precisions still in the range or better than 1%. In the case of SPA59 carbonate samples smaller than 1 mg can be used for $^{230}\text{Th}/\text{U}$ dating. However, this is exceptionally small due to U concentrations of 10–168 $\mu\text{g}/\text{g}$. More realistically, speleothem samples often have U concentrations of less than 1 $\mu\text{g}/\text{g}$. To achieve high spatial resolution dating on such samples the efficiency of Th isotope measurements is crucial. For example, a 150-year-old speleothem with a U concentration of around 0.8 $\mu\text{g}/\text{g}$ U has a ^{230}Th concentration of about 20 fg/g. Thus, for a total of 1–2 fg ^{230}Th only 100 mg of carbonate are needed and for a more precise dating a sample size of 500 mg with a total of 10 fg ^{230}Th is sufficient which is notably small for such a young sample. Therefore, the MIC procedures offer the option to precisely date carbonates younger than 1 ka using less than 500 mg.

However, the MIC procedure for high precision measurements has two important restrictions. Firstly, the ion beam intensities measured on miniaturised channeltrons should be smaller than the specification intensity of 10,000 cps. This minimises changes of ion counter response to incoming ion beams between two subsequent bracketing standards. Ideally, the bracketing standard TEDDi is run with ^{229}Th and ^{230}Th intensities of around 4000 and 6000 cps, respectively, and the ^{229}Th intensity of a spiked sample should be around 4000 cps with a $^{230}\text{Th}/^{229}\text{Th}$ ratio between 0.001 and 1. Secondly, the MIC array cannot be used in conjunction with an RPQ. Therefore, samples with a significant ^{232}Th tailing contribution should be measured using the centre SEM located behind the RPQ. It is suggested to measure only samples with a $^{230}\text{Th}/^{232}\text{Th}$ ratio $>10^{-3}$ with the MIC procedure.

The strength and advantage of the MIC procedure is the simultaneous measurement of low-level beams. This not only reduces the sample sizes it also circumvents potential problems with unstable ion beams often associated with ICPMS and to a greater extent with laser ablation applications. The results for Th isotope measurements on solutions indicate the potential of the MIC application for static laser ablation measurement of low level ^{234}U and ^{230}Th ion beams together with ^{238}U on a Faraday cup. This is an important pre-requisite for precise *in situ* LA MC-ICPMS measurements of U–Th isotopes [11].

5. Conclusions

This study presents a MIC procedure for Th isotope measurements of samples with $^{230}\text{Th}/^{232}\text{Th} >10^{-3}$. The excellent results for the HU aliquots as well as carbonate samples AC-1 and SPA59 demonstrate accuracy of the MIC procedures. The application of MIC enables simultaneous static measurements of low level beams, in this case of ^{230}Th and ^{229}Th , and reduces the sample size required for $^{230}\text{Th}/\text{U}$ dating of carbonates by optimising Th isotope measurements. This also allows faster Th isotope measurements and hence faster sample throughput. Compared to a peak jump routine the sample size for $^{230}\text{Th}/\text{U}$ dating which is limited by the ^{230}Th abundance can be reduced by at least a factor of two. Quantities of about 10 fg of ^{230}Th can be used for high precision $^{230}\text{Th}/^{229}\text{Th}$ measurements.

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References

- [1] S.J. Goldstein, C.H. Stirling, *Rev. Mineral. Geochem.* 52 (2003) 23.
- [2] D.A. Richards, J.A. Dorale, *Rev. Mineral. Geochem.* 52 (2003) 407.
- [3] M.E. Wieser, J.B. Schwieters, *Int. J. Mass Spectrom.* 242 (2005) 97.
- [4] J. Fietzke, V. Liebetrau, A. Eisenhauer, C. Dullo, *J. Anal. Atom. Spectrom.* 20 (2005) 395.
- [5] D.L. Hoffmann, J. Prytulak, D.A. Richards, T.R. Elliott, C.D. Coath, P.L. Smart, D. Scholz, *Int. J. Mass Spectrom.* 264 (2007) 97.
- [6] K.W.W. Sims, J. Gill, A. Dossoto, D.L. Hoffmann, C. Lundstrom, R. Williams, L. Ball, D. Tollstrup, S. Turner, J. Prytulak, J. Glessner, J. Standish, T. Elliott, *Geostand. Geoanal. Res.* 32 (2008) 65.
- [7] M.T. McCulloch, T. Esat, *Chem. Geol.* 169 (2000) 107.
- [8] S. Holzkämper, C. Spötl, A. Mangini, *Earth Planet. Sci. Lett.* 236 (2005) 751.
- [9] S. Richter, S.A. Goldberg, P.B. Mason, A.J. Traina, J.B. Schwieters, *Int. J. Mass Spectrom.* 206 (2001) 105.
- [10] D.L. Hoffmann, D.A. Richards, T.R. Elliott, P.L. Smart, C.D. Coath, C.J. Hawkesworth, *Int. J. Mass Spectrom.* 244 (2/3) (2005) 97.
- [11] D.L. Hoffmann, C. Spötl, A. Mangini, *Chem. Geol.*, submitted for publication.