High precision U-series dating of scleractinian cold-water corals using an automated chromatographic U and Th extraction

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ABSTRACT

High-precision U-series dating of scleractinian cold-water corals is a key chronological tool for studies of past environmental and climate conditions. Here, we tested and optimized an automated chemical extraction system (ESI prepFAST-MC equipped with an Eichrom TRU-resin chromatographic column) for its ability to purify U and Th isotopes for mass spectrometric U-series dating at the sub-‰ precision level. Chemical yields are constantly high, on average around 90% for both U and Th. Analytical blanks are comparable to manual purification (< 0.15 pg U, 0.15 pg Th for a typical sample of 50 mg) and memory effects due to the recycling of the column are mostly insignificant as the carry-over fraction is about 10^{-5} for Th and 10^{-3} for U isotopes. However, it was found that the built-in UTh (TRU-resin) column must be pre-conditioned for analysis using $> 1\,\mu g\,g^{-1}$ Th and U in order to achieve the above mentioned chemical yields. This conditioning has no impact on the Th/U data. The automated chemical preparation protocol described here is compared to conventional high precision U-series dating with manual sample purification. For the 34 cold-water corals extracted from a sediment core collected from a coral mound off Angola, the differences between $^{230}Th/^{238}U$- and $^{234}U/^{238}U$-ratios and U-series ages measured with the two analytical methods are smaller than the respective analytical uncertainty of < 3.0‰, 0.8‰ and 3.0‰, respectively. Overall, ages of the studied corals span 34,000 years and perfectly meet quality control constrains, such as initial seawater $\delta^{234}U_0$. Finally, our record of coral ages indicates vigorous coral growth under warm and cold climate conditions in the temperate south-eastern Atlantic, contrasting climate influenced coral occurrences in the north-eastern Atlantic.

1. Introduction

Precise age determination is of great value in many fields, including earth sciences, paleoclimatology and archeology. Various methods have been invented with the U-series disequilibrium dating now being a key instrument for Quaternary Research (Bourdon et al., 2003). Its practicality depends on several factors including the composition of the sample material, i.e. complete U and Th fractionation during mineral formation and the mineral's subsequent closed-system behavior. U-series methods are applicable to a large variety of materials, for instance corals, speleothems, and travertines, but also archeological material such as bones and teeth (Bourdon et al., 2003). Today, the possible dating range spans from 0 to up to 800,000 years (Cheng et al., 2013), given that the material provides a sufficient number of U and Th atoms for precise isotope measurements using modern mass spectrometry. Over the past decades, improvements of U-series dating greatly

increased the precision to partly even ε-level (0.1‰) (Cheng et al., 2013). Aside from high precision measurements using multi-collector inductively coupled plasma source mass spectrometers (MC-ICP-MS), rapid age screening methods have been developed reaching %-precision levels using far less complex quadrupole mass spectrometers (ICP-QMS) (Douville et al., 2010) or in-situ laser ablation (LA) techniques (Potter et al., 2005; Spooner et al., 2016).

Present methodologies for high precision U-series dating are based on chemical purification of U and Th from the host material, often carbonate, and commonly follow four steps: (1) Samples are manually pretreated to obtain pure and ideally pristine secondary carbonate material. (2) After dissolution in acid the sample is spiked with a solution containing artificial Th and U isotopes (^{229}Th, ^{233}U, and ^{236}U) which is needed to determine the U and Th concentration of the sample. (3) The sample is processed through ion exchange chemistry to purify U and Th from the matrix elements and to separate Th from U if required.

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(4) Ultimately, purified U and Th solutions or admixtures of both are used to conduct isotope ratio measurements on the above mentioned mass spectrometers (Douville et al., 2010). Due to the vast sample throughput of modern mass spectrometers and the efficient chemistry through which numerous samples can be manually processed in parallel, U-series age determination has become an available and widely used chronological tool. Today, ion exchange chemistry and mass spectrometry require clean laboratory environments and the manual handling of ultra-pure and in cases hazardous acids (HNO_3, HCl, HF). To cope with the growing instrumental throughput and to develop more easy-to-handle purification pathways, the need for further developments and high throughput semi-automated sample preparation systems arises. This is of particular importance for the retrieval of geochronological information from individual marine carbonate organisms such as cold-water corals. To constrain the spatial and temporal occurrence of cold-water coral habitats, it is desirable to date a large number of fossil individuals by U-series dating (Frank et al., 2009).

Several attempts for automated sample preparation have been successfully achieved using custom made chromatographic devices. An example for automated sample preparation with respect to Th and U is the flow-injection technique developed by Benkhedda et al. (2005). Here, Th and U were separated from urine samples using Eichrom TRU resin with an on-line method. Avivar et al. (2012) describe a solid-phase extraction method based on the use of valves and syringes together with UTEVA resin. An automatic system operated with pressurized nitrogen gas was developed by Miyamoto et al. (2015), where the eluted fractions were collected off-line. In recent years, the technology to handle highly concentrated acid solutions in chromatographic devices has been largely improved, such that numerous applications for the measurement of rare elements and isotopes have been automated (Romaniello et al., 2015).

Consequently, we here explore the present-day capabilities of such a commercially-available chromatographic device for the purification of U and Th from secondary carbonates, with the aim of performing sub-‰ precision U-series age determination on corals. A protocol is developed that yields chemical purification from matrix elements and between U and Th, low sample carry-over, and analytical blank levels negligible regarding common U-series dating applications. We demonstrate that ultra-high precision dating of cold-water corals at better than ‰-level is feasible with the automated protocol and chemical yields are comparable to manual analytical practice. Hence, we open a new pathway for small and automated systems for U-series dating reducing the infrastructure needs for such highly laboratory-demanding methods.

Lastly, we provide a new dataset to the active discussion on the climate driven occurrence of cold-water corals in the North and South Atlantic (Frank et al., 2011, 2009; Mangini et al., 2010; Wienberg et al., 2010).

2. Material and methods

2.1. Automated chemical extraction system (ACES)

The automated chromatographic extraction of Th and U is carried out with the prepFAST-MC system (ESI, Omaha, NE, USA), equipped with a 200 μl "UTh column" (part number CF-ThU-0200) filled with Eichrom TRU resin. The system is used as an off-line separation and purification system only to collect fractions of purified Th and U solutions from the previously dissolved and spiked samples. However, the system can also be operated on-line, as an autosampler directly coupled to the desolvating systems of the ICP-MS interface.

Over the course of this study, two UTh columns were used successively. About 100 samples and standards were processed with the first column in order to develop the U and Th separation protocol and to optimize it for cold-water coral high-precision U-series dating. The same column was then used to apply this protocol to 34 coral samples of
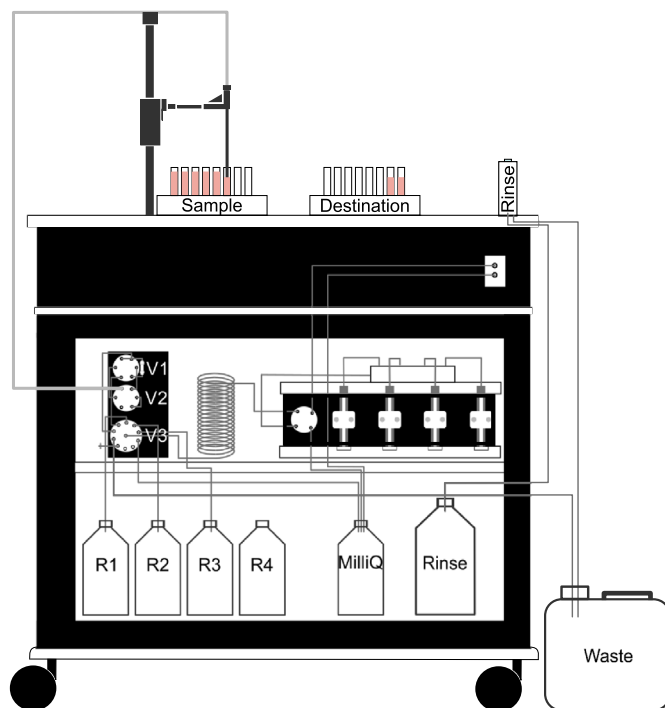

Fig.1. Automated chemical extraction system (ACES) ESI prepFAST-MC including the multi-position valves V1-V3, the reagent containers R1-R4, the sample loop and the autosampler ESI SC-4DX on top with 4 × 60 sample positions. Modified after "prepFAST-MC SC-4 DX System Complete Install" (ESI).

unknown ages. Afterwards, a new UTh column was used to test the developed protocol on a virgin column to assess possible alterations compared to the column in use.

The prepFAST-MC (schematic buildup shown in Fig. 1) is a low pressure chromatography system including an SC-4 DX autosampler, developed by Elemental Scientific (Omaha, NE, USA). The system itself consists of two 6-port 2-position valves, one 10-port multi-position valve, a syringe pump (S400V) with a fill-dispense valve, and a 13 ml sample loop (Romaniello et al., 2015). Four syringes are operated to draw in up to six different reagents or the sample itself to the loop and column.

In this study, an elution protocol was developed from pre-built method blocks that are included in the system's software, with the purpose of purifying Th and U from a $CaCO_3$ matrix and separating both elements from each other (Table 1). The automated protocol is similar to the manual method described in Vivone et al. (2012).

To reduce sample carryover due to the reuse of the column, three subsequent cleaning steps are applied prior to each sample, blank or standard treatment. First, 6 ml (30 column volumes, CV) of reagent R1

Table 1
Protocol for the automated purification of Th and U with the 200 μl UTh column.

Step	Purpose	Cycles & volume	Reagent
1	Clean column	1 × 6 ml	R1
2	Clean column	1 × 6 ml	R2
3	Clean column	1 × 6 ml	R4
4	Condition column	1 × 4 ml	R3
5	Load sample	1 × 1. 2 ml	R3
6	Wash out matrix	1 × 1.5 ml	R3
7	Elute Th	3 × 0.5 ml	R1
8	Elute U	3 × 0.5 ml	R2
Reagents:	R1 = 1 M HCl + 0.1 M HF		
	R2 = 0.1 M HCl + 1 M HF		
	R3 = 1.5 M HNO_3		
	R4 = MilliQ		

(1 M HCl + 0.1 M HF) is passed through the sample loop and column and flushed out into the waste or possibly in a vial if storage is needed for further studies. Next, 30 CV of reagent R2 (0.1 M HCl + 1 M HF) is flushed through the system. Here, HF strongly complexes Th and efficiently cleans the valves, tubing, sample loop and column. Finally, the system is rinsed with 30 CV of MilliQ water (18.2 MΩ high-purity water, Merck) removing all acids from the valves and tubing. Following upon cleaning of the system and column, the ion exchange resin is preconditioned with 20 CV of reagent R3 (1.5 M HNO_3), which presets the TRU resin's capacity factor for Th and U (Horwitz et al., 1993). Then the sample, dissolved in 6 CV of R3, is loaded onto the ion exchange column and the matrix elements are subsequently washed out flushing 7.5 CV of R3 through the sample loop and ion exchange resin. The solutions can be passed into the waste or again into a vial for further studies. The Th fraction is then eluted in three steps of 2.5 CV (total 7.5 CV) by switching to R1 and finally the last three steps of 2.5 CV of R2 elute U. The eluted Th and U fractions are dispensed into predefined vial positions. The complete sequence of cleaning, solution uptake, flushing, and elution takes about 1 h 15 min per sample, hence 19 samples can be processed within 24 h.

2.2. Samples

To develop and test the final protocol a large fossil cold-water coral fragment (4.6 g) was used. This coral fragment was taken in 36–40 cm core depth from the coral-bearing sediment core MD13-3443G, retrieved in the Gulf of Cadiz during the R/V Marion Dufresne MD194 "Gateway" cruise (van Rooij, 2013). The sample had been previously investigated using classical U-series dating which yielded an age of > 500,000 years. For experiments with the automated chemical extraction system (*ACES*), this sample was crushed, homogenized using a porcelain mortar and dissolved in supra-pure (sp) 3 M HNO_3. Aliquots corresponding to 50 mg of the coral material were taken from the bulk solution and the acid concentration was adjusted to 1.5 M HNO_3. Apart from the test sample, aliquots of the Harwell uraninite (HU-1) reference material, assumed to be in radioactive equilibrium (Cheng et al., 2000a), were used to test the chemistry. The solution of HU-1 contained 13.7 µg g^{-1} ^{238}U and 0.23 ng g^{-1} ^{230}Th. For the purpose of better visibility, a typical elution profile of Th and U as extracted with the above protocol for the ACES was measured with an admixture of ^{232}Th and ^{238}U elemental standards, with the concentration adjusted to 1 µg g^{-1} Th and U, respectively.

Finally, the performance of the developed method was tested with the classical purification and the ACES on the coral-bearing sediment core GeoB20933-1, which was retrieved in 2016 during R/V Meteor expedition M122 "ANNA" (Hebbeln et al., 2017). The gravity core (9°49.331′S, 12°46.565′E) was collected at 338 m water depth from a cold-water coral mound (Scary mound; naming follows the informal denomination given in Hebbeln et al., 2017) along the Angolan slope. The core has a total recovery of 9.83 m and is composed of fossil cold-water coral fragments (mainly *Lophelia pertusa* and to a minor degree *Madrepora oculata*) and other shells embedded in fine hemipelagic sediments over its entire length. From this core, 34 fragments of L. *pertusa* (*n* = 32) and *M. oculata* (*n* = 2) were sampled at different core depths.

The state of preservation of the fossil skeleton remains was variable, attested by visual inspection of traces of boring organisms or bio-erosion. Prior to the chemical treatment, coral fragments were thoroughly mechanically cleaned with a dremel tool in order to remove any visible coatings and carbonate not resulting from coral growth. Following the protocol of Douville et al. (2010), coral fragments of about 50 mg were thereafter leached in 0.5 M nitric acid, weighed, and dissolved in 2 M HNO_3. Then a precisely weighed amount of triple spike, composed of ^{229}Th, ^{233}U, and ^{236}U, was added and the sample solution was evaporated on a hotplate. For each sample, an aliquot was prepared with manual drip chromatography (labeled as "A") and with the ACES protocol outlined above (labeled as "B"). The final acid concentration was

adjusted to 7 M HNO_3 and 1.5 M HNO_3 for sample batch A and B, respectively. Batch A was treated according to the extraction method of Douville et al. (2010).

2.3. Measurement protocols

Mass-spectrometric measurements of the chemical yield and the concentration of residual matrix elements were carried out with an Inductively Coupled Plasma Source Quadrupole Mass Spectrometer (Thermo Fisher Scientific iCAP-Q) in combination with an Elemental Scientific Apex HF desolvator and SC-4 DX autosampler at the Institute of Environmental Physics at Heidelberg University. All samples were dried down after the chromatographic purification and either dissolved in (sp) 0.5 M (2.5%) HNO_3 or in a composition of (sp) 1% HNO_3 + 0.05% HF in order to keep Th and U blank levels low during the measurement and to obtain the comparability between the different sample fractions. The chemical yield was determined by evaluating absolute count rates compared to reference solutions following instrumental blank correction. The reference U and Th solution, corresponding to a sample of the previously mentioned test coral from MD13-3443G, spiked after ACES chemistry, was measured every five samples to correct for the instrumental drift via linear interpolation. Specifications and protocols for U-series measurements with ICP-QMS are given in Douville et al. (2010). Blaser et al. (2016) recently described the here used ICP-QMS regarding minor and trace element measurements of marine sediment leaches. Our yield detection protocol closely follows the one of Blaser et al. (2016).

In contrast to simple counting to obtain the chemical yields, isotopic measurements of ^{229}Th, ^{230}Th, ^{232}Th, ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U for high-precision U-series age calculations of the GeoB20933-1 coral samples were ultimately performed on a Multi-collector ICP-MS (Thermo Fisher Scientific Neptune *Plus*) equipped with a desolvator (CETAC Aridus) and an autosampler (Elemental Scientific SC-2 DX). The measurement procedure and data treatment are described in detail in Arps (2017). They follow the method developed in Fontugne et al. (2013) and Matos et al. (2015) and the measurement protocol is presented in Table 2. Depending on the concentration of ^{234}U and ^{230}Th, the procedure is either to measure ^{234}U and ^{230}Th in semi-static mode on the Faraday cup (FC, for signals above 2 mV, 10^{13} Ω resistor) or on the secondary electron multiplier (SEM, when diluted to < 125,000 cps). With a transmission efficiency of 1–3%, a minimum concentration of 1.5 pg g^{-1} of the individual isotopes is required to measure on the 10^{13} Ω resistor. Isotope ^{238}U is typically measured on a 10^{10} Ω resistor, while the remaining isotopes are measured on 10^{11} Ω resistors. Final solutions are diluted such that the isotope with the highest abundance, i.e. ^{238}U, has an intensity of ~ 30 V (equivalent voltage on a 10^{11} Ω resistor). The Th and U fractions are mixed to measure the analyzed isotopes simultaneously. Generally, the entire Th fraction is used and about 5–10% of the U fraction is admixed which reduces the tailing of U by 90–95% compared to a solution containing the entire Th and U fractions.

A standard-sample bracketing technique (i.e. standard-sample-standard measurements using the Harwell Uraninite HU-1 standard) is used for each sample measurement. The instrument baseline is assessed as a noise counting for the signals of each detector. Measurement sequences are preceded by the data acquisition of correction factors for hydride ions (H +), peak tailing (i.e. abundance sensitivity) and chemical blank which are monitored several times over the course of the day. Measurements of each sample last about 20 min and the samples are measured with integration times of 1.049 s to 2.097 s, and approximately 80 to 100 scans, with 3 s idle time between the magnetic field jumps. With this configuration average precisions of 1.8‰ (2σ) for Th ratios and of 0.8‰ (2σ) for U ratios are achieved. Standards measured with intensities above 20 mV (on a standard 10^{11} Ω) or above 11 mV (on a 10^{13} Ω) vary by 0.6‰ (2σ) or 6 ε -units (1ε = 10^{-4}), which in theory allows for ε-precision measurements of isotope ratios

Table 2
Measurement routine and collector configuration for U-series measurements. "H-as" refers to measurements carried out to correct for hydride ions (H +) and abundance sensitivity (tailing). Isotopes and other amu in () are measured on SEM. Table modified after Arps (2017).

Faraday cups	L1	Center	H1	H2	H3
Amplifier	10^{11} Ω	10^{13} Ω/(SEM)	10^{11} Ω	10^{11} Ω	10^{10} Ω
H-as U SEM		(228.50)			
		(230.50)			
		(231.50)			
		(233.50)			
		(236.50)			
		(236.70)			
		(237.05)			
		(237.50)			
		(239.00)			
		–			^{238}U
H-as U IC2	...	...	...	...	...
H-as Th SEM		(227.50)			
		(228.50)			
		(229.50)			
		(230.50)			
		(231.50)			
	^{232}Th	(^{233}U)			
H-as Th IC2	...	...			
Chemistry Blank	^{233}U	(^{234}U)	^{235}U	^{236}U	^{238}U
	^{229}Th	(^{230}Th)		^{232}Th	
		(^{229}Th)	^{230}Th		
Standard	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
	^{229}Th	(^{230}Th)		^{232}Th	
		(^{229}Th)	^{230}Th		
Sample	^{233}U	^{234}U	^{235}U	^{236}U	^{238}U
	...	...		...	
		...	...		
Standard	...	...	...	...	...

and ages but requires measurements with such intensities. However, cold-water corals selected here do not provide sufficiently high [U] and [Th] which may be overcome by increasing the sample size if possible.

The idle or decay time between mass jumps was set to 3 s to drop the initial signal of the amplifier to ≤ 100 ppm, which is far below our achieved measurement precision of permil to ε-scale. The instrument was tuned to maximize signal-to-noise ratios and to reach a signal stability of better than 3% in standard deviation over the course of 80 to 100 scans. Johnson Nyquist noise, instrument blank, and the most dominating counting statistics limit the achieved signal-to-noise ratio of the amplifiers. For a signal-to-noise ratio of better than 2‰ for each isotope, intensities need to be above 8 mV, 24 mV, and 48 mV for the 10^{13} Ω, 10^{11} Ω, and 10^{10} Ω detectors, respectively.

2.4. Data treatment and corrections

The first correction applied to the data originates in the finite abundance sensitivity of the instrument which generates a scattering tail of the ^{238}U- and the ^{232}Th-beam at lower masses. This is measured on the central SEM including a retarding potential quadrupole (RPQ) at half mass to correct for the isotopes that are measured on the SEM. For the isotopes measured on Faraday cups that lack an RPQ, the scattering tail is measured on the ion counter (IC2), which is an additional SEM (without RPQ) positioned at the deflection unit L5. The 237/238 intensity ratio is typically in the range of 0.3–0.7 ppm (with RPQ). A second correction applied to the data counteracts the influence from hydrated ions. For correction of U hydride (U-H +), the isotope on 239 amu is monitored over the course of the day. For correction of Th hydride (Th-H +) the isotope on 233 amu is measured with an in-house ^{232}Th solution (^{230}Th/^{232}Th = 1.04 × 10^{-6}). Usually, both values are in the range of 10 ± 9 ppm. After correcting for tailing and hydrides the mass bias is determined, for which the natural ratio of ^{235}U/^{238}U isotopes is used due to the lack of natural Th-isotopes. The residual

differences of U isotopes in standards with respect to its certified value demonstrate the necessity to normalize using a bracketing method. Each sample measurement is bracketed by two measurements of the standard Harwell Uraninite (HU-1), which is diluted to the same signal intensity as the one of the sample. The HU-1 standard is in secular equilibrium and the activity ratios of (^{234}U/^{238}U) and (^{230}Th/^{238}U) are supposed to be one (Cheng et al., 2000a). The reproducibility of the HU-1 standard is (^{234}U/^{238}U) = 1.00002 ± 0.00082 and (^{230}Th/^{238}U) = 1.0004 ± 0.0018 (1σ standard deviation spanning two years of measurements in Heidelberg). Hence, any residual offset of the (^{234}U/^{238}U) activity ratios due to systematic uncertainties of the detector calibration methods is used for the correction of the activity ratios of the samples. No significant deviation was found between the (^{235}U/^{238}U) ratios of standards and samples. Isotope ratios were used to calculate U-series ages according to the decay equations of Ludwig and Titterington (1994) and the error propagation accounts for the statistical uncertainties, but also for detrital ^{232}Th-correction if significant. For age calculations, the half-lives of ^{234}U and ^{230}Th published by (Cheng et al., 2000b) were used.

3. Results and discussion

3.1. TRU resin U and Th purification

For the method development, numerous experiments were carried out with the coral test sample to assess the system's response to parameter changes. Measurements revealed a systematic increase of the chemical yield over time, which was apparently independent of the tested parameters (acid volumes, molarities, admixtures HCl–HF, etc). Moreover, significant amounts of up to 80% of Th and 50% of U were missing and not retrieved in the matrix fraction or in any additional rinses. After the column had been repeatedly used for coral samples or aliquots of the HU-1 standard solution, the initially applied protocol yielded significantly higher results compared to the beginning, when the column was unused. Hence, it was tested whether column loading with larger quantities of Th and U (here a solution containing 1 μg g^{-1} of both elements) would yield an oversaturated resin, i.e. a breakthrough of both elements into the matrix solution. Instead, the purification improved to yields of now ~90% of both elements. This behavior was further examined by using the developed protocol for U and Th separation for the coral sample on a first-use (virgin) UTh column (Fig. 2). Especially for Th, the chemical yield achieved with a new, previously unused column was very low, only about 15%. U yields were about 50–55%. Following a preloading of the resin with the above
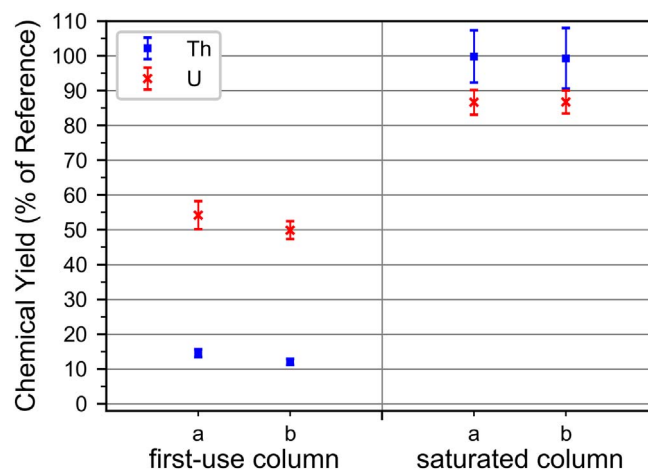

Fig. 2. Chemical yields for U and Th achieved with a first-use (virgin) column and a saturated column, each tested with two aliquots (a and b) of the test sample. The spike isotopes ^{229}Th and ^{236}U were measured and the count rates compared to a reference solution, a sample which was spiked after chemistry.
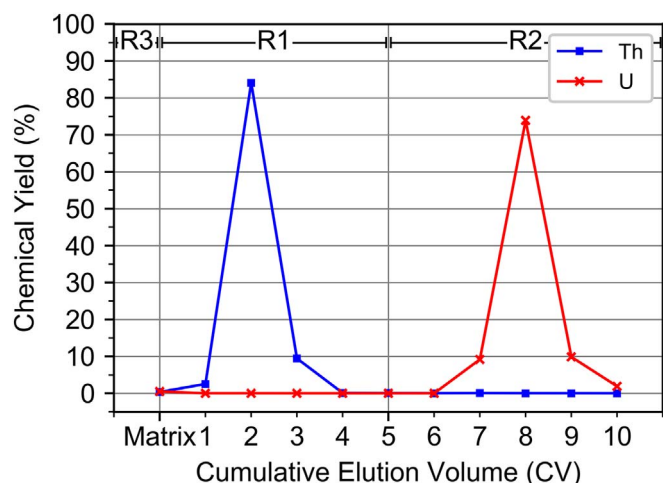
Fig. 3. Elution profile for Th and U. The elution was carried out in steps of 0.2 ml, corresponding to 1 CV (column volume). Here, a solution containing solely 1 μg g^{-1} ^{232}Th and 1 μg g^{-1} ^{238}U was used.

mentioned solution, yields immediately increased to about 100% for Th and to 85–90% for U. Such an observation of lacking Th and U recovery during manual preparation is known for long, but since its occurrence was not necessarily systematic this problem was neither resolved nor investigated in detail. Here, we suggest that the TRU resin is capable of capturing and retaining Th ions permanently. Only after preloading the column, i.e. occupying the permanent ion traps, we achieve an accurate separation.

3.2. U and Th elution

Upon preloading of the column the behavior of TRU resin in the built-in UTh column under treatment with the reagents R1–R3 used in the protocol was further tested with the solution containing 1 μg g^{-1} ^{232}Th and 1 μg g^{-1} ^{238}U. After the matrix washout, both elements were eluted in steps of 0.2 ml, which corresponds to one column volume (CV). The elution profile (Fig. 3) clearly shows the sequential elution of both elements with the different reagents. The matrix washout step with 1.5 M HNO$_3$ does not affect either Th or U, but both elements are retained within the resin. With the use of reagent R1 (1 M HCl + 0.1 M HF), the Th fraction is completely eluted within only 3 CV (0.6 ml). Switching to reagent R2 (0.1 M HCl + 1 M HF), U is eluted from the resin with 4 CV. Both elements can thus be effectively separated from each other. The total chemical yield achieved with this protocol is about 95% for Th and U, respectively.

3.3. Sample carry-over effect

To prove that the Th and U atoms are not released from the resin again and hence lead to a high memory effect, aliquots of coral samples were processed with the saturated column and with manual drip chromatography, respectively. Here, the manual protocol closely followed the one described in Douville et al. (2010), i.e. UTEVA resin was used. The potential sample carryover arising from the reuse of the same column was determined by processing the previously mentioned 1 μg g^{-1} Th-U solution on the preloaded column, directly followed by a Blank. Blanks consisted only of R3 (1.5 M HNO$_3$). Comparing the Th and U concentration in the Blank with that of the previously processed solution, a sample carryover of 0.031 ± 0.004‰ for Th and 2.3 ± 0.1‰ for U (with respect to the 1 μg g^{-1} solution) was determined. While the carryover of Th can be neglected as it is significantly lower than measurement uncertainties, the one for U has to be taken into account if samples with largely differing U concentrations are processed successively. In this work, however, only cold-water coral

samples were processed with the ACES, which all revealed U concentrations between 3 and 4.5 μg g^{-1} and similar isotopic compositions. Considering a sample with 4.5 μg g^{-1} U being processed previous to one containing 3 μg g^{-1} U, a net increase of 0.0035 μg g^{-1} in the U content is estimated. This does not induce a significant deviation of the calculated U-series age. In addition, the sample carryover was found to be reducible by more extensive column cleaning with R1 and R2 prior to the next sample processing.

Analytical blank levels achieved with the ACES are comparable to the manual drip chromatography after repeatedly flushing the system with acid to reduce the memory effect from the previous sample. For Th and U, average blank values of 0.15 pg and 0.5 pg, respectively, were measured for a typical sample of 50 mg.

3.4. Column lifetime and reproducibility

The performance of the ACES was tested on 34 cold-water coral samples, of which five samples were additionally replicated, leading to a total of 39 cold-water corals used for the evaluation of the developed U-Th separation method. The corals span a measured age range between 500 and 34,000 years. The U concentrations of the coral samples and the U isotopic composition are rather similar from one sample to another, whereas the ^{230}Th content varies by three orders of magnitude. Total Th chemical yields range between 75% and 100% (Fig. 4, upper graph), with a mean value of 90 ± 6%. For U, the measured values range between 85% and 95% which results in an average U yield of 89 ± 4% (Fig. 4, lower graph). The consecutive use of the same column does not show any change in the achieved yields and the Th carryover effect is negligible, as assessed with Blanks measured in between samples. Additionally, samples were processed from larger to smaller core depths, i.e. from expected older to younger ages, corresponding to an increasing ^{230}Th content. Nevertheless, U shows a weak increase in the Blanks related to the carry-over effect from 0.02 to 0.1 ng, which however remains insignificant regarding the ~150 ng U loaded per sample. In addition, further cleaning of the columns after the series of samples reset the Blank to its lowest value prior to the treatment of the 39 samples. Finally, regarding the lifetime of the column and resin, we have passed a total number of ~140 samples and standards over the first UTh column with no significant change of its properties or the quality of Th and U purification. The second column was used only to test the need for pre-loading to conduct high-precision measurements on a largely virgin column. Hence, we have not yet sufficient data to accurately determine the lifetime of the column, but presume that several hundred samples may be processed prior to column exchange. Note here that the top of the column where the
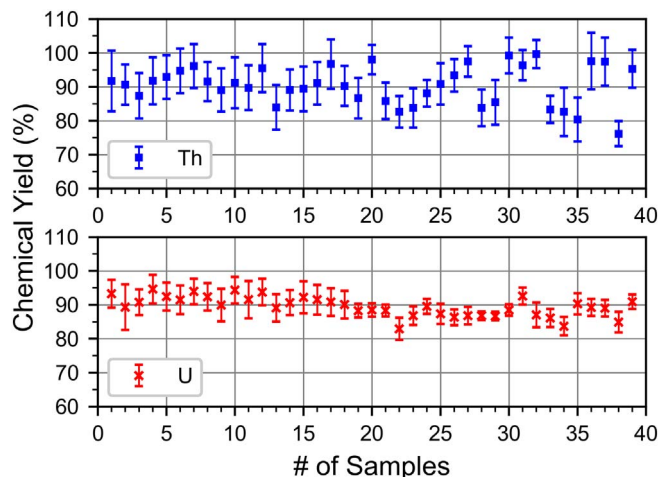

Fig. 4. Th and U yield of 39 cold-water coral samples processed successively with ACES. On average, a Th yield of 90 ± 6% and a U yield of 89 ± 4% was achieved.

sample is dispatched from the sample loop shows some brownish deposits upon the use of a large amount of samples. This is most likely due to the deposition of traces of colloids or suspended non-carbonate materials that remain in solution after dissolution of the carbonate.

3.5. Matrix removal

For analyzing Th and U solutions in an ICP-MS source, the remaining matrix concentration must be reduced to a minimum level. Resulting from the calcium carbonate skeleton of cold-water corals, Ca is the major matrix element that has to be considered. According to Douville et al. (2010) $< 1\,\mu g\,g^{-1}$ Ca is sufficient to avoid loss of sensitivity and cloaking of the sample and skimmer cones of ICP-MS instruments. In order to determine the matrix removal efficiency of the ACES method, the eluted Th and U fractions were merged, adjusted to a total volume of 2.4 ml and the Ca concentration was determined using the ICP-QMS with appropriate certified standards. In all cases, the Ca concentration was below $1\,\mu g\,g^{-1}$, corresponding to a maximum of 2.4 µg Ca in the extracted sample solution. Concerning a typical coral sample with 50 mg and assuming pure $CaCO_3$, 20 mg of Ca are loaded onto the column during each separation. This implies that the Ca concentration is reduced by a factor of 10^4.

3.6. Comparing ACES and manual method

Regarding the time spent for the preparation of 34 coral samples with the manual protocol on one hand and the ACES on the other hand, the significant decrease in laboratory work by the use of the ACES becomes clear. For the automated protocol, about 1 h of work is required for the preparation of the system, including the placement of the samples, the desired reagents and tubes for the eluted fractions. Once the automated extraction procedure has been started, it may only be necessary to fill up reagents in between or to empty the waste container, depending on the number of processed samples. These steps only take a few minutes, however. In contrast, the manual preparation of 34 samples was carried out in two batches of 17 samples each, with about 5 h of laboratory work required per batch.

The ultimate test of the developed ACES protocol is a direct comparison with conventionally prepared samples via manual column chromatography using UTEVA resin (Douville et al., 2010). It was performed on the basis of 34 cold-water coral samples and yielded results in very good agreement, regarding elemental concentrations and isotopic compositions (Table 3). An Age – Age plot of the 34 U-series ages (Fig. 5.1) reveals an excellent linear correlation with an r^2 of 0.999. The corresponding residuals scatter around zero and do not reveal systematic offsets (Fig. 5.2). Hence, ages obtained using manual preparation employing individual columns per sample yield identical results to the ACES.

This observation also holds for individual isotope ratios used to determine coral ages (Table 3). Overall the data is of high quality with ^{238}U concentrations being in typical ranges for L. *pertusa* corals (~ 2.9–$4.3\,\mu g\,g^{-1}$), ^{232}Th concentrations are on average $< 1\,ng\,g^{-1}$, yielding ($^{230}Th/^{232}Th$) activity ratios of 75 for the youngest sample and > 1000 on average. Hence, age corrections based on initial ^{230}Th derived from seawater are mostly negligible, with the exception of the youngest coral for which this correction amounts to 10% using a seawater ($^{230}Th/^{232}Th$) ratio of 8 ± 4. The initial $\delta^{234}U$ ratio, expressed as the ‰-deviation from secular equilibrium, was reproduced to a relative external precision of $< 1‰$ in both methods and yields values similar to the one expected for the global mean ocean. Corals of ages up to 13,000 years BP (before present, present = 1950) reveal initial $\delta^{234}U$ values identical to modern seawater of $146.8 \pm 0.1‰$ (Andersen et al., 2010), $146.7 \pm 0.4‰$ with manual preparation and $146.8 \pm 0.5‰$ with ACES, whereas last glacial values are lower by on average 6–7‰, with mean values of $140.6 \pm 0.9‰$ and $139.7 \pm 1.7‰$ for both preparations, respectively. Those lower values are in good agreement

with a previously documented decrease of global seawater U isotopic composition (Chen et al., 2016; Esat and Yokoyama, 2010, 2006; Reimer et al., 2009). However, this depletion carries unique novel insights to the oceanic U cycle and links to a sluggish northern-southern hemisphere exchange of U during the last glacial that will be subject of further studies.

The obtained ages indicate that coral mound formation off Angola took place at least since the last glacial period until today. The 9.8 m-long core record shows several recurring periods of increased mound aggradation, indicative of locally dense coral populations (Frank et al., 2009) (Fig. 6), followed by periods of locally reduced coral occurrence displayed in a significant decrease of the mound aggradation rate. Coral mound aggradation rates calculated for the Scary Mound vary between 200 cm kyr^{-1} and 0–15 cm kyr^{-1} (Fig. 6), whereas the low rates are indicative of a slowdown or even temporary stagnation in mound aggradation. These values are comparable to previously observed coral mound accumulation rates in other regions such as the north-eastern Atlantic, Mediterranean Sea or South Atlantic off Brazil (Douarin et al., 2014; Douville et al., 2010; Eisele et al., 2014; Frank et al., 2011, 2009; López Correa et al., 2012; Mangini et al., 2010; Matos et al., 2015; Wienberg et al., 2010). The quality of the developed analytical procedure is attested by the overall decreasing ages towards the top. This implies that corals at the Angolan Margin have been present most of the time during the last 34,000 years, however with a potential period of significantly reduced or even absent coral cover between 13,000 and 19,000 years BP. This period may indicate a dramatic environmental change of coral habitats off Angola. Nevertheless, in contrast to observations off Mauritania and the Gulf of Cadiz, where coral mounds predominantly evolved during glacial climate periods (Eisele et al., 2011; Frank et al., 2011; Wienberg et al., 2010), the temperate southeast Atlantic reveals balanced growth during both glacial and interglacial periods and is as such a unique cold-water coral habitat at present. Details about past coral occurrence and mound aggradation along the Angolan margin in relation to environmental change will be subject of further studies. The here demonstrated technique of automated high-quality sample preparation using ACES for U-series dating via MC-ICP-MS revealed a first unique finding regarding coral developments off Angola and will allow for efficient preparation of fossil corals in the future to tackle further scientific questions.

4. Conclusions

The tested and optimized automated U and Th extraction system yields overall identical chemical purification and analytical yields as well as precision and accuracy compared to conventional chemical preparation methods for high-precision U-series dating (Cheng et al., 2000a; Douville et al., 2010; Fietzke et al., 2005; Frank et al., 2004; McCulloch et al., 2010; Yu et al., 2006). Previously developed methods make use of various kinds of ion exchange resins and eluent acids, in cases including Ca removal in an iron co-precipitation step. Such extraction methods are available since the late 80's and have been further developed to ultimately provide the highest quality age data of speleothems, corals and other secondary carbonates. In recent years several attempts to conduct chemistry using automated systems have been successful. Interestingly, we observed a lack of Th and U recovery for first-use (virgin) UTh ion exchange columns provided by ESI. Accurate separation of Th and U was only achieved after pre-loading the column. The carry-over effect is negligible for Th, while U is released from the resin leading to a minor carry-over effect.

Systematically high chemical yields are achieved when processing samples subsequently with the same column. Cold-water corals typically reveal U concentrations of a few $\mu g\,g^{-1}$, whereas the Th concentrations lie around a few ng g^{-1}, thus three orders of magnitude lower. After the column had been loaded with $1\,\mu g\,g^{-1}$ Th and U, respectively, the chemical yield was about 90% for both Th and U.

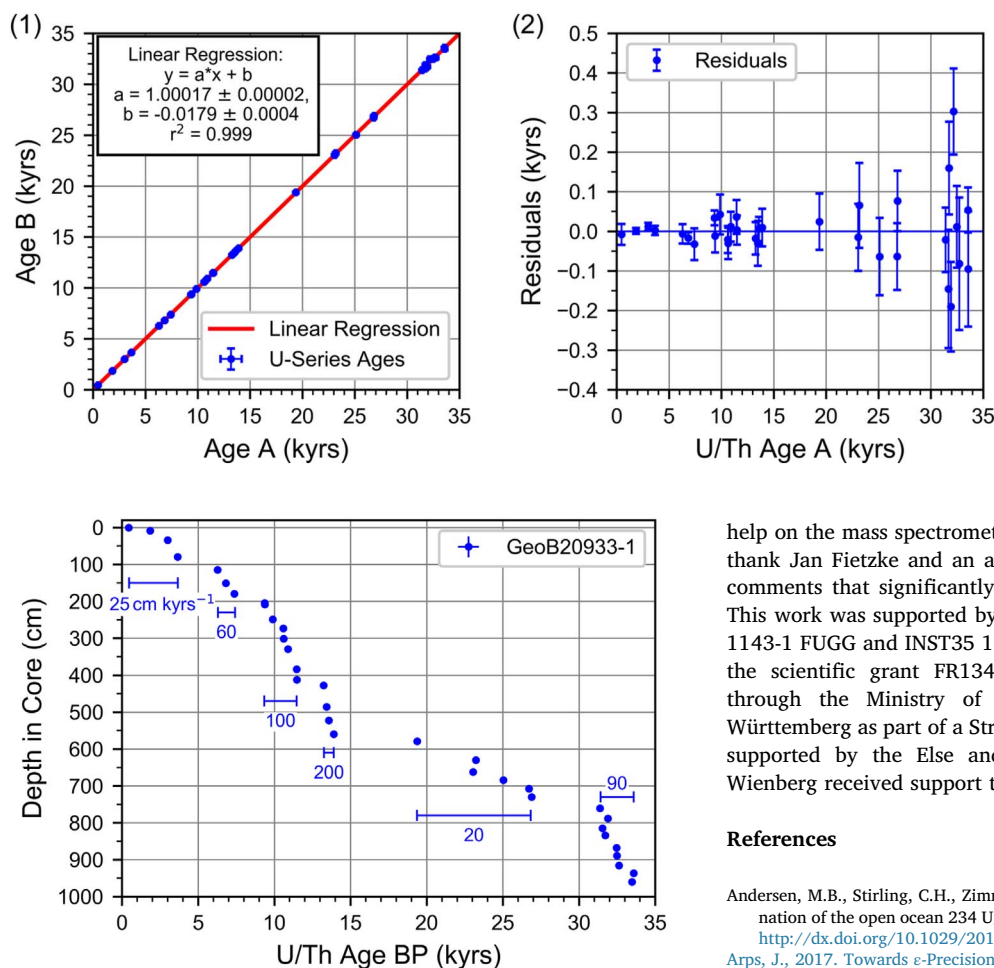The application of the ACES offers numerous advantages over

Table 3

Elemental concentrations, isotopic compositions and corresponding U-series ages for 34 cold-water corals from GeoB20933-1. All uncertainties are 2σ. A are results from manual preparation, B are results from ACES preparation. Age is the corrected U-series age according to Cheng et al. (2000a), for the initial $^{230}Th/^{232}Th$ a value of 8 ± 4 was assumed. Half-lives used for the calculation of the ages are taken from Cheng et al. (2000b), $T_{1/2,230} = 75{,}690$ yrs. and $T_{1/2,234} = 245{,}250$ yrs. All samples were measured at the Institute of Environmental Physics, Heidelberg University, from September to November 2016.

Lab #	Depth (cm)	^{238}U (µg g⁻¹) A	±	B	±	^{232}Th (ng g⁻¹) A	±	B	$^{230}Th/^{238}U$ (activity ratio) A	±	B	±	$\delta^{234}U$ (‰) A	±	B	±	Age (kyrs) A	±	B	±
7917	0.5	3.4998	±0.0001	3.4997	±0.0001	0.7978	±0.0016	0.7345	0.0055	±0.0001	0.0052	±0.0001	146.1	±0.4	146.5	±0.4	0.465	±0.029	0.445	±0.026
7918	8.5	3.2945	±0.0001	3.2959	±0.0001	0.1131	±0.0003	0.1140	0.0195	±0.0001	0.0193	±0.0001	146.2	±0.6	145.5	±0.7	1.862	±0.007	1.845	±0.008
7919	34.0	4.1428	±0.0001	4.1436	±0.0001	0.2193	±0.0004	0.2091	0.0313	±0.0001	0.0313	±0.0001	145.3	±0.3	146.4	±1.7	3.014	±0.012	3.007	±0.011
7920	79.5	3.3365	±0.0001	3.3405	±0.0001	0.1798	±0.0004	0.1407	0.0380	±0.0001	0.0379	±0.0001	145.5	±0.5	146.4	±1.5	3.669	±0.014	3.658	±0.012
7921	114.5	3.6818	±0.0001	3.6826	±0.0001	0.7511	±0.0014	0.6382	0.0648	±0.0002	0.0645	±0.0002	145.5	±0.4	145.1	±0.7	6.305	±0.032	6.282	±0.025
7922	151.0	3.9610	±0.0001	3.9604	±0.0001	0.1864	±0.0003	0.1729	0.0697	±0.0002	0.0696	±0.0002	143.9	±0.5	146.0	±1.5	6.848	±0.017	6.823	±0.017
7923	179.5	2.9020	±0.0001	2.9073	±0.0001	0.9476	±0.0017	0.8536	0.0761	±0.0002	0.0757	±0.0008	144.9	±1.0	145.6	±0.4	7.424	±0.047	7.378	±0.040
7924	204.5	4.2098	±0.0012	4.2050	±0.0001	0.3014	±0.0007	0.2780	0.0940	±0.0002	0.0943	±0.0004	142.5	±0.5	143.2	±0.7	9.345	±0.024	9.366	±0.019
7925	208.5	4.2889	±0.0001	4.2889	±0.0001	1.4397	±0.0026	1.2946	0.0952	±0.0002	0.0951	±0.0015	143.4	±0.5	144.2	±0.5	9.396	±0.049	9.381	±0.041
7926	249.0	3.8309	±0.0001	3.8328	±0.0001	1.6244	±0.0029	1.4764	0.1000	±0.0002	0.1002	±0.0012	143.1	±0.5	143.3	±1.4	9.874	±0.059	9.905	±0.051
7927	273.0	3.7822	±0.0001	3.7958	±0.0009	0.4988	±0.0010	0.5964	0.1064	±0.0003	0.1061	±0.0014	142.8	±0.5	141.9	±2.0	10.617	±0.032	10.593	±0.039
7928	301.5	3.2610	±0.0001	3.2667	±0.0001	0.5768	±0.0011	0.6520	0.1069	±0.0003	0.1065	±0.0013	142.5	±0.7	141.8	±1.2	10.663	±0.037	10.623	±0.041
7929	329.5	4.2511	±0.0001	4.2466	±0.0001	0.8629	±0.0015	0.9144	0.1092	±0.0003	0.1092	±0.0015	141.7	±0.8	141.5	±1.1	10.903	±0.038	10.906	±0.039
7930	384.0	4.0354	±0.0001	4.0373	±0.0001	0.3357	±0.0006	0.3843	0.1144	±0.0003	0.1144	±0.0009	142.0	±0.4	141.8	±1.4	11.483	±0.032	11.478	±0.040
7931	412.5	3.8623	±0.0001	3.8645	±0.0002	0.6794	±0.0013	0.7210	0.1144	±0.0003	0.1146	±0.0016	141.7	±0.6	140.9	±1.0	11.464	±0.039	11.491	±0.043
7932	428.0	3.9791	±0.0001	3.9784	±0.0001	0.7737	±0.0013	0.8234	0.1310	±0.0003	0.1310	±0.0017	139.6	±1.2	140.3	±0.5	13.259	±0.041	13.239	±0.041
7933	486.0	2.9177	±0.0001	2.9228	±0.0001	0.6928	±0.0011	0.7433	0.1333	±0.0003	0.1330	±0.0017	140.1	±1.1	140.0	±0.7	13.485	±0.046	13.447	±0.056
7934	522.5	3.2602	±0.0001	3.2618	±0.0001	0.5825	±0.0012	0.5281	0.1342	±0.0004	0.1342	±0.0005	140.5	±0.6	142.7	±2.1	13.592	±0.045	13.591	±0.039
7935	560.0	3.1546	±0.0001	3.1542	±0.0001	0.3586	±0.0007	0.3988	0.1367	±0.0003	0.1369	±0.0011	139.3	±1.0	139.4	±0.6	13.896	±0.042	13.907	±0.047
7936	579.5	3.7280	±0.0001	3.7261	±0.0001	0.4926	±0.0007	0.5315	0.1853	±0.0005	0.1857	±0.0016	135.1	±0.9	135.6	±0.6	19.356	±0.046	19.389	±0.070
7937	630.0	3.8634	±0.0001	3.8638	±0.0001	2.3470	±0.0049	2.4640	0.2188	±0.0005	0.2194	±0.0057	132.7	±0.7	132.5	±0.6	23.184	±0.094	23.255	±0.108
7938	662.5	3.5047	±0.0001	3.5050	±0.0001	1.1640	±0.0022	1.2274	0.2174	±0.0005	0.2176	±0.0026	133.5	±1.0	134.6	±0.5	23.070	±0.081	23.064	±0.084
7939	684.5	3.5585	±0.0001	3.5607	±0.0001	1.4368	±0.0023	1.5321	0.2344	±0.0005	0.2341	±0.0037	132.6	±0.4	132.8	±1.0	25.109	±0.081	25.058	±0.099
7940	708.0	3.6685	±0.0001	3.6667	±0.0001	2.3213	±0.0042	2.2247	0.2485	±0.0005	0.2486	±0.0018	131.6	±0.4	134.0	±2.6	26.786	±0.102	26.741	±0.110
7941	730.0	3.4141	±0.0001	3.4158	±0.0001	0.6046	±0.0010	0.6366	0.2480	±0.0005	0.2481	±0.0014	131.9	±1.1	128.9	±1.0	26.826	±0.069	26.921	±0.080
7942	761.0	3.9654	±0.0001	3.9651	±0.0001	0.5635	±0.0013	0.5895	0.2837	±0.0007	0.2834	±0.0011	128.2	±0.4	127.1	±1.3	31.407	±0.097	31.410	±0.092
7943	788.5	3.9217	±0.0001	3.9219	±0.0001	1.9592	±0.0066	2.0213	0.2871	±0.0009	0.2884	±0.0050	128.9	±0.6	128.2	±1.2	31.737	±0.134	31.921	±0.123
7944	815.0	3.5182	±0.0001	3.5242	±0.0001	2.7824	±0.0056	2.8573	0.2872	±0.0007	0.2861	±0.0073	128.4	±0.7	127.8	±0.6	31.688	±0.134	31.566	±0.147
7945	834.5	3.5848	±0.0001	3.6150	±0.0001	1.3487	±0.0024	1.4903	0.2879	±0.0006	0.2858	±0.0038	127.4	±0.5	124.0	±3.1	31.919	±0.088	31.751	±0.156
7946	868.0	3.7649	±0.0001	3.7656	±0.0001	0.8825	±0.0022	0.9449	0.2894	±0.0011	0.2902	±0.0027	126.8	±0.5	120.3	±2.1	32.169	±0.140	32.495	±0.130
7947	889.5	3.8120	±0.0001	3.8142	±0.0001	1.2962	±0.0020	1.3503	0.2921	±0.0005	0.2922	±0.0033	126.9	±0.4	126.0	±0.6	32.524	±0.074	32.524	±0.105
7948	916.0	3.0770	±0.0001	3.0803	±0.0001	2.8950	±0.0052	2.9940	0.2953	±0.0006	0.2947	±0.0078	127.8	±0.5	126.9	±0.5	32.722	±0.142	32.661	±0.167
7949	937.0	3.4565	±0.0001	3.4554	±0.0001	0.8571	±0.0015	0.7998	0.2998	±0.0006	0.3004	±0.0009	125.7	±0.7	125.9	±0.3	33.547	±0.092	33.628	±0.056
7950	960.0	4.1955	±0.0001	4.1936	±0.0001	0.4442	±0.0008	0.4888	0.2997	±0.0006	0.2994	±0.0017	125.5	±0.8	126.4	±1.0	33.580	±0.085	33.509	±0.150

Fig. 5. (1) Age-age plot and linear regression for the 34 coral samples from GeoB20933-1. "Age A" refers to the U-series ages resulting from manual sample preparation, "Age B" refers to the ACES preparation. Error bars correspond to 2σ-uncertainties, but are smaller than the marker size. (2) Residuals resulting from the linear regression scatter around zero, suggesting that no systematic offset occurs between method A and method B.
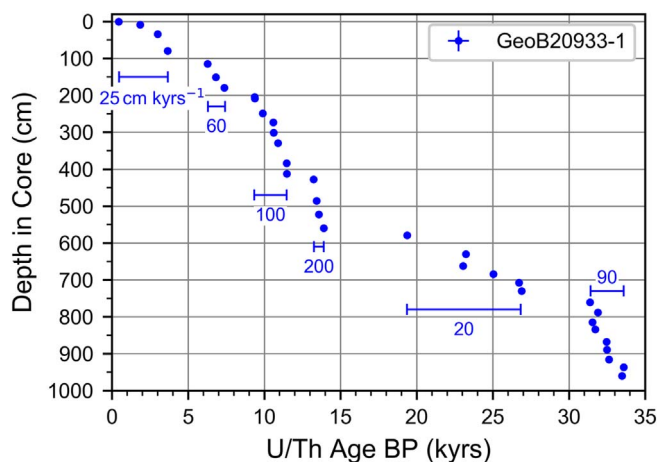

Fig. 6. Depth-age relation for sediment core GeoB20933-1. Ages are displayed in kyrs BP (thousand years before present, present = 1950). Blue numbers denote vertical mound accumulation rates for different time periods, given in cm per kyrs. Error bars correspond to 2σ-uncertainties, but are smaller than the marker size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

manual laboratory work. Using a pre-configured protocol guarantees the identical treatment of samples and reduces the risk of manually induced errors and uncertainties. An outstanding benefit of the automated procedure is the decrease in laboratory work required for the time-consuming conventional protocol, and the resulting increase of the sample throughput. This should allow for the generation of large datasets of U-series ages with minimal effort and a robust setup, which even bears the potential to be carried out in conventional laboratory environments or coupled directly to ICP-MS sources.

Our study focused on the chronology of past cold-water coral occurrence, but the protocol could be easily adjusted for different types of samples, such as speleothems, carbonate crusts or water samples. It therefore also provides efficient U and Th purification for a number of different objects of interest, apart from U-series dating, for instance U isotopic measurements in ocean water.

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