



Precision measurement of $\delta^{234}\text{U}$ in annually banded tropical corals

Sahra Greve¹, Norbert Frank^{1,2}, Sophie Warken^{1,2}, Paolo Montagna^{3,4}, Amos Winter⁵, Serguei Damián Rico-Esenaro^{6,7}, Juan P. Carricart-Ganivet⁶, Joan-Albert Sanchez-Cabeza⁸, Ana Carolina Ruiz-Fernández⁸, Carlos Alonso-Hernández⁹, Miguel Gomez-Batista¹⁰, Marco Taviani^{4,11}, Steffen Hetzinger¹²

5 ¹Institute of Environmental Physics, Heidelberg University, 69120 Heidelberg, Germany

²Institute of Earth Science, Heidelberg University, 69120 Heidelberg, Germany

³Institute of Polar Sciences, ISP-CNR, Via Gobetti 101, 40129, Bologna, Italy

⁴Stazione Zoologica ‘Anton Dohrn’, Naples, Italy

⁵Department of Earth and Environmental Systems, Indiana State University, Terre Haute, IN USA

10 ⁶Laboratorio de Esclerocronología de Corales Arrecifales, Unidad Académica de Sistemas Arrecifales, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México, Puerto Morelos, Q. Roo 77580, México

⁷Departamento El Hombre y su Ambiente, Universidad Autónoma Metropolitana Unidad Xochimilco, Coyoacán, Cd. de México 04960, México

⁸Unidad Académica Mazatlán, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México, 82040

15 Mazatlán, Mexico

⁹IAEA Marine Environment Laboratories 4 Quai Antoine 1er, MC-98000 Monaco, Principality of Monaco

¹⁰Centro de Estudios Ambientales de Cienfuegos (CEAC), Cienfuegos, Cuba

¹¹Institute of Marine Sciences, ISMAR-CNR, Via Gobetti 101, 40129, Bologna, Italy

¹²Christian-Albrechts-Universität zu Kiel, Institut für Geowissenschaften, Kiel, Germany

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Correspondence to: Sahra Greve (sgreve@iup.uni-heidelberg.de)

Abstract. Tropical corals preserve geochemical $^{238}\text{U}/^{234}\text{U}$ ratios that provide valuable records of past seawater uranium isotope compositions. Variations in the coral skeletons and thus seawater are likely indicative of freshwater contributions from submerged groundwater discharge and river runoff, or reflecting coral diagenesis. Advances in multi-collector ICP-MS allow
25 precise determinations of $^{238}\text{U}/^{234}\text{U}$ ratios, enabling the reconstruction of subtle (typically $>1\%$) environmental changes in these marine records. In this study, we evaluate the reliability of coral-based $\delta^{234}\text{U}$ records across multiple genera, sampling strategies, and intra-skeletal variability. Analyses of reference material NBS-CRM-112A demonstrate reproducibility within $\pm 0.4\%$. Replicate sampling across coral structures and colonies indicates measurable intra-band heterogeneity ($\pm 0.6\%$),
30 although local hydrodynamics and submarine groundwater discharge can introduce small inter-colony offsets. No species-dependent isotope fractionation was detected, underscoring the robustness of $\delta^{234}\text{U}$ as a geochemical proxy. These findings demonstrate that coral skeletons provide reliable archives of up to sub-annual $\delta^{234}\text{U}_{\text{sw}}$ for detecting subtle climatic and hydrological signals.

1 Introduction

35 Geochemical element and isotope composition of tropical coral skeletons serve as robust archives of environmental reconstructions (Druffel, 1997). Coral based climate reconstructions with up to weekly resolution span over timescales ranging



from decades to centuries and even millennia (Tierney et al., 2015). It is well appreciated that aragonite coral skeletal U/Ca ratios provide results that are very close to that of seawater. However, these may be modulated by temperature, carbonate ion concentration, and even salinity (Ourbak et al., 2006). U/Ca ratios can vary by more than 30% on annual time scales. In contrast, negligible isotope fractionation occurs as U is transferred from the seawater into the coral aragonite (Chen et al., 2018). Contemporary studies have shown that $\delta^{234}\text{U}$ values in pristine coral skeletons reflect the $\delta^{234}\text{U}$ composition of ambient seawater ($\delta^{234}\text{U}_{\text{sw}}$) at the time of coral growth (Gallup et al., 1994; Henderson, 2002; Esat & Yokoyama, 2006, 2010; Wang et al., 2017; Kipp et al., 2022; Li et al., 2023) although freshwater discharge, whether from rivers or submarine groundwater modulate locally and regionally the oceans $^{234}\text{U}/^{238}\text{U}$ activity ratio. Typically, the U concentration is diluted (reduced) by freshwater, while the $^{234}\text{U}/^{238}\text{U}$ activity ratio, today given as permille deviation from radioactive equilibrium $\delta^{234}\text{U}$, increases in most cases (Dunk et al., 2002). Consequently, tropical coral $\delta^{234}\text{U}$ ratios of modern or fossil specimens are often more variable than the open ocean $\delta^{234}\text{U}$ ratio (Chutcharavan et al., 2018), which has recently been reassessed as $145.55 \pm 0.28 \text{ ‰}$ (Wang et al., 2017; Kipp et al., 2022; Li et al., 2023). Lastly, understanding U isotopes and their decay products contribute important information regarding the precision and accuracy of the $^{230}\text{Th}/\text{U}$ - disequilibrium dating system. This requires U series closed system behaviour and the absence of initial ^{230}Th . Tropical coral α - recoil displacement of ^{234}Th (^{234}U) and ^{230}Th , as well as skeleton diagenesis cause coupled and time dependent variance of reconstructed initial $\delta^{234}\text{U}$ ratios of corals (Thompson et al., 2003; Villemant & Feuillet, 2003; Scholz et al., 2004). In this context, $\delta^{234}\text{U}$ has been used as a screening tool for diagenetic alteration, with values deviating significantly from modern seawater ($\sim 145.55 \text{ ‰}$) indicating potential U-series open-system behaviour and unreliable age determinations (Henderson et al., 1993; Gallup et al., 1994; Thompson et al., 2003; Scholz et al., 2004; Frank et al., 2006; Chutcharavan et al., 2018). In summary, any significant deviation of a tropical corals initial $\delta^{234}\text{U}$ with respect to seawater must be related to (i) influences of freshwater, (2) coral diagenesis, and (3) U-series open system behaviour has provided new opportunities to use $\delta^{234}\text{U}$ in well-preserved tropical and deep-sea corals to infer ice-volume influences on the global ocean $\delta^{234}\text{U}$ composition (Robinson et al., 2004a; Esat & Yokoyama, 2006, 2010; Chutcharavan et al., 2018). Moreover, the freshwater influence on the regional $\delta^{234}\text{U}$ composition has made it possible to reconstruct deglacial freshwater injection into the North Atlantic and submerged meltwater discharge into the Southern Ocean (Cheng et al., 2013; Li et al., 2023). Thus, the ocean $\delta^{234}\text{U}$ composition through time has become an important new toolbox. These developments stem from profound technical advancement in recent decades of uranium isotope measurements, which improved from ‰ (Chen et al., 1986) to (sub-)epsilon precision for repeated measurements of near secular equilibrium materials (Kipp et al., 2022; Kerber et al., 2023; Hu et al., 2025). Epsilon precision of U isotope measurements can, however, only be achieved through repeated analysis of the same high U concentration solution of a sample or standard using multi-collector inductively coupled plasma source mass spectrometry (MC-ICP-MS) equipped with multiple high ohmic resistors ($10^{10} - 10^{13} \text{ Ohm}$) accounting for the four orders of magnitude in signal intensity difference between ^{238}U to ^{234}U , and by simultaneously and precisely measuring the instrument's tailing (Kerber et al., 2023; Hu et al., 2025), and also accounting for scattering signals (ghost signal) (Kerber et al., 2023). High precision measurements are typically normalized to uranium



reference materials such as NBS CRM 112A (Cheng et al., 2013; Wang et al., 2017; Kipp et al., 2022; Hu et al., 2025) and
70 Harwell uraninite 1 (HU-1) (Hoffmann et al., 2007; Cheng et al., 2013).

For routine individual measurements of corals and seawater analytical precision is today typically in the order of 3-10 epsilon
(Kipp et al., 2022; Kerber et al., 2023; Li et al., 2023). Precision measurements of tropical and deep-sea corals permit
reconstructing millennial trends in regional seawater at ± 1 to 2‰ (Chutcharavan et al., 2018; Li et al., 2023), while observed
freshwater influences often reach >4 ‰ deviation from such trends (Greve et al., 2026). The fine-scale chronological control
75 provided by annual density banding in tropical corals offers a unique opportunity to resolve past seawater $\delta^{234}\text{U}$ variability at
sub-annual to annual resolution. This capability potentially enables the detailed reconstruction of freshwater fluctuations in
annual $\delta^{234}\text{U}$ time series (Greve et al., 2026). Tropical coral reefs host remarkable biodiversity, and multiple coral genera like
massive *Porites*, *Acropora*, *Siderastrea*, *Montastrea*, and *Orbicella* are commonly used in U/Ca proxy records. Each genus
exhibits distinctive skeletal architectures and growth morphologies, which pose varying analytical challenges due to
80 differences in skeletal densities, porosities, and growth rates (de Villiers et al., 1995; Sadler et al., 2014; Ross et al., 2019).
Moreover, the skeletal architecture can vary not only among genera but also within individual colonies at micro- and
macroscales, potentially affecting geochemical signals and diagenetic alteration pathways (Perrin, 2003; DeLong et al., 2016;
Reed et al., 2021). To validate that $\delta^{234}\text{U}$ values in coral skeletons accurately reflect the $\delta^{234}\text{U}$ composition of ambient seawater,
we conducted a series of methodological tests using various coral genera to determine the quality of $\delta^{234}\text{U}$ measurements.
85 These include (1) assessment of analytical reproducibility using reference materials and repeated measurements of coral
aliquots, (2) procedural replicates of full chemical preparation, and (3) skeletal structure replicates sampled from different
places within the same coral colony. In addition, comparative analyses were conducted (4) across different coral genera and
(5) among individuals of the same species collected from the same reef. Together, these tests provide community-wide
confidence that coral-based $\delta^{234}\text{U}$ records reliably reconstruct, at (sub)annual temporal resolution, local and past seawater
90 uranium isotope compositions.

2 Material and Methods

2.1 Corals samples

For this methodological study several annual banded tropical corals from different species and environments were selected
(Table 1). First, the optimal sample masses were determined between 50 and 100 mg using subsamples from a beached *Porites*
95 *sp.* colony collected at Moruroa Atoll in the Pacific Ocean. A 1 g sample was extracted using a Dremel handheld saw fitted
with a diamond blade. The carbonate was ultrasonically cleaned and dissolved in 7N HNO_3 . This solution was subdivided into
aliquots containing 20, 30, 35, 40, 45, 50, 55, 60, 70, 80, 100, 120, and 150 mg coral material. Each subsample was spiked
with 0.1 ml of TriSpike solution and processed following the procedure described in 2.3. The following tests were conducted
on an *Orbicella faveolata* core to determine the reproducibility. An approximately one-meter-long (97 cm) coral core was
100 collected at a depth of approximately 10 m in March 2016 from the Cayo Santa Maria reef, Cuba (79.10 W, 22.66 N). The



core was dated by sclerochronology using radiographic density images; it exhibited green bands with elevated Mg content, related to the presence of the endolithic green algae *Ostreobium* (Cuny-Guirriec et al., 2019; Alonso-Hernández et al., 2022). To further investigate $\delta^{234}\text{U}$ variability for different coral species from similar local environmental conditions, eleven coral samples were collected at Rancho Luna (Cuba) in 2016 using an underwater drill from ten different live coral colonies co-
 105 occurring within an 800 m² area. The water depth of the corals ranged from 3 to 8 m. The selected species are: *Siderastrea siderea*, *Mycetophyllia lamarckiana*, *Acropora palmata*, *Agaricia agaricites*, *Meandrina meandites*, *Acropora cervicornis*, *Colpophyllia natans* (two cores), *Diploria labyrinthiformis*, *Montastrea cavernosa*, and *Orbicella faveolata*. The upper skeletal portions of each core, corresponding to the years 2015 and part of 2016, were sub-sampled and carefully cleaned mechanically using a Dremel tool to remove any residual organic matter.

110 To investigate the feasibility of sub-annual sampling we selected a 16.7 cm-long core of a live *Pseudodiploria strigosa* colony in 2004 from Los Roques (140 km offshore Venezuela) at 2 m water depth. The coring was again conducted using an underwater drill. The core spans approximately 10 years of coral growth (1995-2004) and was sub-sampled at semi-annual (twice per year) to seasonal resolution. A semi-annual resolution was achieved by taking one sample from a high-density band and one from a low-density band, while seasonal resolution was achieved by subdividing each band and sampling the upper
 115 and lower halves, resulting in 4 samples per year. The age model was established using both X-ray images and alignment with $\delta^{18}\text{O}$ values to a nearby previously dated coral by Hetzinger et al. (2008). To evaluate intra-colony replication of $\delta^{234}\text{U}$ signals across density bands, two *Orbicella annularis* cores were analysed: CPR1990 (60 cm) collected in September 1990 from Pinnacles Reef and TM2020 (90 cm) sampled in December 2020 from Turromote Reefs, La Parguera, Puerto Rico. The chronology of both cores was developed using computed tomography (CT) scans and U-series dating. Nine growth layers were
 120 sampled mechanically twice to assess the reproducibility for a given growth band. To assess the spatial variability of $\delta^{234}\text{U}$ within a single species across a reef, two *Orbicella faveolata* (BOC1 and BOC2) cores were collected in 2016 from La Bocana Reef, Puerto Morelos National Park, Mexican Caribbean (20° 52.490' N, 136 86° 51.044' W) (Rico-Esenaro et al., 2022). We selected this reef because it is heavily influenced by submarine groundwater discharge (SGD), with coastal freshwater fluxes of ~300 m³ day⁻¹ m⁻² (Null et al., 2014). The two 150 cm long cores were extracted two meters apart, within the same reef,
 125 using an underwater hydraulic drill. One-centimetre-thick slabs were cut from each core and radiographed for later age modelling using sclerochronology (Rico-Esenaro et al., 2019; Rico-Esenaro et al., 2022). These cores were also used to assess the impact of different sampling techniques. Two sampling strategies were employed for each growth band: (1) to obtain bulk samples, solid sections were cut from annual density bands using a handheld Dremel tool fitted with a diamond saw blade and (2) finely powdered samples were collected from the same bands by milling along the growth axes.

130 **Table 1: Summary of samples and analytical tests conducted in this study. Listed are reference materials and coral samples analysed for uranium isotope composition ($\delta^{234}\text{U}$) by MC-ICP-MS, including the type of test performed and number of samples measured.**

sample ID	Location	Species	No. of Samples	Purpose	Publications



NBS-CRM-112A			66	Interlab standard consistency	Hu et al., 2025; Wang et al., 2017; Cheng et al., 2013
Seawater Mix			12	Internal standard consistency	
CSM_1	Cayo Santa Maria, Cuba (22°40'N 79°5'W)	<i>Orbicella faveolata</i>	20	Assess measurement reproducibility	Alonso-Hernandez et al., 2022
	Moruroa Atoll, French Polynesia (21°51'50"S 138°53'42"W)	<i>Porites sp.</i>	12	Effect of sample mass on $\delta^{234}\text{U}$ precision	
RL_species name	Rancho Luna, Cuba (22° 1' 53" N 80° 26' 28" W to 22° 0' 56" N 80° 24' 42" W)	<i>Siderastrea siderea</i> , <i>Mycetophyllia lamarckiana</i> , <i>Acropora palmata</i> , <i>Agaricia agaricites</i> , <i>Meandrina meandites</i> , <i>Acropora cervicornis</i> , <i>Colpophyllia natans</i> , <i>Diploria labyrinthiformis</i> , <i>Montastrea cavernosa</i> , and <i>Orbicella faveolata</i>	11	Compare interspecific variability	
ROQ_V	Los Roques, Venezuela (11° 46' 12" N, 66° 45' 0" W)	<i>Pseudodiploria strigosa</i>	26	Semi-annual (twice per year) to seasonal resolution	Hetzinger et al., 2008
CPR1990	La Parguera, Puerto Rico (17°56'07"N 67°01'09"W)	<i>Orbicella annularis</i>	4	Assess intra-skeleton reproducibility	
TM2020	La Parguera, Puerto Rico (17°55'50"N 66°58'26"W)	<i>Orbicella annularis</i>	14	Assess intra-skeleton reproducibility	
BOC1	Puerto Morelos, Mexico (20°52.5'N 86°51'W)	<i>Orbicella faveolata</i>	31	Bulk vs. powder comparison/intra-reef reproducibility	Rico-Esenaro et al., 2019; Rico-Esenaro et al., 2022
BOC2	Puerto Morelos, Mexico (20°52.5'N 86°51'W)	<i>Orbicella faveolata</i>	30	Bulk vs. powder comparison/intra-reef reproducibility	Rico-Esenaro et al., 2019; Rico-Esenaro et al., 2022

2.2 Reference Materials

135 We used an in-house seawater U isotope standard (IUP-SW) as reference material to assess the reproducibility of the mass spectrometric measurements. This standard is composed of eastern Atlantic seawater from various depth and has an isotopic composition, within uncertainty, identical to the open ocean seawater assessed by Kipp et al. (2022). In addition to this standard we made use of an in-house NBS-CRM-112A uranium metal solution (Cheng et al., 2013; Wang et al., 2017; Kipp et al., 2022;



Hu et al., 2025), with a concentration of 50 ppb. This standard was measured at the start and at the end of each sample sequence.
140 All measurements have been conducted with a bracketing standard, namely Harwell uraninite (HU-1) reference material (Hoffmann et al., 2007; Cheng et al., 2013).

2.3 Sample treatment

The separation of uranium from the sample matrix followed the protocol established by Wefing et al. (2017), and modified by Kerber et al. (2023). Between 50 and 100 mg of the coral sample underwent ultrasonic cleaning in MilliQ water and dissolution
145 in 7 M HNO₃. To serve as a concentration reference, 100 µL of TriSpike solution, a mixture of 3.86778 ng/g ²³⁶U, 0.018055 ng/g ²²⁹Th and 0.038556 ng/g ²³³U was added to each sample. About 15 samples and one analytical blank were prepared in the same batch. Uranium was separated from the matrix using an ion exchange columns filled with U/TEVA resin (300 µL bed volume) (Horwitz et al., 1992). Before loading samples, the columns were preconditioned by rinsing three times with 7N HNO₃. Elution was performed subsequently with 3 x 500 µL of 3 M HCl followed by 1 x 500 µL of 1 M HCl. The column
150 chemistry was repeated using the same column to ensure complete separation from Ca, Mg, and other potential matrix elements. Chemical yields are better than 90%. The final uranium fraction was evaporated and then redissolved in 1.2 mL 1 % HNO₃ + 0.05% HF. All samples were centrifuged to remove potential residual particles from the U/TEVA resin before mass spectrometer measurement.

2.4 ICP-MS concentration and calcium assessment

Prior to δ²³⁴U analysis by MC-ICP-MS, a pre-screening routine was conducted using an inductively coupled plasma source quadrupole mass spectrometer (Thermo Fisher iCAP Qs) to determine calcium and uranium concentrations after uranium chemical purification. For each sample, a 50 µL aliquot was diluted 1:10 with 0.5 M HNO₃, and the analysis was performed in standard mode, i.e., not using a collision cell gas. Calcium and uranium concentration standards were frequently analysed to calibrate the ⁴³Ca and ²³⁸U signal intensity and to monitor instrumental drift. Results were corrected for instrumental base
160 line and drift. Samples with calcium concentrations below 10 ppm were deemed sufficient to minimize potential matrix effects in the ICP-MS source and were selected for further δ²³⁴U analysis by MC-ICP-MS. Uranium concentrations of the samples were quantified to dilute samples to uranium concentrations of ~50 ppb matching the concentration of the bracketing standard used in MC-ICP-MS analysis.

2.4 MC-ICP-MS U isotope measurements

165 Static isotopic measurements of ²³³U, ²³⁴U, ²³⁵U, ²³⁶U, and ²³⁸U were performed at the Institute of Environmental Physics, Heidelberg, using a MC-ICP-MS (Thermo Fisher Neptune Plus), coupled to an ARIDUS II desolvating system, equipped with an microflow PFA nebulizer, and an ESI SC-2DX autosampler. The cup configuration and corresponding resistors used are shown in Table 2 and correspond to the first line of the Th and U isotope measurements described in detail in Kerber et al. (2023, 2025). Prior to each analytical sequence composed of an interspaced series of standards, reference materials, blanks



170 and samples, amplifier gains were calibrated. For the 10^{11} Ohm and 10^{10} Ohm resistors we employed the instruments electronic
supplying a constant voltage to the amplifier. Until June 2024 the gain of the 10^{13} resistor was calibrated using a repeated
measurement of $^{235}\text{U}/^{236}\text{U}$ in cup combinations C/H1 and H1/H2. From June 2024 onwards, the MC-ICP-MS instrument was
updated allowing for an electronic gain calibration of the 10^{13} Ohm resistors. In addition, prior to each analytical sequence,
the tailing of mass ^{238}U was assessed using electron multiplier measurements on half-masses (228.5, 233.5, 236.5, 236.7,
175 237.05, and 237.5) (Kerber et al., 2023). In contrast to recent approaches (Hu et al., 2025), the tailing pattern was modelled
using a piecewise cubic Hermite interpolating polynomial (PCHIP), which was found to best reproduce the observed tailing
behaviour (Kerber et al., 2023).

Table 2: Cup configuration and selected amplifier resistor settings

Cup	L1	C	H1	H2	H3
Mass number	233	234	235	236	238
Resistor Ω	10^{11}	10^{13}	10^{11}	10^{11}	10^{10}

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Each sample and standard were measured in static mode over 60 cycles, with an integration time of 4 seconds per cycle.
Between each measurement, the system was rinsed for several minutes with an acid solution (1% HNO_3 + 0.05% HF).
Instrumental noise and solution blank levels were confirmed through measurements before each sample and standard analysis.
Complete chemical procedural blanks were further measured with each series. Data evaluation was performed using a custom
185 Python script developed by the Institute of Environmental Physics for U-Th dating analysis (Kerber et al., 2025). This script
encompasses instrumental background corrections, identification and correction of signal outliers, adjustment for mass bias
accounting for hydride formation, and addressing the above mentioned ^{238}U tailing. Instrumental mass bias was corrected
based on the $^{235}\text{U}/^{238}\text{U}$ ratio, using the natural isotopic ratio reported by Richter et al. (2010) for HU-1 and CRM-112A and by
Kipp et al. (2023) for coral samples. All isotope measurements were normalized to the NBS-CRM-112A standard (Cheng et
190 al., 2013; Wang et al., 2017; Kipp et al., 2022; Hu et al., 2025). The $\delta^{234}\text{U}$ value is reported in permille (‰) and calculated
from the activity ratio using the formula:

$$\delta^{234}\text{U} (\text{‰}) = \left(\frac{A_{234\text{U}}}{A_{238\text{U}}} - 1 \right) * 1000$$

with the decay constants $\lambda_{238} = 1.55125 * 10^{-10}$ (Jaffey et al., 1971) and $\lambda_{234} = 2.82206 * 10^{-6}$ (Cheng et al., 2013). Internal
measurement uncertainties are reported as 2σ standard mean error. Reproducibility of mass spectrometric measurements was
195 assessed through repeated measurements of the reference material NBS-CRM-112A and the inhouse IUP-SW seawater
standard. To ensure interlaboratory comparability, both HU-1 and NBS-CRM-112A standards were routinely analysed. When
assuming a certified reference isotope composition of CRM-112A of -38.5‰ our HU-1 standard implies a mean offset of -
0.9‰ from secular equilibrium material. Analytical performance was assessed through repeated measurements of the NBS-

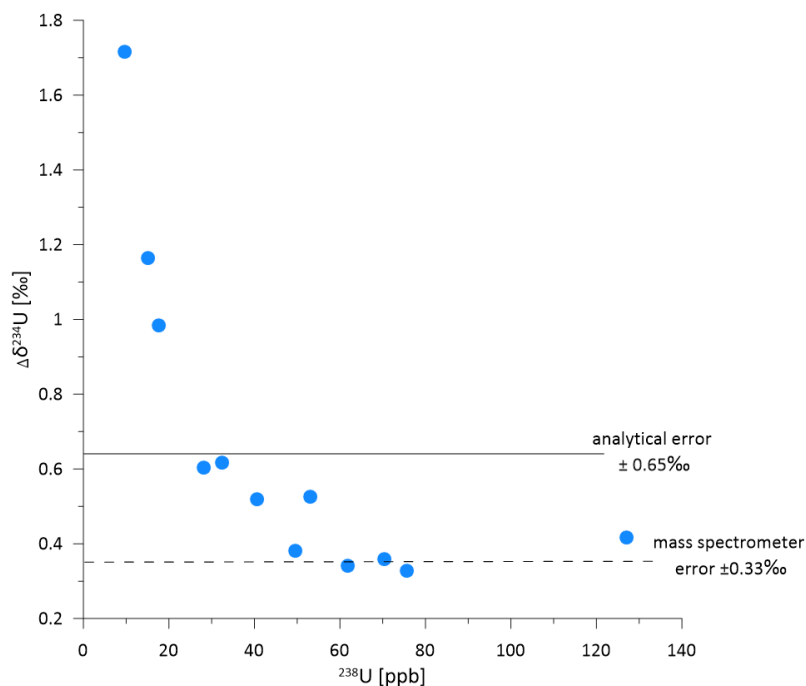


CRM-112A reference material, yielding an external reproducibility of $\pm 0.4\%$, consistent with values reported for established
 200 high-precision $\delta^{234}\text{U}$ methodologies (Wang et al., 2017; Kipp et al., 2022).

3 Results

3.1 Reproducibility

Procedural blanks were measured between each sample and standard. These yielded an average ^{234}U background of 6 cps,
 consistent with Kerber et al. (2025). All chemical blanks ($n = 20$) were below this threshold and are thus negligible. Our
 205 assessment of necessary uranium concentration to yield optimal precision for $\delta^{234}\text{U}$ measurement was conducted with twelve
 coral samples of variable size and thus total uranium concentration. It appears that the measurement uncertainty decreases
 exponentially with increasing U concentration (Figure 1). At concentration levels of >20 ppb in the measured solution, the
 analytical error decreased to $\pm 0.6\%$ and plateaued at $\pm 0.3\%$ for U concentrations >40 ppb, up to the maximum measured
 concentration of 174.4 ppb. Therefore, all measurements were conducted at > 40 ppb in solution.



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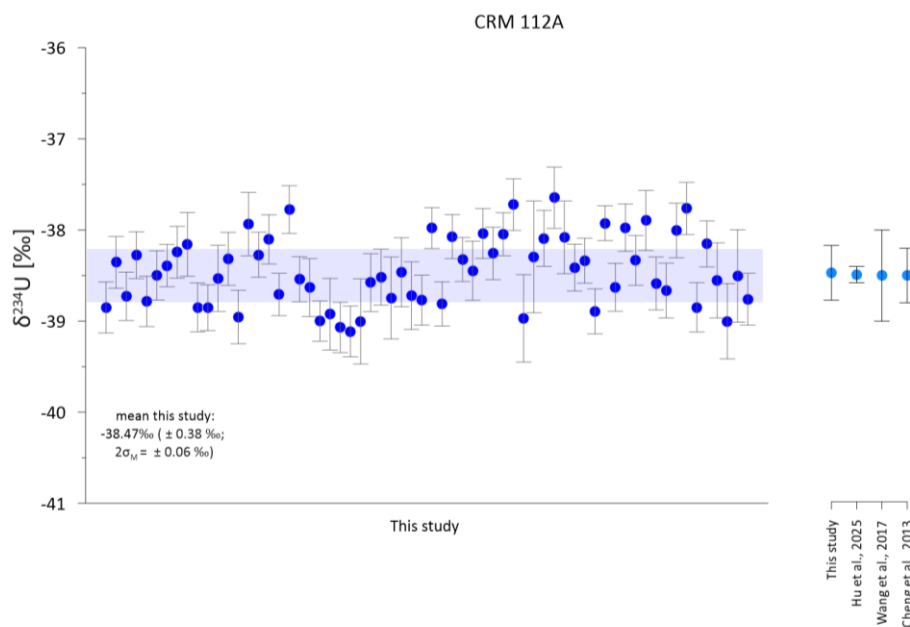
Figure 1: $\delta^{234}\text{U}$ measurement precision against ^{238}U concentrations of 12 coral samples. The error decreases from 1.7‰ to 0.6‰ with a solution containing more than 20 ppb uranium. At concentrations exceeding 40 ppb uranium, the error plateaus at 0.3‰ until the maximum uranium concentration of 128.40 ppb is reached.

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External analytical uncertainty was assessed through repeated measurements of the NBS-CRM-112A standard within each measurement batch. Across 66 analyses, the mean value for CRM-112A was -38.5% with a standard deviation of $\pm 0.4\%$



(Figure 2). These results are consistent with the certified value of CRM-112A. The methodology applied here allows theoretically for ϵ -level precision for $\delta^{234}\text{U}$ measurements (Kipp et al., 2022; Hu et al., 2025) when repeating sample solutions frequently. While our technological setup is identical to the one used by Hu et al. (2025) achieving a similar level of analytical precision with our standard solutions requires prolonged measurements of approximately 2.8 hours per standard, corresponding to ~ 5000 individual scans with 2 s integration time. For coral samples, this would necessitate relatively large sample sizes, thereby limiting temporal resolution. Given the typically larger natural variability in $\delta^{234}\text{U}$ observed in coral records (Greve et al., 2026), such high analytical precision is not critical for the scope of this study, but may become increasingly relevant for future high-resolution investigations. The reproducibility of individual measurements of $\pm 0.42 - 0.60\%$ achieved here is characteristic of well-established precision MC-ICP-MS protocols routinely applied to natural samples, when using a standard bracketing approach and integration time of 4 s and 60 scans, i.e. a total measurement duration of 4 minutes. The reproducibility was also assessed with repeated measurement of an in-house seawater standard, which yields a mean $\delta^{234}\text{U}$ value of 145.7% with a standard deviation of $\pm 0.3\%$, thus comparable precision to NBS-CRM-112A (Figure 3).



230 **Figure 2: 66 measurements of the external NBS-CRM-112A standard in this study yielded a mean $\delta^{234}\text{U}$ of $-38.5\% \pm 0.4\%$, with a $2\sigma_M$ of $\pm 0.06\%$ ($n = 66$), indicating high analytical precision.**

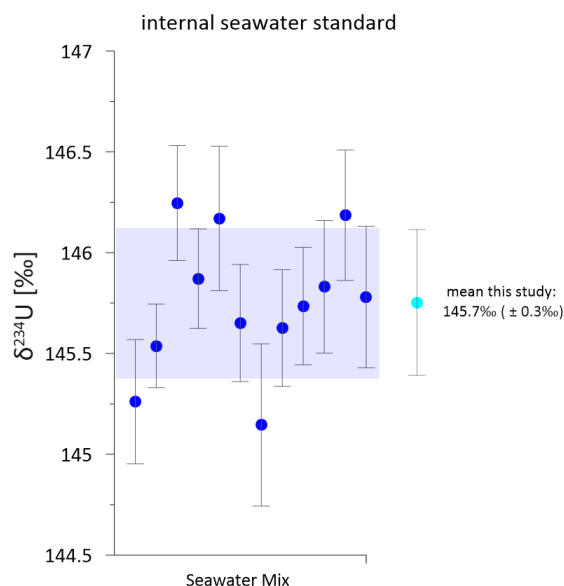


Figure 3: Measurements of the internal seawater U standard yielded a mean $\delta^{234}\text{U}$ of 145.7‰ ± 0.3‰ (n = 12), consistent with expected marine values.

- 235 A total of 20 MC-ICP-MS replicate measurements from individual coral samples were performed, spanning an isotopic range from 144.4‰ to 146.1‰. The overall standard deviation across all these replicates was ±0.3‰, indicating consistency with the repeated measurements of reference material and in-house seawater standard. However, the maximum deviation between individual replicates can reach ±1‰ in some cases (n=3 out of 20) (Figure 4a). Figure 4b shows nine additional full sample replicates for $\delta^{234}\text{U}$ measurements performed on aliquots of the TM2020 *Orbicella annularis* coral samples from Puerto Rico.
- 240 These replicates comprise pairs of subsamples taken from the same growth band but from different spatial positions within the skeletal structure. These measurements yield an isotopic range of $\delta^{234}\text{U}$ from 144.5‰ to 147.1‰, with a resulting standard deviation of ±0.6‰ (n = 9) (Figure 4).

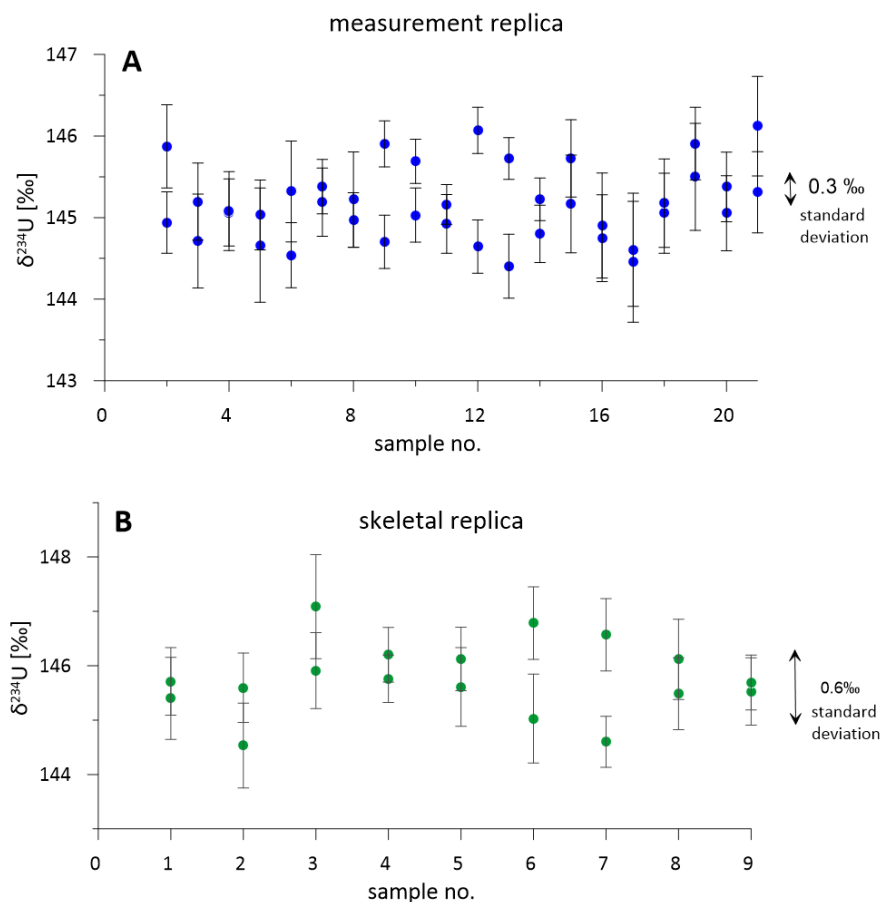


Figure 4: A: 20 replicate measurements of $\delta^{234}\text{U}$, with values ranging from 144.4‰ to 146.1‰. The standard deviation across all samples was 0.3‰. The maximum difference between replicate pairs was 1‰, resulting in an uncertainty of 0.5‰ for individual points. B: Nine chemical replicates from the same growth band of the Puerto Rico coral yielded $\delta^{234}\text{U}$ values from 144.5‰ to 147.1‰, with 0.6‰ standard deviation among replicates.

3.3 Temporal resolution

250 The $\delta^{234}\text{U}$ values measured from the *Pseudodiploria strigosa* core at both semi-annual and seasonal resolution are presented in Figure 5a. Semi-annual $\delta^{234}\text{U}$ values ranged from approximately 143‰ to 148‰ over the period 1996–2002. Seasonal measurements exhibit a similar range, from ~142‰ to 148‰, but capture finer intra-annual variability that is not evident in the lower-resolution dataset. To assess the effect of sampling resolution, a relative deviation was calculated between each semi-annual sample and the mean of its corresponding seasonal samples. These residuals are also plotted in Figure 5a and
 255 generally are $< \pm 2\%$. From 1996 to 1999 the deviation between seasonal and semi-annual $\delta^{234}\text{U}$ is $\pm 0.5\%$, moderately higher than analytical precision of $\pm 0.3\%$, while beyond 1999 to 2002 this difference increased to $\pm 1\text{--}2\%$. In the absence of a detailed



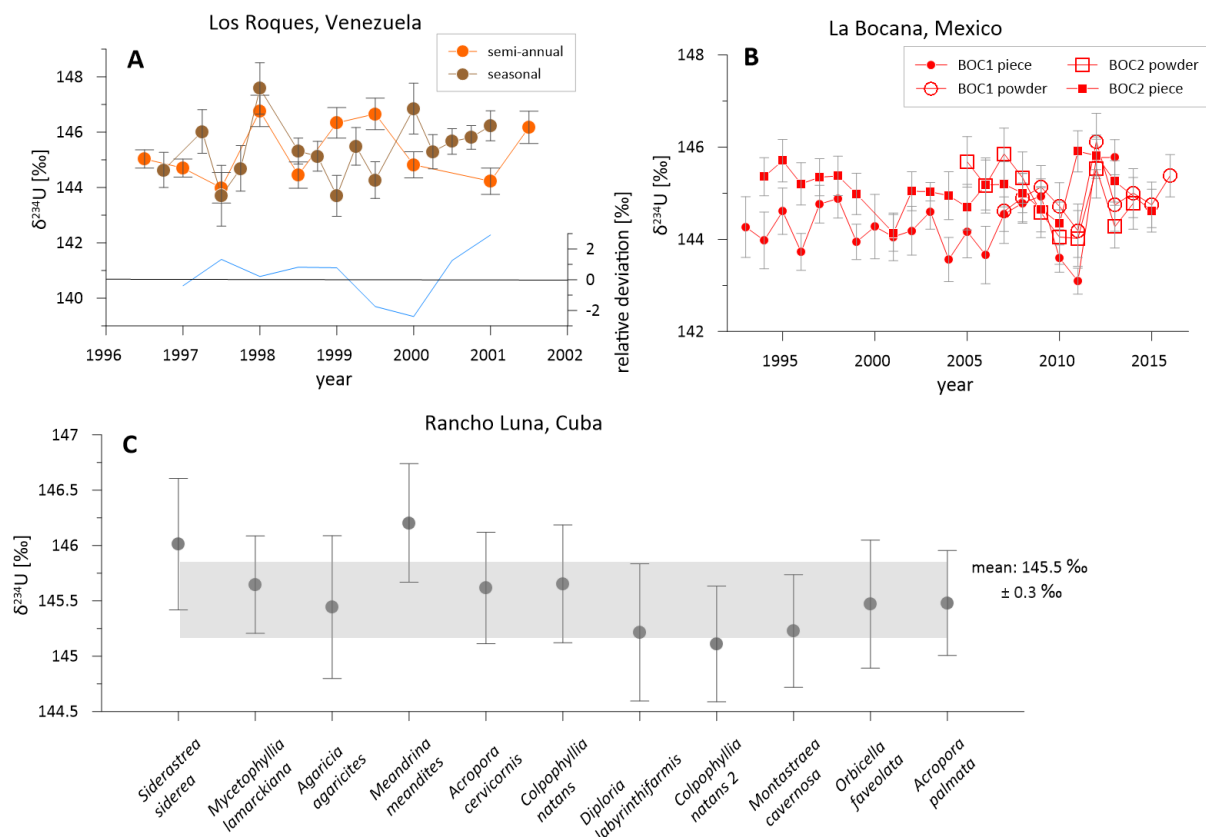
U/Ca map of the sampled coral piece, it is difficult to distinguish whether these deviations arise from analytical effects or reflect natural variability related to heterogeneous U distribution within coral growth bands, potentially coupled to a seasonal $\delta^{234}\text{U}$ cycle. Nonetheless, for most of the record, deviations remain $<1\%$, indicating consistency between annual and seasonal resolution at such precision.

3.4 Species variability

Eleven coral samples representing ten different species from Rancho Luna Bay, Cuba, exhibited $\delta^{234}\text{U}$ values ranging from $146.2\% \pm 0.5\%$ (*Meandrina meandrites*) to $145.1\% \pm 0.5\%$ (*Colpophyllia natans*) (Figure 5c). A second specimen of *Colpophyllia natans* yielded a $\delta^{234}\text{U}$ value of $145.6\% \pm 0.5\%$. The mean value across all samples was 145.5% with a standard deviation of $\pm 0.3\%$. Thus, $\delta^{234}\text{U}$ values for a given year appear species independent within analytical precision achieved here.

3.5 Spatial variability and sampling technique comparison

To further investigate the spatial variability of $\delta^{234}\text{U}$ over time within the same reef environment, two colonies of *Orbicella faveolata* (BOC1 and BOC2), growing approximately two meters apart, were analysed over the same 20 years from 1995 to 2015 (Figure 5b). BOC1 exhibited slightly lower $\delta^{234}\text{U}$ values, with a mean of $144.3\% \pm 0.6\%$, compared to BOC2 with a mean of $145.1\% \pm 0.4\%$. The two values are identical within two sigma uncertainty, but the largest offset in absolute values of 0.8% exceeds reproducibility of $\pm 0.4\%$, but is similar to the punctuated differences occurring between sample replicates, and for different time resolutions. Nevertheless, both records display similar temporal trends, with a strong positive correlation ($r = 0.70$, $p < 0.001$) across the two decades-long time series (Table 3). Correlation coefficients between solid samples pieces, cut with the diamond saw blade, and finely powdered samples, milled along the growth axis, are summarized in Table 3. Significant correlations were observed between both BOC1 sampling methods and between the BOC1 and BOC2 bulk samples. In contrast, correlations involving the powdered samples from BOC2 were weaker, although still positive ($r > 0.4$), and did not reach statistical significance.



280 **Figure 5: A: Comparison of seasonal (brown) and semi-annual (orange) $\delta^{234}\text{U}$ values measured in coral samples from Los Roques, Venezuela, between 1996 and 2002. Uncertainty bars represent analytical uncertainty (2σ). The blue line shows the relative deviation (%) between the two records. While overall trends are similar, notable divergence occurs around 2000–2001. B: Temporal $\delta^{234}\text{U}$ records from two neighbouring coral colonies (BOC1 and BOC2) collected at La Bocana, Puerto Morelos, Mexico. Both bulk (solid symbols) and powdered (open symbols) samples are shown. Despite spatial heterogeneity in absolute $\delta^{234}\text{U}$ values, particularly between colonies, the temporal trends are significantly correlated ($r = 0.7$, $p < 0.001$). C: $\delta^{234}\text{U}$ values measured in 10 different coral species collected from Rancho Luna in Cuba in 2016. The species include massive, branching and encrusting growth forms. Despite biological and morphological differences, all species exhibited consistent $\delta^{234}\text{U}$ values within analytical uncertainty (mean = 145.5‰ \pm 0.3‰, shaded band).**

285

Table 3: Pearson correlation coefficients (r) between $\delta^{234}\text{U}$ records obtained from bulk and powdered samples of two coral colonies (BOC1 and BOC2) at La Bocana, Mexico. All correlations are based on overlapping time intervals. Bold values indicate statistically significant correlations ($p < 0.05$).

290

	BOC1 bulk	BOC1 powdered	BOC2 powdered
BOC1 bulk			
BOC1 powdered	0.70		
BOC2 powdered	0.29	0.48	
BOC2 bulk	0.69	0.54	0.41



4 Discussion

4.1 $\delta^{234}\text{U}$ Measurements

The accuracy of $\delta^{234}\text{U}$ measurements in this study is supported by 66 analyses of the reference material NBS-CRM-112A, which yielded a mean $\delta^{234}\text{U}$ value of -38.5‰ ($\pm 0.4\text{‰}$). These results fall well within the range reported by previous studies, which have documented $\delta^{234}\text{U}$ values for NBS-CRM-112A (Cheng et al., 2013; Wang et al., 2017; Hu et al., 2025) (Figure 2). The analytical precision reported in this study reflects recent improvements in data processing, including refined outlier detection, hydride correction, and mass bias adjustments (Kerber et al., 2023; Kerber et al., 2025). While ϵ -level precision in $\delta^{234}\text{U}$ measurements has recently been demonstrated under optimized analytical conditions (Hu et al., 2025), the reproducibility reported here is sufficient to resolve environmentally meaningful variability in seawater $\delta^{234}\text{U}$. Given that total procedural replicates displayed slightly greater variability ($\pm 0.6\text{‰}$; Fig. 4) compared to NBS-CRM-112A standard measurements and that observed $\delta^{234}\text{U}$ dispersion in natural coral archives commonly exceeds analytical uncertainty, the method applied here still represents robust reproducibility for carbonate-based uranium isotope analysis. The precision achieved in this study therefore allows for the resolution of even minor subtle variations in seawater $\delta^{234}\text{U}_{\text{sw}}$. For example, a recent work has reported modern variability in $\delta^{234}\text{U}_{\text{sw}}$ on the order of 1.3‰ (Kipp et al., 2022). Even slight differences of this magnitude can be resolved with confidence in annual banded corals using the methodology presented here. For example, during past climatic shifts, such as the Last Glacial Maximum, characterized by low sea level and extensive global ice volume, with enhanced weathering rates, the $\delta^{234}\text{U}_{\text{sw}}$ values decreased by approximately $6\text{‰} \pm 2\text{‰}$ (Henderson, 2002; Esat & Yokoyama, 2006; Chutcharavan et al., 2018). Further, modern hydrological settings of ground- and riverine water ($\delta^{234}\text{U} = 70\text{‰}$ - 1000‰ (Dunk et al., 2002)) can be traced using high resolved $\delta^{234}\text{U}$ in coral skeleton (Greve et al., 2026). These shifts highlight the sensitivity of the $\delta^{234}\text{U}$ signal to changes in global continental weathering and hydrological balance, reinforcing its value as a paleoenvironmental tracer.

4.2 Sampling strategy

Several studies have explored the spatial variability of trace element concentrations and isotopic compositions within coral skeletons, often identifying differences among microstructural components such as the theca, septa, and dissepiments (Perrin, 2003; DeLong et al., 2016; Reed et al., 2021). Additionally, variations in coral growth rates under different environmental conditions have been shown to influence geochemical signatures (Felis et al., 2003). In the present study, the relatively large material demand for uranium isotope analysis of 50 mg necessitated the integration of multiple skeletal components into single 'bulk' samples. Despite this approach, replicate $\delta^{234}\text{U}$ measurements taken along the same growth band, each incorporating different proportions of skeletal microstructures, revealed no statistically significant differences in $\delta^{234}\text{U}$ values (Figure 4b). This suggests that, at the resolution applied here, intra-band heterogeneity in $\delta^{234}\text{U}$ is minimal or remains within analytical uncertainty. While some degree of microstructural variability likely exists, its influence on the bulk $\delta^{234}\text{U}$ signal appears negligible regarding the precision, reproducibility and accuracy obtained here. The results support the validity of using integrated skeletal material for high-resolution isotope analysis when sample quantity is limited.



Additional tests comparing sampling methods (bulk vs. milled powder) on two neighbouring *Orbicella faveolata* colonies revealed further insights (Figure 5b). In the first coral, $\delta^{234}\text{U}$ values from bulk and powdered samples were identical, suggesting
325 homogeneity in internal skeletal composition or minimal structural influence on uranium incorporation. This consistency implies that either sampling approach is reliable when structural heterogeneity is low. In contrast, the second coral, located only two meters away, exhibited a measurable difference between the adjacent first sample (Table 3). In addition, significant deviations are visible between bulk and powdered samples. These discrepancies illustrate a variable degree of microscale heterogeneity between coral colonies. It is interesting to note that both corals reveal 0.8‰ to 1‰ differences over almost two
330 decades, after which the variability of $\delta^{234}\text{U}$ increases, but absolute values merge. In the absence of further mineralogical and geochemical studies of both corals, the origin of small but systematic deviations and intra-skeletal heterogeneity in U isotopes remains unknown. These findings highlight the importance of skeletal structure and sampling scale in $\delta^{234}\text{U}$ analysis, underscoring the need for consistency in sampling methods when comparing records across colonies. Note that the temporal pattern is preserved even if small systematic biases exist between individual corals or over several decades of growth. Since
335 such differences do not exceed the analytical reproducibility by more than a factor of two, we can safely interpret isotope variability larger than 1‰ as originating in seawater.

The temporal resolution achievable in $\delta^{234}\text{U}$ analyses is largely constrained by the amount of available coral material. Seasonal sampling does not consistently resolve into well-defined semi-annual averages (Figure 5a). Moreover, the semi-annual records are not merely smoothed versions of the seasonal signals, suggesting that averaging does not fully preserve intra-annual
340 variability, likely because uranium concentrations vary among individual growth bands and throughout seasons. This discrepancy may also result from the sampling process itself. During sawing an uneven loss of material may disproportionately affect the averaging of seasonal values, which are better defined when using semi-annual coral chips extracted with a diamond wire saw. Achieving high-resolution $\delta^{234}\text{U}$ records requires careful sampling techniques, such as micro-drilling or wire sawing; however, micro-drilling may introduce bias if the sampled material does not integrate multiple skeletal components.

345 4.3 $\delta^{234}\text{U}$ variability across coral genus and colonies

Species-specific differences in the incorporation of trace elements and isotopes into the coral skeleton are well documented and often attributed to variations in biomineralization strategies, growth rate, morphologies, and ecological preferences (de Villiers et al., 1995; Sadler et al., 2014; Ross et al., 2019; Canesi et al., 2023). The species analysed in this study are all common throughout the Caribbean (Veron, 1995), yet they represent a broader range of morphotypes, including massive,
350 branching, encrusting, and plate corals, that are typically used in paleoclimate reconstructions. Among these, genera such as *Siderastrea*, *Orbicella* and *Diploria* are frequently used in climate proxy studies and are known to show species-dependent variations in elements such as Sr, Mg, and Li (Giry et al., 2010; DeLong et al., 2011). U/Ca ratios have also been reported to vary among species (de Villiers et al., 1995; Sadler et al., 2014; Ross et al., 2019). Here, we find that all the analysed corals, regardless of species, exhibit $\delta^{234}\text{U}$ values consistent with the open ocean value (Figure 5c). This supports the robustness of
355 $\delta^{234}\text{U}$ as a geochemical proxy, largely unaffected by biological or ecological variability during uranium incorporation.



The analysis of two neighbouring corals from La Bocana (Mexico) reveals notable spatial heterogeneity in $\delta^{234}\text{U}$ values (Figure 5b). Similar small-scale geochemical variability has previously been observed for Sr/Ca ratios and $\delta^{18}\text{O}$ within single reef systems (Alpert et al., 2016; Sayani et al., 2019). In this region, SGD is a prominent feature, with numerous point sources contributing freshwater inputs across the reef (Null et al., 2014). Groundwater on the Yucatán Peninsula exhibits $\delta^{234}\text{U}$ values lower than open-ocean seawater (Schorndorf et al., 2023), consistent with the lower $\delta^{234}\text{U}$ values recorded in BOC1. This suggests that BOC1 may have been more strongly influenced by SGD than BOC2 between 1992 to 1998 and in 2004, 2006, and 2010. Otherwise, both records show identical values within uncertainty. Indeed, analysis of coral growth parameters (e.g. density, linear extension rate and calcification rate) revealed significant differences in calcification rates among these colonies (Rico-Esenaro et al., 2022). These differences were attributed to variations in the local hydrological conditions of each habitat and/or to colony-specific morphological traits. For example, colony BOC1 exhibits a symmetrical growth pattern, while BOC2 displays a more irregular morphology. However, no direct correlation between the growth parameter and $\delta^{234}\text{U}$ values is possible. Previous hydrodynamic studies indicate that seawater inflow occurs primarily above the reef crest, while groundwater and deeper water outflow are restricted to two main channels, one at the southern reef edge and another near La Bocana, the coring site (Coronado et al., 2007). Although detailed microcurrent mapping at this reef is lacking, studies from comparable systems indicate that water flow is strongly modulated by reef topography and benthic structure (Monismith, 2007; Pomeroy et al., 2023). Such localized dynamics may contribute to the observed minor differences in $\delta^{234}\text{U}$ values between the two colonies. Indeed, Hernández-Terrones et al. (2021) demonstrated differing degrees of mixing across SGD point sources in this reef, further supporting the role of spatial hydrological variability in shaping the observed coral $\delta^{234}\text{U}$ signals. Despite this offset, the temporal $\delta^{234}\text{U}$ trends in both corals remain highly correlated ($r = 0.7$, $p < 0.001$) (Table 3), indicating a common response to external drivers and overall changes in freshwater fluxes over decadal time periods.

5 Conclusion

This study demonstrates that $\delta^{234}\text{U}$ measurements in tropical coral skeletons are robust, with a precision of full chemical, species and sampling replicates of $\pm 0.6\%$. Factors contributing to a reproducibility that exceeds our internal error of 0.4% by a factor of two include micro-heterogeneity on a seasonal scale, and local reef microcurrents. These improvements allow for the detection of subtle $\delta^{234}\text{U}$ variations ($< 1\%$) associated with changes in seawater Uranium isotope composition, including those linked to climatic events. Sampling strategy and intra-skeletal heterogeneity were found to introduce minor systematic differences and decreased reproducibility of seawater $\delta^{234}\text{U}$ reconstructions. Although the integration of multiple skeletal structures helped to minimize variability, some colonies exhibited microstructural heterogeneity that affected results at fine spatial scales ($< 1\%$).

The temporal resolution is limited solely by sample availability, but seasonal and semi-annual measurements highlight the sensitivity of $\delta^{234}\text{U}$ to transient environmental events. The isotopic concordance between corals species confirms the lack of fractionation observed using the $^{238}\text{U}/^{235}\text{U}$ ratios (Chen et al., 2018) and underscores the robustness of $\delta^{234}\text{U}$ as a geochemical



proxy of freshwater contributions to the reef environments, supporting its application across diverse coral taxa. Importantly, local hydrodynamics, such as submarine groundwater discharge, may drive local changes in $\delta^{234}\text{U}$ on time scales of years to decades with even very local differences in $\delta^{234}\text{U}$ between neighbouring corals near discharge points. Despite this, strong inter-colony correlations indicate that $\delta^{234}\text{U}$ time series reliably capture regional-scale environmental variability, provided that local reef conditions are well-constrained.

Credit authorship contribution statement

SG: Conceptualization; Investigation; Data curation; Formal analysis; Writing – original draft.

395 NF: Conceptualization; Methodology; Validation; Supervision; Resources.

SW: Methodology; Validation; Resources.

PM: Resources; Methodology.

AW: Resources; Methodology; Writing - Review & Editing.

SDRE: Resources; Formal analysis; Methodology.

400 JPCG: Resources; Formal analysis; Methodology.

JASC: Resources; Writing - Review & Editing.

ACRF: Resources; Writing - Review & Editing.

CAH: Resources.

MGB: Resources.

405 MT: Resources.

SH: Resources; Methodology.

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